

CLAY MINERALOGY OF COTTONWOOD LIMESTONE

by

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INTRODUCTION

Interpretation of Clay Minerals in Sediments

With the improvement of the X - ray and differential thermal analysis (DTA) techniques in the last fifteen years, and with the acquisition of modern instruments by many laboratories, great emphasis has been placed on research in clay mineralogy.

One of the many branches of this field deals with the occurrence of clay minerals in sedimentary rocks. Detailed investigations provide a clue to the origin and the history of a sediment. Observations of recent sediments indicate that the clay mineral assemblage is a result of the source area, environmental conditions, diagenesis, and weathering. The determination of the genesis of a sediment is hindered by the lack of sufficient data, and the uncertainties grow when dealing with ancient sediments. Therefore it is not surprising to find contrary statements in the literature; but, good progress towards the solution of many problems has been definitely made (Grim, 1958; Weaver, 1958a; 1958c; 1959).

Two concepts of the origin of minerals have generally evolved. Grim (1953; 1958) favored the theory that the environment of deposition is the most important factor in determining which clay mineral assemblage will occur, whereas Weaver (1958a; 1958c; 1959) believed that a clay mineral assemblage reflects mainly the type of rock composing the source area.

According to Grim certain clay mineral associations are typical for certain environments. For example: a highly saline environment is

characterized by montmorillonite, illite, chlorite, and sepiolite-attapulgite minerals. However, no representative composition of fluvial sediments was given and all mineral combinations are possible.

Grim concluded that two layered minerals, such as kaolinite, are not in equilibrium with a marine environment. Therefore, an alteration of kaolinite to three layered minerals such as illite and chlorite was suggested, although this change might be slow and incomplete. Formation of illite and chlorite from montmorillonite was also proposed.

Evidence was presented (Grim and Johns, 1954) that degraded illite and chlorite will regenerate very quickly when fresh-water mud enters a marine environment. The formation of partially altered minerals, such as illite-montmorillonite and chlorite-montmorillonite will be controlled mainly by the availability of Potassium and Magnesium. Bentonitic montmorillonites, however, will not be changed beyond the mixed-layered stage, because of a deficiency of the interlayer charge.

Weaver (1959) cited proposed alteration products of clay minerals given by different authors in previous years and proceeded to show that nearly every clay mineral can be changed to every other clay mineral. Weaver suggested that the structural relationships of the different clays should be considered. He did not believe that any basic change will take place in the structure of a clay mineral when it is exposed to a new environment. His assumption was based on structural considerations and on observations of several thousand sediments in the southern part of the United States.

He reasoned in following way: the stable low-temperature muscovite or illite is the 1M and 1M1 type, and the stable high-temperature variety is the 2M polymorph or common muscovite (Yoder and Eugster, 1955; Smith and Yoder, 1956). Except for glauconite and mixed layer illite-montmorillonite, the 1M illite is relatively uncommon; the 2M illite is common in ancient sediments. It is unlikely that the 2M illite was formed by marine diagenesis and more likely that it was detrital and was derived from muscovite or illite in the source area. Most chlorite, of ancient sediments is trioctahedral, whereas most montmorillonite is commonly dioctahedral. This excludes any formation of chlorite from montmorillonite and suggests that most chlorites are of detrital origin.

Weaver considered only adsorption as a factor in the alteration of clay mineral such as the formation of illite and chlorite from degraded illite and chlorite.

Both Grim's environment and Weaver's source area-concept are supported by several studies. Degens, Williams, and Keith (1957), for example, found that in 70 samples of Pennsylvanian rock, the illite-to-kaolinite ratio was statistically higher in marine and brackish-water shales than in fresh-water shales. Age studies on the sediments of the Mississippi delta, on the other hand, showed that the illites were mainly detrital (Hurley, et al., 1961).

Also Weaver (1959) observed the relationships between clay mineral suites and environments. According to him it is, however, not obvious whether these relationships were caused by physical and chemical sorting or by chemical alterations of the detrital clays. Observations in river deltas

showing that one clay mineral-type decreases towards the sea, while others increase, are commonly taken as evidence of alteration. This phenomenon can also be explained by preferential flocculation, current sorting, different source areas, floods, and periodic variations of river detritus (Weaver, op. cit.).

Previous Work in the Area

The clay mineralogy of Kansas rocks has been reported by several authors in recent years. Swinford (1955) studied the Upper Permian rocks of south-central Kansas, and reported that illite and chlorite are the dominant minerals. Montmorillonite is common in the upper part of the section. Kaolinite occurs in only small quantities.

Several theses at Kansas State University have dealt with the clay mineralogy of Permian and Pennsylvanian rocks in the vicinity of Manhattan. Applying X-ray and DTA-methods Mc Pherron (1956) investigated most of the units of shale from the Beattie Limestone of the Council Grove Group to the Matfield Shale of the Chase Group. He discovered illite, chlorite, and interlayered chlorite-vermiculite in all of his samples, whereas kaolinite, montmorillonite, and other interlayered minerals occur only in some. He observed that some montmorillonite was present as a mixed layer mineral directly above and below the chert-bearing limestones. He believed this occurrence to be due to the devitrification of volcanic ash.

Watkins (1957), studying five Pennsylvanian and six Permian limestones, reported illite to be most abundant followed by chlorite. The chlorite

was Fe-rich and poorly crystalline in all samples. Illite-montmorillonite was a common interlayered mineral. No kaolinite was found.

Asmussen (1958) examined the clay of the Johnson Shale, Red Eagle Limestone, Roca Shale, Grenola Limestone, Eskridge Shale, and Blue Rapids Shale of the Council Grove Group. Illite and Fe-rich chlorite are major constituents and many variations of interlayered minerals are in all samples. Some montmorillonite is in the Neva Limestone.

Hargardine (1959) found illite to be the most abundant clay mineral in the Grenola Limestone. He distinguished several types of chlorite according to degrees of crystallinity and Fe-content. Superlattices of chlorite and montmorillonite occur in many units. Where the content of chlorite was high, so also was the amount of dolomite.

Bryson (1959) studied the Upper Chase Group and Lower Sumner Group. He related the clay mineral assemblages to the regional structure which was reflected by the depositional environment. Illite and chlorite would characterize a basin facies, whereas interlayered clay minerals would be typical of brackish conditions associated with anticlinal structures that served as source areas. Bryson also considered the degree of weathering of clay minerals.

Huber (1965), in his petrological study of the Crouse Limestone, reported illite as a major constituent and interlayers of chlorite and vermiculite as minor constituents.

All of the above mentioned theses have accumulated a detailed knowledge about the clay minerals in northeastern Kansas, especially in the Manhattan area.

Purpose of Study

This study is mainly concerned with the distribution of clay minerals within one stratigraphic unit investigated over an extended area. By confining the study to only one unit one variable, the influence of time during deposition, is fairly well eliminated. Thus any evaluation of source area and depositional environment with respect to clay mineral genesis is facilitated. It is hoped to consider also effects of diagenesis and weathering.

The Cottonwood Limestone Member of the Beattie Limestone is well suited because it crops out for more than 200 miles in a northerly band through Kansas. The thickness ranges from 6.5 to 7.5 feet and the member is recognized easily in the field. In addition the non-clay petrology, paleontology, and paleoecology has been carefully studied by Imbrie, Laporte, and Merriam (1959) and Laporte (1962). Parish (1952) studied the insoluble residue of the Cottonwood in the Manhattan area, and Wilbur (1956) listed the heavy minerals.

The results of all these investigations are of great value; for any conclusions drawn in this study can be checked with the results of previous work.

DESCRIPTION OF THE COTTONWOOD LIMESTONE

The Cottonwood Limestone, Florena Shale, and Morrill Limestone, in ascending order, are members of the Beattie Limestone, which belongs to the Council Grove Group of the Gearyan Stage, Permian System (old nomenclature in Kansas : Wolfcampian Stage, see O'Connor, 1963). The Beattie Limestone originated in a marine environment, whereas the underlying Eskridge Shale and the overlying Stearns Shale were formed in brackish environment; this sequence constitutes one of the many cyclothem known in Pennsylvanian and Permian stratigraphy.

The Cottonwood Limestone can be observed from southern Nebraska to northern Oklahoma and in subsurface the limestone is traced westward to the Kansas-Colorado line (Imbrie, Laporte, and Merriam, 1959). The outcrops of the Cottonwood are about six feet thick. In central and northern Kansas it forms a prominent ledge with a "bush line" and can easily be distinguished in the field and in aerial photos. These features disappear in southern Kansas where the Cottonwood contains many beds of shale.

Laporte (1962, pp. 525-534) described the following five facies of the Cottonwood Limestone by means of isopachous data, lithology, and faunal provinces (Plate I):

a) Bioclastic facies: buff to yellow, cherty, fine-grained limestone composed of finely comminuted fossils, especially the algal-foraminiferal intergrowth Osagia, echinoderms, and bryozoans. It forms the lower half of the Cottonwood from southern Nebraska to central Kansas. The average thickness is three feet.

b) Fusuline facies: buff to gray, cherty, fine-grained limestone with abundance of small fusulines. It forms the upper half of the Cottonwood from southern Nebraska to central Kansas, and averages three feet in thickness.

c) Platy Algal facies: buff to gray, massive, fine-to medium-grained limestone composed of very abundant broken thalli of the calcareous alga, Anchicodium; some Osagia is also present. For about 40 miles across central Kansas the Cottonwood is composed of this facies. The thickness ranges from less than three feet to more than seven feet, and averages about four and a half feet.

d) Shelly facies: interbedded dark-gray to reddish-gray limestone and calcareous shale, with a very diverse, abundant, and well-preserved fauna that includes brachiopods, molluscs, and ammodiscid foraminifers. From central Kansas to northern Oklahoma this facies ranges in thickness from one to six feet and averages four and a half feet. There is a progressive thinning southward.

e) Silty Osagia facies: medium crystalline, reddish-gray to light-gray limestone with several thin shaly interbeds. Molluscs, Osagia, and quartz silt characterize this facies. From northern Oklahoma to the southern limit of its outcrop the facies thins progressively from about four feet to less than one foot.

According to Laporte (1962, p. 534), the five facies can be reduced to two facies provinces.

"The silty Osagia and shelly facies belong to a southern facies province, characterized by a diverse, well-preserved fauna with minor but significant amounts of detrital quartz. The bioclastic, fusuline, and platy algal facies belong to a northern facies province, characterized by a restricted biota, which is finely comminuted, in a fairly pure carbonate matrix."

Using 40 chemical analyses Laporte (1962, p. 527) calculated the mineral percentages of the five facies. These data are in Table 1 and are in agreement with the percentages of insoluble residue reported by Parish (1952, pp. 93-114) for the Cottonwood Limestone in the Manhattan area.

EXPLANATION OF PLATE I

The Cottonwood Limestone is shown in a cross-section with north at the right that parallels its outcrop. Localities of samples for this study are indicated. They include the Spillway outcrop (SP), Intersection K 177 - K 13 (I), Stagg Hill (ST), Mc Donnell Creek (MD), and Deep Creek (DC), in the Manhattan area. Additional samples were taken from outcrops in Chase County (CH), Greenwood County (GR), Cowley County (CO), and Pawnee County (PA), Oklahoma.

PLATE I

KANSAS

OKLAHOMA

PA






CO

GR

CH

DCARDST I SP



-  SILTY OSAGIA FACIES
-  SHELLY FACIES
-  PLATY ALGAL FACIES
-  FUSULINE FACIES
-  BIOCLASTIC FACIES



FACIES OF THE COTTONWOOD LIMESTONE
(LAPORTE, 1962)

Table 1

Cottonwood Facies Mineralogy

(Laporte, 1962, p. 527)

	Calcite	Dolomite	Silica	Clay	Minor Constituents
Bioclastic	84.9	2.4	3.6	7.5	1.3
Fusuline	87.7	1.8	2.8	6.2	0.9
Platy Algal	91.7	0.7	1.2	6.2	0.4
Shelly					
lime-rich	81.1	2.6	4.7	9.6	1.6
clay-rich	46.9	3.3	13.1	32.6	3.3
Silty <u>Osagia</u>					
lime-rich	75.7	2.8	8.3	10.4	2.7
clay-rich	40.5	2.2	31.8	19.7	5.5

METHOD OF INVESTIGATION

Field Procedure

This study of the clay mineralogy consisted of two phases. The first phase involved a detailed investigation of the clay mineralogy of the Cottonwood Limestone in the Manhattan area from five localities in Riley and Pottawatomie County (Plate II). Then the clay mineralogy of the Cottonwood was also determined in central Kansas, southern Kansas, and northern Oklahoma from four localities that are 40 to 50 miles apart. These locations were picked to include each of the facies that was described by Laporte.

Samples were taken from different levels within the Cottonwood and, if possible, from the overlying Florena Shale and the underlying Eskridge Shale. From five to eight samples were collected at each outcrop so that each bed was included. Weathered parts as far as this is possible on surface outcrops were avoided.

Samples of the Cottonwood Limestone were collected from the following sites:

- (1) Manhattan area:
 - (a) Spillway section (SP) of the Tuttle Creek Reservoir, Pottawatomie County (SW $\frac{1}{4}$, sec 18, T. 9 S., R. 8 E.)
 - (b) Intersection K 177 - K 13, Roadcut on southwestern side of intersection, Riley County (NW $\frac{1}{4}$, NW $\frac{1}{4}$, sec 25, T. 9 S., R. 7 E.)
 - (c) Stagg Hill, Roadcut on east side of highway, Riley County (NE $\frac{1}{4}$, NE $\frac{1}{4}$, sec 26, T. 10 S., R. 7 E.)
 - (d) Mc Dowell Creek, Outcrop on west side of highway, Riley County (SE $\frac{1}{4}$, NE $\frac{1}{4}$, sec 21, T. 11 S., R. 7 E.)
 - (e) Deep Creek, Road cut on south side of Interstate 70, Riley County (NE $\frac{1}{4}$, sec 26, T. 11 S., R. 8 E.)

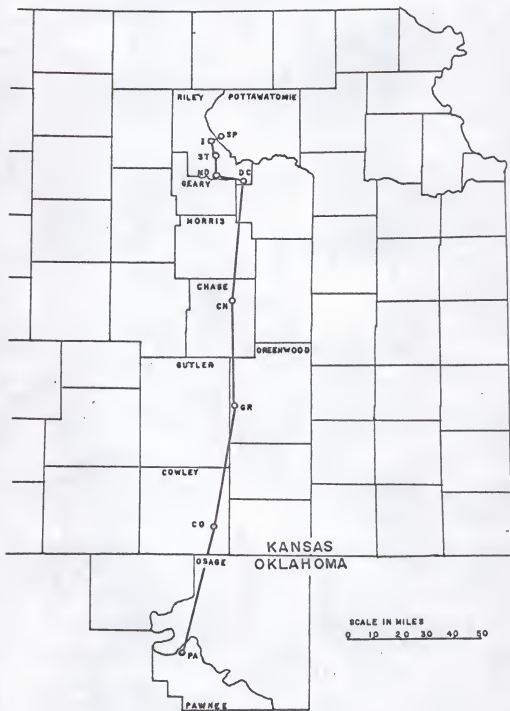
- (2) Chase County, Kansas:
Section on both sides of highway K 13 about 1 mile west of Strong City, about 30 feet west of railroad track (NW $\frac{1}{4}$, sec 17, T. 19 S., R. 8 E.)
- (3) Greenwood County, Kansas:
Roadcut on both sides of U.S. 54, 0.3 mile east of Butler county line (SE $\frac{1}{4}$, SW $\frac{1}{4}$, sec 3, T. 26 S., R. 8 E.)
- (4) Cowley County, Kansas:
Stream gully northeast of road 0.3 mile east of Hooser (NW $\frac{1}{4}$, NW $\frac{1}{4}$, sec 36, T. 33 S., R. 7 E.), for samples CO 1.- CO 5.
Roadcut on both sides of U.S. 166 (SE $\frac{1}{4}$, NE $\frac{1}{4}$, sec 11, T. 34 S., R. 7 E.), for sample CO 6.
- (5) Pawnee County, Oklahoma:
Outcrop north of road (SE $\frac{1}{4}$, sec 2, T. 23 N., R. 4 E.)

The outcrops in the Manhattan area and in Chase County belong to the bioclastic and fusuline facies. Samples from Greenwood County represent the platy algal facies. In Cowley County the shelly facies is present. The section in Pawnee County, Oklahoma, is not included in Laporte's investigation (Plate I), the correlation of this outcrop does not seem to be assured. (See Discussion of Results.)

EXPLANATION OF PLATE II

Map showing location of samples of Cottonwood Limestone.

PLATE II



LOCATION OF SAMPLES

Laboratory Procedure

Preliminary Investigation.--About 60 samples of insoluble residue from the Cottonwood Limestone in the Manhattan area, which are part of Parish's thesis (1952), were available in the Geology department at Kansas State University. The fine fraction of these samples was used for a preliminary investigation of the clay minerals. X-ray recordings of ten samples, however, showed only a monotonous illite-quartz association. A fractionation of grain sizes into 2 microns, 1 micron, 0.2 micron, and 0.2 - 0.08 micron revealed only that quartz disappeared below a one micron size and that the peak resolution of illite decreased with decreasing grain size. It was concluded that Parish's acid treatment (1 : 1 diluted HCl) destroyed some of the clay minerals. Thus any insoluble residues which are treated in such a way are of no value for clay mineral studies.

Preparation of Clay Size Material.--Because clays are only a minor constituent in most of the Cottonwood samples (Table 1), they had to be concentrated in order to get useful results from the X-ray analysis. The concentration was accomplished by removing the carbonates with acetic acid. A careful treatment was applied to prevent dissolution of certain clay minerals. Some types of chlorite and montmorillonite are known to be soluble in acid. The method used in this investigation is similar to that described by Ostrom (1961).

Each rock sample, roughly a cube of about 20 cm. on a side, was put under a rock trimmer. Its surface was then removed to prevent contamination from adhering soil material and to keep effects of weathering at a minimum. The remaining sample was crushed with mortar and pestle and then sieved. The -60 and -200 mesh fractions were used for preparing oriented slides and for random powder samples.

Oriented Slides.--About 200 grams of the -60 and -200 mesh fractions were put into a three liter beaker. Then the sample was covered with distilled water to prevent a vigorous acid reaction. After a short time of soaking one liter of 0.3 molar acetic acid with a pH of about 3.5 was added. The mixture was stirred at one hour intervals. After the reaction (about 8 hours), the liquid was decanted and more acid added. After 3 or 4 treatments most of the carbonates had been dissolved and a dark layer ($\frac{1}{2}$ cm. thick) of insoluble residue accumulated on some undissolved limestone. Attention was paid that always some undissolved limestone remained so as to prevent alteration of the clays. By this treatment any effect of acid on the clay minerals was held at a minimum. The insoluble residue was then separated from the undissolved limestone by decanting and washed to remove any soluble salts that might cause flocculation. The washing involved: (1) centrifuging, (2) decanting the clear liquid, and (3) adding distilled water. This process was repeated several times until the clays finally stayed in suspension when centrifuged. More distilled water was added to the clays to make a volume of 120 ml. The mixture was agitated in a Waring Blendor for about two minutes and the resulting suspension was

brought into a 140 ml- cylinder (length of 35 cm, internal diameter of 2 cm). After eight hours of settling the -2 micron fraction was removed with a pipette and part of it was placed on a glass microscope slide with an eye-dropper and allowed to dry, thus producing an oriented sample.

Random Powder Samples.--Untreated -200 mesh fractions were mounted in aluminum frames to give random powder samples which were used for the determination of the non-clay minerals. Also, some of the samples of insoluble residue were prepared as random powders to investigate the non-basal spacings of clay minerals.

X-Ray Analysis.--Oriented and non-oriented samples were analyzed with a Norelco Wide Range Diffractometer of the following setting: Ni-filtered Cu K alpha radiation, with 40 kilovolts and 18 milliamperes, scanning speed of 1° (two theta) / min., chart speed $\frac{1}{2}$ inch/min., time constant of 2 seconds, and proportional counter detector. The slit system consisted of: a divergent and antiscatter slit of 1° , and a receiving slit of 0.006 inch. The pulse height analyzer (PHA) was set at a level of 16 volts with a window of 11 volts; the detector voltage was 1.7 kilovolts. A scale factor of 200 or 500, depending on intensities of peaks was used.

All oriented slides were first run from 62 to $1\frac{1}{2}$ degrees (two theta). Then after each additional treatment of glycolation, heating, ion exchange or acid dissolution the slide was analyzed from 15 to $1\frac{1}{2}$ degrees (two theta) which was enough to show any effect on the 001 spacing of the clay minerals. To examine the 060 spacing of illite and chlorite random powder samples

of the insoluble residue were scanned from 70 to 58 degrees (two theta). Most of the untreated samples were investigated as random powders in the range of 35 to 20 degrees (two theta) which includes the strongest reflections of quartz, calcite, dolomite, and the feldspars.

The two theta values of the spacings were converted to Angstrom units using the "Tables for Conversion of X-ray Diffraction Angles to Interplanar Spacing", published by the U.S. Department of Commerce, National Bureau of Standards, Applied Mathematics Series 10 (1950).

Glycol Treatment.--Certain clay minerals, especially montmorillonite and some varieties of vermiculite and chlorite form complexes with organic compounds and cause an expansion of the basal spacing as much as 3 Angstrom units. This feature is used to distinguish the different types of clay minerals.

All oriented slides were treated with ethylene glycol by spraying a thin film of it on the clays, which were then allowed to soak for an hour before X-ray analysis. It was observed in some cases, that montmorillonites did not show full expansion, when x-rayed immediately after glycolation.

Heat Treatment.--Another method to distinguish clay minerals depends on their behavior to heating. For example, kaolinite dehydrates in the range from 550 to 770° C, (depending on crystallinity) and the structure collapses (Richardson, 1961, p. 132). Montmorillonite loses its inter-layer water in the range from 100 to 200° C and collapses to 10 A.U. (Mac Ewan, 1961, p. 188). Vermiculite collapses to 10 A. U. between 150

to 300° C by the loss of the bound and unbound water (Walker, 1961, p. 312). Chlorite and illite are not affected significantly by temperatures below 600° C.

All oriented slides were heated in a muffle furnace to 450° C and to 600° C for 30 minutes each time followed by X-ray analysis.

Acid Treatment.-- Different solubilities of the clay minerals in acid serve as a supplementary means for identification. Types of Fe-rich chlorite are dissolved in warm diluted HCl. Trioctahedral montmorillonite is also destroyed by acid. Dioctahedral Fe-rich montmorillonite (nontronite) is affected somewhat, whereas highly aluminous montmorillonite is fairly resistant to acid treatment (Mac Ewan, 1961, p. 186).

Oriented slides were put into a beaker, carefully covered with 6 normal HCl, and allowed to stand for half a day or even more. After the treatment the acid was poured off, and the slides were dried under air before X-ray analysis.

Ion Exchange Treatment.-- Ion exchange capacity gives information concerning the interlayer charge of a clay mineral. According to Weaver (1958b) this property tells something about the history of a mineral, for example, whether montmorillonite is derived from a pre-existing illite or by alteration of volcanic ash. In the first case the montmorillonite has a high interlayer charge, in the second case it has a low charge (Weaver, 1958b). If mica-derived montmorillonite and vermiculite are treated with KOH or NH_4Cl solutions, respectively, they will readily

contract to 10 A.U. because Potassium or ammonium cations are incorporated in the structure by the inherited high interlayer charge. Montmorillonite and vermiculite, which are not derived from micas, will not contract.

Four samples (SP 4, GR 4, CO 5, PA 1), which contained illite or illite-montmorillonite, were investigated for ion exchange capacity. A small amount of the -2 micron fraction of these samples was put into a beaker and covered with about 50 ml of 1 normal solution of KOH. While stirring at several intervals the mixture was allowed to stand for 15 hours. Thereafter the clays were washed by centrifuging and prepared for oriented slides.

Three samples (SP 4, I 7, PA 2), containing chlorite-vermiculite and chlorite-montmorillonite, were treated with a saturated solution of NH_4Cl . The -2 micron fraction of the clays was mixed with about 50 ml of the solution and boiled for five minutes. Then the clays were washed, and oriented slides were prepared.

Microscopic Study.--Some of the samples of insoluble residue were put on a glass slide, immersed in oil ($n = 1.54$), and observed with a petrographic microscope, although the small grain size made identification difficult. A few thin sections of the Cottonwood Limestone in the Manhattan area, and detrital slides of heavy mineral-separations of Wilbur's (1956) thesis were available for examination.

INTERPRETATION OF X-RAY DIAGRAMS

Because some confusion concerning the nomenclature of clay minerals exists, the types of clay minerals reported in this study are defined and described (compare also Plates III, IV, V, VI, VII).

Illite

A basal spacing of 10 A.U. was identified in all samples, and the submultiples of the basal spacing of 5 A.U., 3.3 A.U., 2.5 A.U., and 2.0 A.U. were generally recorded. The first order reflection 001 at 10 A.U. had the highest intensity followed by 003 and 002. Heating, glycolation, or HCl-treatment did not affect the spacings. All the above mentioned data fit the description of an illite.

A frequently observed broadening of the peaks may be caused either by low crystallinity (imperfections of the structure) or by small grain size; however, only grain sizes in the range of 0.05 - 0.2 micron will broaden a peak significantly (Cullity, 1959, p. 262). The illites in this study had an average grain size in the range of 1 - 1.5 micron, as observed with the petrographic microscope. Therefore it is concluded that broadening of the peaks is mainly due to the low crystallinity of the minerals.

Based on the ratio of peak heights, $\frac{001}{002}$ two types of illite were distinguished. For illite-1 the 002 peak is less than half as high as the 001 peak, thus giving a $\frac{001}{002}$ ratio larger than two. For illite-2 the 002

peak is more than half as high as the 001 peak, but still smaller than 001, thus giving a $\frac{001}{002}$ ratio smaller than two. This distinction seems to be arbitrary, because all gradations between the two extreme values are observed (Table 3), Using this distinction, however, it is possible to establish a regional pattern of illite distribution.

14 A. U. Clay Minerals

The second most abundant peak was recorded between 14 and 15 A.U. The submultiple spacings were at 7.15 A.U., 002, 4.75 A.U., 003, and 3.54 A.U., 004. The first order reflection at about 14 A.U. gave usually the highest intensity. Based on the behavior of the basal spacing after glycolation and heating six minerals were recognized: (1) chlorite, (2) vermiculite, (3) chlorite-vermiculite, (4) vermiculite-chlorite, (5) chlorite montmorillonite, and (6) Ca-montmorillonite.

Chlorite.--Chlorite was identified by the stability of the basal spacing after glycolation and heating; however a decrease in intensity of the peaks after heating was common. Some of the chlorites were completely destroyed by HCl. Peak height ratios of the first two basal spacings did not reveal any regional differentiation of the chlorites. The first order reflection at 14 A.U. had usually the highest intensity. However, in most chlorites which have been reported from the literature, the 002 reflection has the highest intensity. Especially Fe-rich chlorites give weak first and third orders and strong second and fourth orders.

Because the intensities are related to the population of the cation positions and to the nature of these cations (Grim, 1953, p. 97; and Brindley, 1961, p. 270), it is concluded that the chlorite of this study differs from the commonly reported Mg- and Fe-chlorites in respect to cation substitution. Also, small admixtures of vermiculite with the chlorite, which show a strong first order reflection, may have caused the unusual intensities of the chlorite in this study.

Vermiculite.--The 001 spacing of vermiculite collapsed to 10 A.U. after heating to 450° C. The clay mineral expanded slightly (less than one A.U.) upon glycolation.

After heating to 450° C and 600° C many 14 A.U. clay minerals collapsed to values between 14 A.U. and 10 A.U., thus showing a behavior to heat treatment intermediary between that of chlorite and that of vermiculite. All possible gradations were observed. This feature is supposed to be due to random interstratifications of chlorite and vermiculite. Where the interlayered mineral showed a strong resistance to heating, there was probably a high proportion of chlorite. By arbitrarily chosen limits two types of interlayered minerals were distinguished: chlorite-vermiculite and vermiculite-chlorite. The first one contains more chlorite than the second one.

Chlorite-Vermiculite Interlayer.--After heating to 450 and 600° C the 001 spacing of the interlayered mineral changed to values between 14 A.U. and 12 A.U. Upon glycolation a slight expansion of less than one A.U. was observed.

Vermiculite-Chlorite Interlayer.--After heating to 450° C and 600° C the 001 spacing of the interlayered mineral changed to values between 12 and 10 A.U. Upon glycolation a slight expansion of less than one A.U. was observed.

Chlorite-Montmorillonite Interlayer.--Where a 14 A.U. clay mineral expanded by about 1.5 A.U. upon glycolation it was called chlorite-montmorillonite. After heating to 450 and 600° C the interlayered mineral collapsed to values in the range of 14 to 10 A.U.

Ca-Montmorillonite.--The mineral expanded to 17 A.U. when glycolated, and broke down to 10 A.U. when heated to 450 and 600° C. Upon KOH treatment the mineral generally contracted to 10 A.U. The interlayered cation is considered to be Ca⁺⁺.

12 A.U. Clay Minerals

Illite-Montmorillonite Interlayer.--In some of the samples a rather prominent peak at about 12 A.U. was recorded. It shifted to 13 - 13.5 A.U. upon glycolation, and to 10 A.U. after heating to 450 and 600° C. HCl treatment lowered the 001 spacing by one A.U. to about 11 A.U. These data fit a random interstratification of about equal amounts of illite (10 A.U.) and Ca-montmorillonite (14 A.U.). No submultiples of the first order reflection were observed.

Na-Montmorillonite.--The 12 A peak expanded to about 15 A when glycolated. Upon heating to 450° C it collapsed to 10 A. This mineral was observed in only a few samples.

Kaolinite

A few samples showed a very strong and sharp peak at 7.15 A.U. 001. The 002 reflection at 3.58 A.U. had nearly the same intensity and sharpness as 001. The third order reflection 003 at 2.38 A.U., which is significant for the identification of kaolinite, had a considerably lower intensity than the first two reflections. By heating to 450° C the intensity of the 001 peak was reduced by more than half and by heating to 600° C the peak disappeared.

Regularly Interstratified Clay Minerals

Broad peaks at the low angle side of the diffractograms indicated spacings in the range of 20 - 40 A.U., caused by the regular stacking of two or three different clay minerals. Submultiples of these spacings were seldom observed, probably because either a small percentage of these minerals occurred within the assemblage, or the crystallinity was poor.

Five types of interstratified clay minerals were distinguished:

(1) illite-montmorillonite (1 : 1) : A 24 A.U. spacing 001 expanded to 28 A.U. upon glycolation.

(2) illite-montmorillonite (2 : 1) : A 35 A.U. spacing 001 expanded to about 39 A.U. upon glycolation.

(3) illite-chlorite (2 : 1) : A 34 A.U. spacing 001 remained constant after either glycolation or heating.

(4) chlorite-montmorillonite (1 : 1) : A 28 A.U. spacing 001 expanded to about 31 A.U. upon glycolation.

(5) swelling chlorite-montmorillonite (1 : 1) : A 29 A.U. spacing 001 expanded to 34 - 35 A.U. upon glycolation.

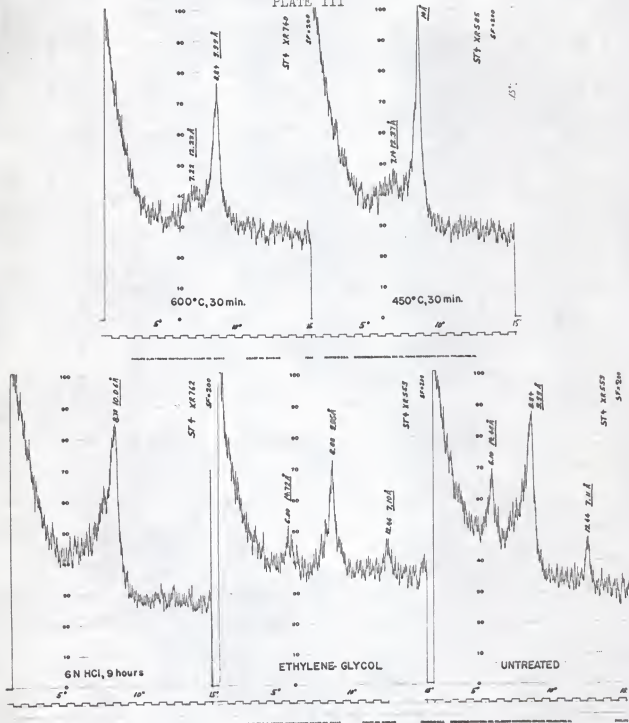
Except for illite-chlorite all other interlayered minerals generally lost the 001 peak after heat treatment of 450° C, which indicated the instability of the interstratified minerals.

Many small peaks were observed at the low angle side of the diffractograms. However, it was not possible to distinguish them with certainty from the background reflections. When some slides were X-rayed twice, without changing the position of the slides, the small reflections, which were thought to represent superlattice clay minerals, disappeared, and other reflections at other angles were observed.

EXPLANATION OF PLATE III

Sample ST 4 of the Cottonwood Limestone of Stagg Hill, Riley County, Kansas represents the northern facies. The clay mineral assemblage contains about 70% illite and 30% randomly interlayered chlorite-vermiculite. The percentages are based on the proportions of the sub-peak areas of the first order reflections recorded from the untreated sample. Note the behavior of the chlorite-vermiculite peak to the different treatments. Glycolation caused a very slight expansion of about 0.3 A.U. Upon heating to 450 and 600° C the 14 A.U. spacing was reduced to 12.4 and 12.2 A.U. respectively. After HCl-treatment the chlorite-vermiculite peak disappeared, which indicates that the mineral is soluble in acid. Solubility of chlorite in acid is generally enhanced by Fe-substitution in the octahedral layer.

PLATE III

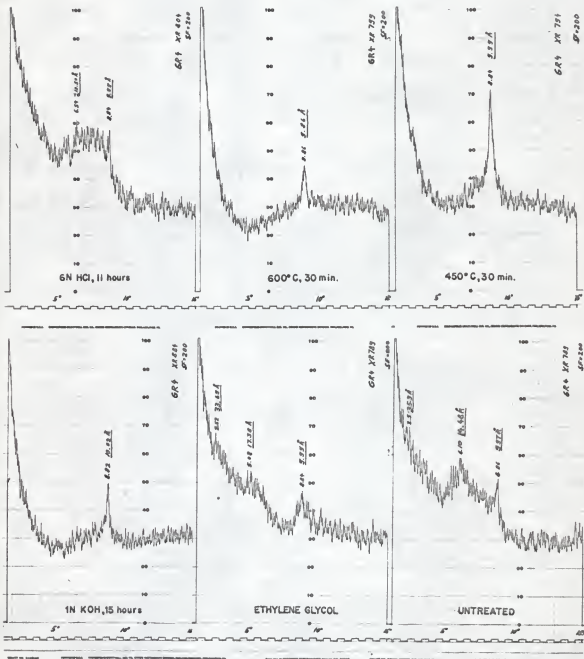


X-RAY DIFFRACTION PATTERN OF SAMPLE ST 4

EXPLANATION OF PLATE IV

Sample GR 4 of the Cottonwood Limestone of Greenwood County, shows mainly illite and Ca-montmorillonite. Some randomly interlayered illite-montmorillonite may be indicated by the small peaks between 14 and 10 A.U. Regularly interstratified illite-chlorite (2:1) may cause the 34 A.U. spacing. The nature of the montmorillonite was investigated by several methods. Upon glycolation the 14 A.U. spacing expanded to 17 A.U. KOH-treatment caused the 14 A.U. spacing to contract to 10 A.U., thus indicating a montmorillonite of a high interlayer charge. After heating to 450 and 600° C the montmorillonite spacing collapsed to 10 A.U. Only a part of the montmorillonite was dissolved by 6 normal HCl after 11 hours.

PLATE IV

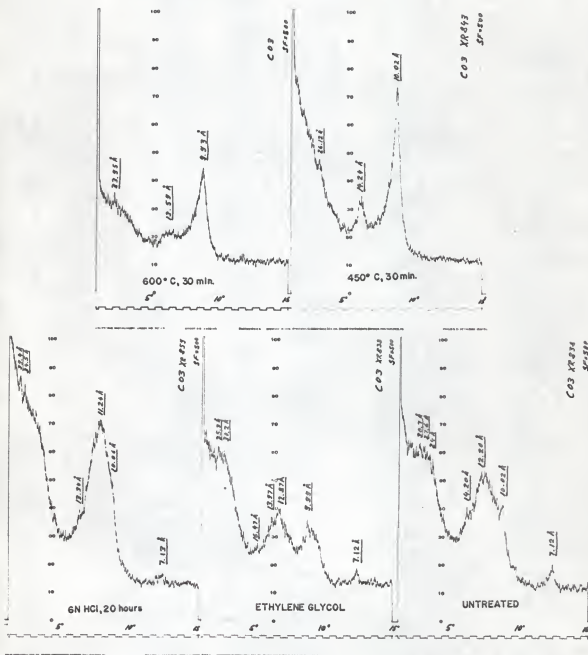


X-RAY DIFFRACTION PATTERNS OF SAMPLE GR 4

EXPLANATION OF PLATE V

Sample of CO 3 of Cowley County represents the southern facies of the Cottonwood and contains an assemblage of illite (10 A.U.), chlorite (14 A.U.), randomly interlayered illite-montmorillonite (12 A.U.), and regularly interstratified clay minerals (24 - 35 A.U.). The superlattice spacings may be caused by 1:1 chlorite-montmorillonite (28 A.U.; 31 A.U. after glycolation), 1:1 swelling chlorite-montmorillonite (about 30 A.U.; after glycolation 35 A.U.), 1:1 illite-montmorillonite (24 A.U.), and 2:1 illite-chlorite (34 A.U. after heating to 600° C). Traces of free montmorillonite are indicated by the small peak at 16.5 A.U. in the glycolated sample. After heating to 450 and 600° C the spacing of randomly interlayered illite-montmorillonite was collapsed to 10 A.U., whereas the spacing of chlorite stayed at about 14 A.U. HCl-treatment caused the reduction of randomly interlayered illite-montmorillonite to about 11 A.U. and of chlorite to about 13 A.U.

PLATE V

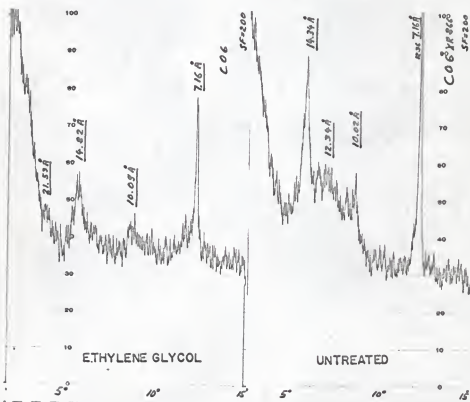
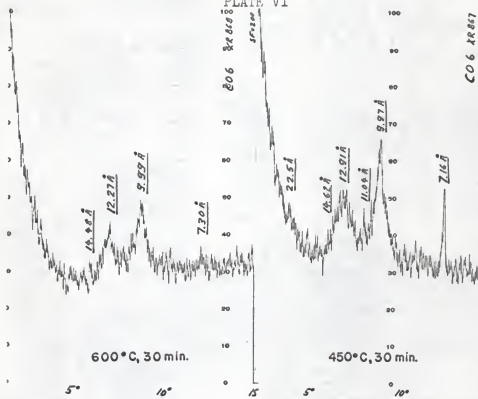


X-RAY DIFFRACTION PATTERNS OF SAMPLE CO 3

EXPLANATION OF PLATE VI

Sample CO 6 represents the Morrill Limestone of Cowley County, Kansas. Illite (10 A.U.), randomly interlayered illite-montmorillonite (about 12 A.U.), randomly interlayered chlorite-vermiculite (14.3 A.U.), and kaolinite (7.16 A.U.) are present. Upon glycolation chlorite-vermiculite expanded to 14.8 A.U., whereas illite-montmorillonite expanded to about 14 A.U. The peak of the latter is not easily recognized probably due to its broadness and to the overlapping peak of chlorite-vermiculite. Upon heating to 450 and 600° C the spacing of chlorite-vermiculite was reduced to 12.9 and 12.3 A.U. respectively, whereas the spacing of illite-montmorillonite collapsed to 10 A.U.

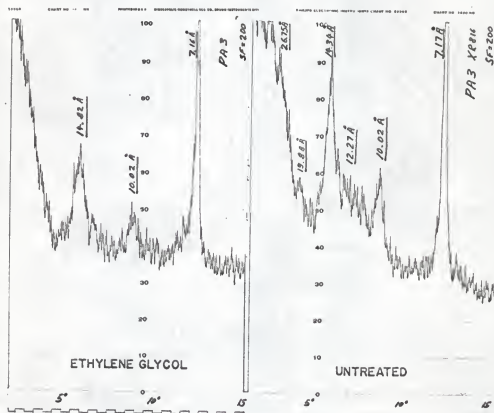
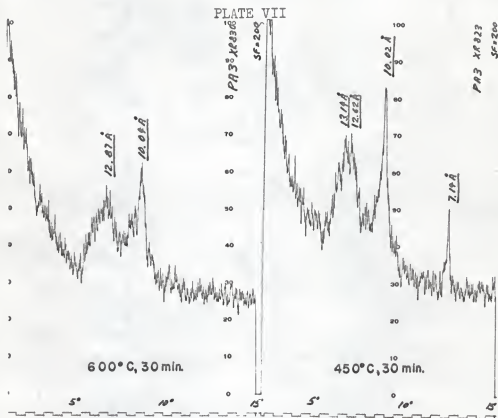
PLATE VI



X-RAY DIFFRACTION PATTERNS OF SAMPLE CO 6

EXPLANATION OF PLATE VII

Sample PA 3 was taken from an outcrop of a limestone in Pawnee County, Oklahoma, which is described as Cottonwood by Greig (1959). The sample contains illite (10 A.U.), randomly interlayered illite-montmorillonite (about 12 A.U.), randomly interlayered chlorite-vermiculite (14.3 A.U.), kaolinite (7.17 A.U.), and traces of a regularly interstratified clay mineral. Note the similarity of these patterns to that of the Morrill Limestone of Cowley County, Kansas, shown on Plate VI (see Correlation Problem in Discussion of Results).



X-RAY DIFFRACTION PATTERNS OF SAMPLE PA 3

Quantitative Evaluations

The percentages of the various clay minerals within an assemblage were determined by comparing the integrated intensities of the basal spacings. The area, bounded by the peak line and the background level, of the 001 reflections of glycolated as well as untreated samples was measured.

For minerals with similar structure the intensity generally increases towards the low angle side of the diffractogram (Johns, Grim, and Bradley, 1954). If the ratio of montmorillonite to illite is 1:1 then a 17 A.U. peak and a 14 A.U. peak would be about four and three times as intense respectively, as the 10 A.U. peak. For equal amounts of 14 A.U. chlorite and 10 A.U. illite the two peaks would be of nearly equal intensity. For equal amounts of kaolinite and illite the 7 A.U. kaolinite peak would be about two to three times as intense as the 10 A.U. peak (Weaver, 1958c, p. 270).

The reflective power of interlayered minerals is somewhat problematic. Bryson (1959) used the arithmetical mean of the reflecting powers of the two minerals, which constitute the random interstratification. Brown and Mac Ewan (1950) and Jonas and Brown (1959) calculated the intensities theoretically. Relating graphically the reciprocal spacing to the intensity they showed that the reflecting power of a randomly interlayered mineral is smaller than each of the single phases.

When comparing peak areas instead of peak heights the difference arising from the two concepts might be reduced somewhat, as can be seen from the diagrams of Brown and Mac Ewan (1950).

An example follows: a reflecting power of one, arbitrarily chosen, is assigned to illite. Thus a 14 A.U. montmorillonite has a reflecting power of three. The two species form a randomly interstratified mineral of equal proportions. After Bryson (1959) the reflecting power of the mineral would be two; after Brown and Mac Ewan (1950), however, the reflecting power would be less than one. This difference may only be of theoretical interest, because the intensities are also influenced by crystallinity, grain size, and the thickness of the clay-film. These variables will affect an interlayered mineral strongly, so that differences in quantitative evaluation arising from the two concepts become negligible. In this study a reflecting power of one was assumed for interlayered illite and montmorillonite.

In conclusion it may be stated that the method of measuring peak areas, because of the above mentioned uncertainties, should be regarded as only semiquantitative. However, it may be sufficiently accurate in a practical study for any variations within a rock sequence show up in a relative pattern, if all samples are treated in the same way.

RESULTS

Quantitative X-Ray Analysis

The percentages of the different clay mineral types in relation to the sum of all clay minerals is given for each sample in Table 2. These data were obtained from the X-ray diffractograms of the oriented slides. Also given is the ratio of the first two basal spacings for illite and for a part of the chlorites (Table 3). For some types of chlorite the ratio could not be determined because of admixtures of kaolinite. In Table 4 the non-clay minerals calcite, dolomite, quartz, and feldspar are recorded for the majority of the samples. The percentages of each of the single phases is given in relation to the sum of all four minerals. The data were obtained from the powdered samples of the untreated -200 mesh fraction. The non-clay mineralogy of the Cottonwood Limestone was mainly investigated to show possible relationships between carbonates and clay minerals. (See Diagenesis, Discussion of Results.) In cases where the percentage of a mineral was less than one percent of the total, "t" was used to indicate traces.

Diagrams were constructed to show the distribution of the clay minerals within the Cottonwood Limestone. Vertical variations in clay mineralogy at each sampling location are given on Plates VIII, IX, and X. The average lateral change along the outcrop belt is given on Plate XI.

Table 2: Percentages of Clay Minerals in Insoluble Clay Fraction of Cottonwood Limestone
(Percentages based on sub-peak area of basal spacing.)

Location of Sample	illite type 1	illite type 2	ill-mont	chl-ver	chl-ver	ver-chl	ver-chl	chl-mont	Ca-mont	Na-kaol mont	ill-mont 1:1	ill-mont 2:1	ill-mont c:1	chl-mont 1:1	sv.chl-mont 1:1
MANHATTAN AREA															
Spillway:															
SteSP	35	68	-	-	-	-	-	55	-	-	-	-	-	10	-
FiaSP	-	-	-	22	-	-	-	10	t	-	-	-	-	-	-
SP 5	72	-	21	-	-	-	-	t	-	-	-	-	-	-	-
SP 4	76	-	-	18	-	-	-	t	7	-	-	-	-	-	-
SP 3	69	-	-	31	-	-	-	t	6	-	-	-	-	-	-
SP 2	70	-	-	30	-	-	-	-	t	-	-	-	-	-	-
SP 1	64	-	36	-	-	-	-	-	t	-	-	-	-	-	-
EskSP 3	81	-	-	19	-	-	-	-	t	-	-	-	-	-	-
EskSP 2	71	-	-	21	-	-	-	8	t	-	-	-	-	-	-
EskSP 1	78	-	8	-	14	-	-	-	-	-	-	-	-	-	-
Intersection K 177 - K 13															
I 8	-	60	-	-	-	-	-	40	-	-	-	-	-	-	-
I 7	-	75	-	-	-	-	-	25	t	-	-	-	-	-	-
I 5	68	-	-	24	-	-	-	-	-	-	t	-	-	-	-
I 3	67	-	-	-	15	-	-	18	-	-	-	-	-	-	-
I 1	70	-	-	-	30	-	-	t	-	-	-	-	-	-	-
Stagg Hill															
ST 6	81	-	t	-	19	-	-	-	-	-	-	-	-	-	-
ST 5	71	-	-	-	29	-	-	-	-	-	-	-	-	-	-
ST 4	73	-	-	27	-	-	-	-	-	-	-	-	-	-	-
ST 3	69	-	-	31	-	-	-	t	-	-	-	-	-	-	-
ST 2	58	-	-	22	-	-	-	20	t	-	-	-	-	-	-
EskST	64	-	-	-	-	-	-	36	-	-	-	t	-	-	-

Table 2 (continued)

Location of Samples	illite type	1	2	ill- chl mont	chl- ver	chl- ver	chl- mont	ver	Ca- mont	Na- mont	kaol	ill- mont	ill- mont	ill- mont	ill- chl	ill- chl	chl- mont	chl- mont	sv. chl- mont	
				1:l	2:l	1:l	2:l	1:l	2:l	1:l	2:l	1:l	2:l	1:l	2:l	1:l	2:l	1:l	2:l	
Mc Dowell Creek																				
MD 5	-	67	-	-	18	-	15	t	t	-	-	-	-	-	-	-	-	-	-	-
MD 4	-	84	-	-	-	16	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MD 3	-	74	-	-	-	-	26	-	-	-	-	-	-	-	-	-	-	-	-	-
MD 2	-	77	-	-	-	23	-	-	t	-	-	-	-	-	-	-	-	-	-	-
EsAMD	-	-	71	-	-	-	29	-	-	-	-	-	-	-	-	-	-	-	-	-
Deep Creek																				
DC 8	-	72	-	-	-	-	t	-	-	-	-	-	-	-	-	-	-	-	-	-
DC 6	-	65	-	28	35	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DC 5	-	69	-	-	-	31	t	-	-	-	-	-	-	-	-	-	-	-	-	-
DC 4	-	-	77	23	-	-	t	-	-	-	-	-	-	-	-	-	-	-	-	-
DC 1	-	-	64	-	36	-	-	-	-	-	-	-	t	-	-	-	-	-	-	-
CHASE COUNTY																				
CH 5	-	74	-	-	13	-	13	-	-	-	-	-	-	-	-	-	-	-	-	-
CH 4	-	77	-	-	23	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CH 3	-	75	-	-	25	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CH 2	-	79	-	-	21	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CH 1	-	75	-	-	25	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 2 (continued)

Location of Samples	illite type	1	2	ill- mont	chl ver	chl- ver- chl mont	chl- ver- chl mont	Ca- mont	Na- mont	kaol mont	ill- mont 1:1	ill- mont 2:1	ill- chl mont 1:1	ill- chl- mont 1:1	sv. chl- mont 1:1
GREENWOOD COUNTY, KANSAS															
GR 5	-	80	-	-	-	-	-	20	-	-	-	-	-	-	-
GR 4	-	55	10	-	-	-	-	20	-	-	-	15	-	-	-
GR 3	-	80	20	-	-	-	-	-	-	-	-	-	-	-	-
GR 2	-	50	10	-	-	-	-	35	-	5	-	-	-	-	-
GR 1	-	60	-	-	t	-	-	30	10	-	-	-	-	-	-
COWLEY COUNTY, KANSAS															
CO 6	-	22	32	-	35	-	-	-	-	11	-	-	-	-	-
CO 5	-	22	56	-	-	-	-	13	-	t	-	-	-	4	-
CO 4	-	32	43	-	18	-	-	-	-	4	-	-	-	3	-
CO 3	-	24	51	14	-	-	-	t	-	-	-	t	6	5	-
CO 2	-	22	49	14	-	-	-	-	-	-	-	-	-	15	-
CO 1	-	22	49	18	-	-	-	-	-	-	-	-	11	-	-
RAWNEE COUNTY, OKLAHOMA															
RA 4	-	17	-	-	18	-	-	-	-	56	-	-	-	-	-
RA 3	-	26	20	-	43	-	-	-	-	20	-	-	-	t	-
RA 2	-	18	15	-	-	50	-	-	-	17	-	-	-	t	-
RA 1	-	17	34	-	-	29	-	t	-	9	-	-	-	6	-

Table 3
Peak Height Ratios $\frac{001}{002}$ for Illite
and Chlorite Minerals in Cottonwood Limestone

Location of Sample	Illite	Chlorite (incl.chl- ver,chl-mont)	Location of Sample	Illite	Chlorite (incl.chl- ver,chl-mont)
MANHATTAN AREA:			CHASE COUNTY, KANSAS:		
Spillway:			CH 5	2.1	1.2
SteSP	3.4	3.6	CH 4	5	---
FlaSP	1.7	1.3	CH 3	3.1	1.2
SP 5	3.7	1.8	CH 2	3.0	1.0
SP 4	3.2	1.2	CH 1	2.0	1.6
SP 3	4.0	1.5			
SP 2	3.0	1.6			
SP 1	3.5	1.5			
EskSP 3	3.1	1.6	GREENWOOD COUNTY, KANSAS:		
EskSP 2	2.8	1.5	GR 5	2.8	---
EskSP 1	2.5	1.2	GR 4	1.4	---
			GR 3	1.5	---
Intersection K 177 - K 13:			GR 2	1.8	---
I 8	1.5	3.8	GR 1	3.1	---
I 7	1.8	4.5	COWLEY COUNTY, KANSAS:		
I 5	3.5	---	CO 6	1.2	---
I 3	3.3	1.1	CO 5	1.4	---
I 1	2.1	2.0	CO 4	1.6	---
			CO 3	1.6	1.8
Stagg Hill:			CO 2	1.7	1.2
ST 6	3.1	1.6	CO 1	1.3	1.0
ST 5	2.1	1.5			
ST 4	2.3	1.5			
ST 3	2.5	2.0			
ST 2	1.3	1.5			
EskST	3.6	2.7			
Mc Dowell Creek:			PAWNEE COUNTY, OKLAHOMA:		
MD 5	2.1	2.4	PA 4	1.1	---
MD 4	3.8	1.3	PA 3	1.9	---
MD 3	3.3	2.3	PA 2	1.5	---
MD 2	3.8	1.8	PA 1	1.3	---
EskMD	1.8	2.8			
Deep Creek:					
DC 8	2.5	1.9			
DC 6	2.3	1.1			
DC 5	2.1	1.4			
DC 4	1.9	---			
DC 1	1.7	0.9			

Table 4

Percentages of Non-Clay Minerals According to X-Ray
Analysis of Untreated -200 Mesh Powder of Cottonwood Limestone







Location of Sample	Calcite	Dolomite	Quartz	Feldspar
MANHATTAN AREA				
Spillway				
SteSP	10	5	75	10
SP 5	90	-	10	-
SP 4	85	-	15	-
SP 3	85	-	15	-
SP 2	90	-	10	-
EskSP 3	60	15	20	5
EskSP 2	35	35	25	5
EskSP 1	55	15	25	5
Intersection K 177 - K 13				
I 8	85	-	15	-
I 7	90	-	10	-
I 5	90	-	10	-
I 3	90	-	10	-
I 1	85	-	15	-
Stagg Hill				
ST 6	85	-	15	-
ST 4	80	5	15	-
ST 3	78	10	12	-
ST 2	70	15	15	-
EskST	-	70	25	5
Mc Dowell Creek				
MD 4	75	-	25	-
MD 3	85	-	15	-
MD 2	85	-	15	-

Table 4 (continued)

Location of Sample	Calcite	Dolomite	Quartz	Feldspar
Deep Creek				
DC 8	85	-	15	-
DC 6	90	-	10	-
DC 5	85	-	15	-
DC 4	90	-	10	-
DC 1	85	-	10	5
CHASE COUNTY, KANSAS				
CH 4	85	8	7	-
CH 3	90	-	10	-
CH 2	93	-	7	-
GREENWOOD COUNTY, KANSAS				
GR 5	92	4	4	-
GR 3	95	-	5	-
COWLEY COUNTY, KANSAS				
CO 6	88	-	8	4
CO 4	55	-	40	5
CO 3	41	4	51	4
CO 2	65	6	25	4
CO 1	40	-	50	10
PAWNEE COUNTY, OKLAHOMA				
PA 4	-	-	90	10
PA 3	85	-	15	-

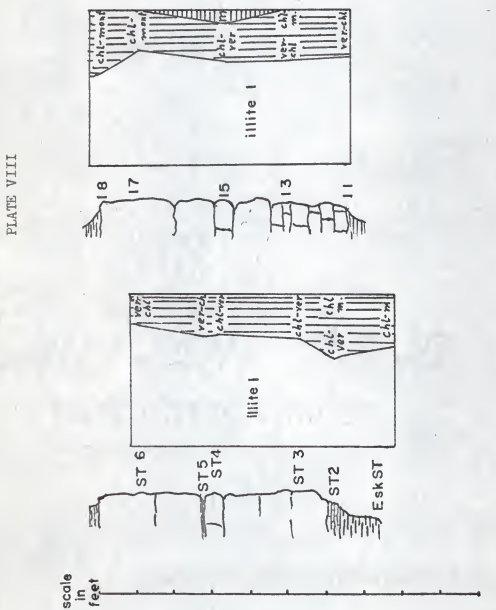
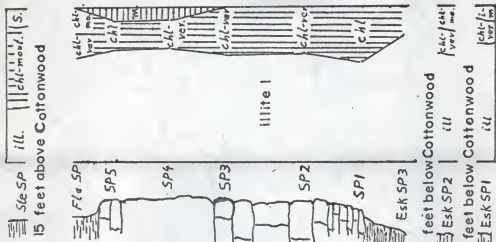
EXPLANATION OF PLATE VIII

The percentages of clay minerals in the Cottonwood Limestone at each single point in a vertical sequence are represented graphically and related to the percentages of the other points. Using these diagrams the vertical differences in clay mineralogy for each outcrop become visible. The sketches at the left of each diagram indicate from what part of the unit or units samples were taken. The following patterns were used to represent the clay mineral groups on the diagrams:

	illite
	chlorite minerals (incl. chlor.-verm., verm.-chlor., chlor.-mont.)
	montmorillonite
	illite-montmorillonite
	kaolinite
	superlattice minerals, regularly interstratified

The 3 outcrops shown on this Plate display only minor vertical changes in clay mineralogy within the Cottonwood.

PLATE VIII



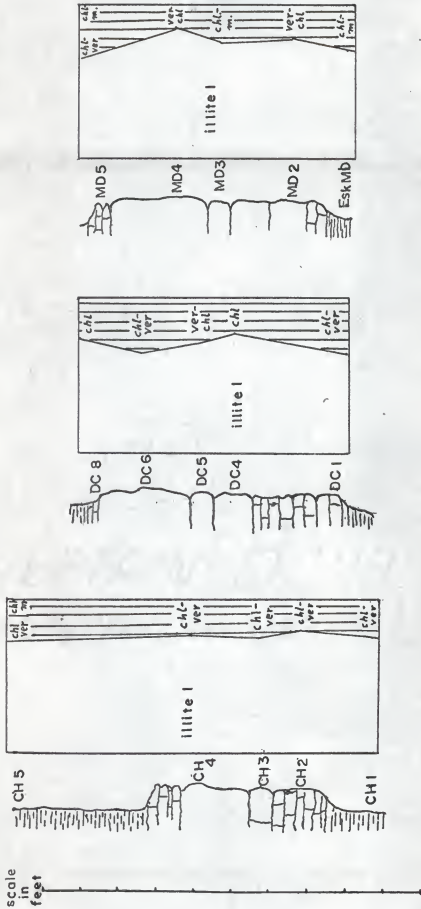
VERTICAL VARIATIONS IN CLAY MINERALOGY OF COTTONWOOD LIMESTONE AT STAGG HILL, INTERSECTION K 177 - K 13, AND SPILLWAY, RIBBY COUNTY, KANSAS

EXPLANATION OF PLATE I

Vertical variations in clay mineralogy of Cottonwood Limestones.

Diagrams show a monotonous clay assemblage, especially in the outcrop of Chase county.

PLATE IX



Chase County

Deep Creek

McDowell Creek

VERTICAL VARIATIONS IN CLAY MEMBERSHIP OF COTWOOD LIMESTONE AT MC DOWELL CREEK, DEEP CREEK, RILEY COUNTY, KANSAS, AND IN CHASE COUNTY, KANSAS

EXPLANATION OF PLATE X

Vertical variations in clay mineralogy of Cottonwood Limestone.

Vertical variations in clay mineralogy are much stronger in the strata of the southern facies (represented on this Plate) than in the limestone of the northern facies (Plates VIII and IX).

Note the similar clay mineral association in the limestone of Rawnee County, Oklahoma, and in the Morrill limestone of Cowley County, Kansas.

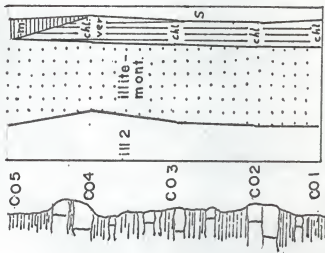
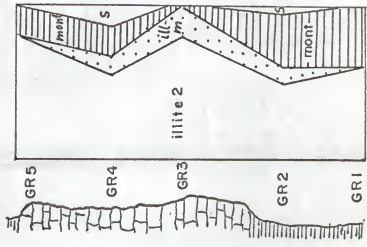
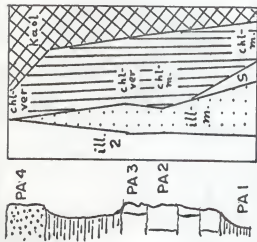


PLATE X

Morrill 5 feet above
Cottonwood

Pawnee County, Oklahoma

Cowley County, Kansas

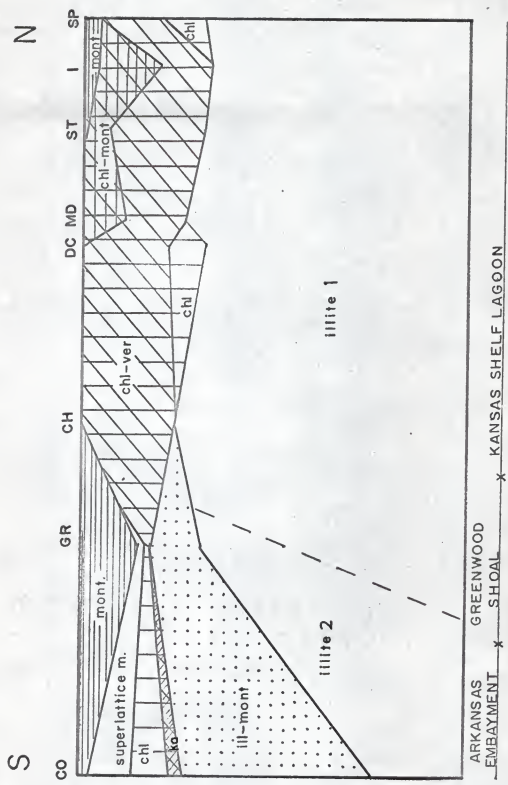
Greenwood County, Kansas

VERTICAL VARIATIONS IN CLAY MINERALOGY OF COTTONWOOD LIMESTONE IN GREENWOOD AND COWLEY COUNTIES, KANSAS, AND IN PAWNEE COUNTY, OKLAHOMA

EXPLANATION OF PLATE XI

Regional distribution of clay minerals in Cottonwood Limestone.

PLATE XI



REGIONAL DISTRIBUTION OF CLAY MINERALS IN COTTAGEWOOD LIMESTONE

Percentages of the types of clay at each sampling point were indicated graphically and connected by lines. Actual values between the investigated locations may not always coincide with the values represented by the lines; however, the general trend is indicated.

Samples of the Manhattan area and Chase County contain mainly illite type 1 and randomly interlayered chlorite-vermiculite. Some montmorillonite (5 to 10%) occurs in the outcrops of Spillway and Intersection K 177 - K 13, the two northernmost sampling locations. The ratio of illite to chlorite-vermiculite is generally constant. The average percentages of illite and chlorite-vermiculite in the Manhattan area and Chase County are 72% and 28% respectively. They do not change more than about $\pm 10\%$ in this region.

The percentages of clay minerals in the outcrop of Greenwood County change vertically somewhat more. Illite ranges from 55% to 80% within the Cottonwood. The rest is formed by montmorillonite, randomly interlayered illite-montmorillonite, and regularly interstratified clay minerals.

Vertical changes of the clay mineralogy within the Cottonwood of Cowley County, Kansas, are fairly small; whereas the outcrop in Pawnee County, Oklahoma, displays strong vertical variations within a short range, mainly because the percentage of kaolinite increases abruptly in the overlying red sandstone.

The average lateral variation in clay mineralogy along the outcrop belt of the Cottonwood Limestone, as shown on Plate XI, reveals two different

clay mineral facies: a northern facies that contains illite and chlorite-vermiculite in a constant ratio, and a southern facies that contains an assemblage of illite, illite-montmorillonite, chlorite, and regular interstratified minerals. The illite of both facies is different, as is shown by the different peak height ratio. The small amount of kaolinite, observed in the Florena Shale in Cowley county also emphasizes the two facies.

Acid Treatment

When X-rayed after treatment with HCl some samples showed a complete destruction of the chlorite peaks, whereas others did not. This behavior may be explained by different Fe - content or different crystallinity. Nearly all samples at Deep Creek, Intersection K 177 - K 13, and Stagg Hill lost the 14 A.U. peak after HCl treatment. Spillway and Mc Dowell Creek samples showed only traces of the 14 A.U. peak.

There seems to be a relation between acid solubility and peak height - ratio (e.g. Esk-ST vs. all other ST samples). Where the solubility is high the $\frac{001}{002}$ ratio is low; this may be caused by a higher content of iron. The basal spacings of the illite-montmorillonites in the southern facies were shifted from 12 A.U. to 11 A.U. by HCl treatment.

Because particle size, concentration of acid, time of reaction, and temperature affect the solubility of clay minerals in acid more quantitative results would be obtained if these variables could be held

constant. A clay fraction, which would still be in suspension when treated with acid, should provide better results than those of the oriented slide that was used in this study.

Ion Exchange Treatment

KOH Treatment.--In sample SP 4 only a part of the 14 A.U. peak, which represents chlorite-vermiculite plus montmorillonite, collapsed to 10 A.U., indicating that the montmorillonite had a high interlayer charge. The remaining 14 A.U. peak was due to chlorite-vermiculite. In sample GR 4 most of the 14 A.U. spacing (montmorillonite) collapsed to 10 A.U., whereas in sample CO 5 all 14 A.U. montmorillonite collapsed to 10 A.U. In sample PA 1 the illite-montmorillonite peak was shifted from 12 A.U. to 11 A.U. The chlorite-montmorillonite spacing decreased slightly from 14.5 to 14 A.U.

NH₄Cl Treatment.--In sample SP 4 almost no change was observed on the peaks of chlorite-vermiculite and montmorillonite. In sample I 7 the chlorite-montmorillonite basal spacing was shifted from 14.4 to 12.6 A.U. In sample PA 2 the chlorite-montmorillonite basal spacing collapsed from 14.4 to 13.6 A.U., and the illite-montmorillonite basal spacing collapsed from 12 to 10.7 A.U.

Microscopic Study

Thin sections of the Cottonwood Limestone in the Manhattan area showed in some cases single flakes of muscovite with a length of about

10 microns. The insoluble residue samples of the Cowley County outcrops revealed sericite (up to 10 microns in size) and also grains of sericitized feldspar. Chlorite and twinned plagioclase grains of an oligoclase-andesine composition were observed in the same samples.

DISCUSSION OF RESULTS

Clay mineral suites of sedimentary rocks are a product of many factors which work from the time a sediment is forming until the present. The most important of these factors are:

(1) source area: it ultimately determines what kind and what percentage of minerals will be delivered into a sedimentary basin; tectonic activity and climate are influencing factors.

(2) environment of deposition: it controls the alterations taking place on certain clay minerals. For example, in a marine environment with high salinity Potassium adsorption is greater than in a brackish environment.

(3) diagenesis: upon increasing temperature and pressure during burial of a sediment the mineral assemblages change in an attempt to approach chemical equilibrium.

(4) weathering: the mineral assemblages again are changed when the rock is exposed to atmospheric conditions.

A sedimentary rock is the result of a complex interaction of these four variables throughout time in an attempt to maintain chemical and physical equilibrium between the phases and the environment. In this part of the study an attempt is made to evaluate each of these variables in order to obtain a true picture of the clay mineral-formation and thereby to reconstruct the history of the sedimentary rock.

Source Area

Paleogeography.--Imbrie, Laporte, and Merriam (1959) and Laporte (1962) have worked out the paleogeography and paleoecology of the Beattie Formation. By using isopachous data, lithological evidence, and faunal provinces they distinguished several facies which originated in a morphologically differentiated area (Plate XII). Two major basins, the Arkansas embayment in southern Kansas and northern Oklahoma and the Kansas Shelf Lagoon in central and northern Kansas, were separated by the Greenwood Shoal. The Cottonwood sea was bounded on the northeast by a low continental mass and to the west and south by tectonically active lands. This assumption is supported by the clay mineralogy of the Florena Shale which consists of a muscovite-chlorite suite in the northern facies and an illite-montmorillonite suite in the southern facies, thus indicating two different source areas (Imbrie, Laporte, and Merriam, 1958, p. 75).

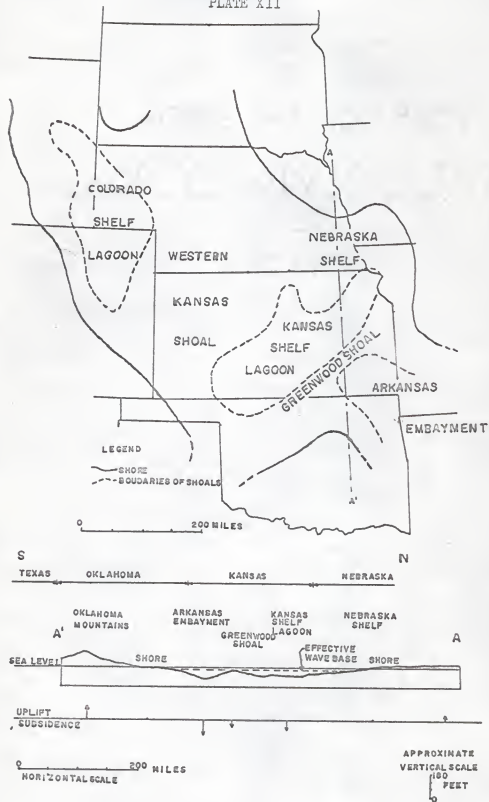
The clay mineralogy of the Cottonwood is in agreement with this conception. As mentioned before, a marked change of the clay minerals from north to south is observed. The illite (type 1) and chlorite-vermiculite assemblage of the north contrasts with the illite (type 2), illite-montmorillonite, chlorite, and regularly interstratified clays in the south.

Illite.--The two types of illite have nearly the same degree of crystallinity, as shown by their similar asymmetric 001 and 003 peaks.

EXPLANATION OF PLATE XII

Paleogeography during deposition of the Cottonwood Limestone, as proposed by Imbrie, Laporte, and Merriam (1959), and by Laporte (1962) in a slightly modified version.

Different rates of subsidence determine the morphology of the basins, which is critical in the formation of the facies.



PALEOGEOGRAPHY OF THE COTTONWOOD SEA
(after LAPORTE, 1962)

They differ in the peak height ratio $\frac{001}{002}$ which is over two in the Manhattan area and in Chase County and less than two in Cowley County. Because the intensities of X-ray reflections are related to the atomic scattering factors of the ions forming the structure (Brindley, 1961, p. 270), it is suggested that the marked difference in peak height ratio is caused by two chemically different illites, each of which was derived from a different source area. A weak diffuse 002 reflection, which would indicate Fe-substitution in the octahedral layer (Weaver, 1958, p. 267) was not observed; therefore, nothing specific is known about the nature of the cations. Both illite types, however, are dioctahedral as demonstrated by the 1.50 A.U. of the 060 spacing.

Chlorite.--The outcrops in Cowley County (southern facies) contain mainly chlorite as 14 A.U. clay, whereas in the northern facies mostly random interlayers of chlorite and vermiculite and some chlorite and montmorillonite were observed. The difference between chlorite and chlorite-vermiculite is not considered to be basic, and therefore need not be inherited from the source area. Only a slight change from the brucite layer of the chlorite to the hydrated interlayer cations of the vermiculite is responsible for that difference. If the alteration continues, a chlorite-montmorillonite interlayer will be formed. Chlorite and chlorite-vermiculite have not been found to differ significantly in crystallinity and in peak height ratio with respect to the two facies. In some cases the chlorite-montmorillonite interlayer showed a somewhat higher $\frac{001}{002}$ ratio than the chlorite-vermiculite interlayer. This may be

explained by the fact that crystallinity and ordering of chlorite-montmorillonite is lower than in chlorite-vermiculite. Therefore sub-multiple basal spacings are weakened, which results in a higher $\frac{001}{002}$ ratio.

In conclusion, sedimentary chlorite minerals of this study do not offer a key to different source areas.

Illite-Montmorillonite Interlayer.--Illite-montmorillonite interlayers comprise the major part of clay minerals in the southern facies. Their formation may be due to: (1) a partly weathered illite, which is derived from a soil, transported to the sea, and deposited without any structural change, (2) a partly collapsed montmorillonite caused by adsorption of Potassium in a marine environment, or (3) postdepositional weathering of an illite by exposure to atmospheric conditions in the present time or in the geologic past.

Because the illite-montmorillonite interlayer occurs in a shale, which does not allow much water movement, the possibility of postdepositional weathering seems to be excluded. The first two points, (1) and (2), are regarded as more important and will be discussed under "environment of deposition".

Montmorillonite.--The montmorillonite, which occurs in Greenwood County, is probably derived from illite or muscovite, as indicated by the collapse of the 14 A.U. spacing to 10 A.U. after KOH-treatment.

Montmorillonite, thus, may represent a weathering product formed either before or after deposition of the Cottonwood Limestone. Because montmorillonite occurs also in the Eskridge Shale, which hampers postdepositional weathering due to low permeability, it is assumed that the mineral was formed before deposition of the Cottonwood. It may have been derived from a soil in the southern source area.

Kaolinite.--Only traces of kaolinite were in the upper part of the Cottonwood Limestone in Cowley County. This mineral increases in the Florence into the Morrill where it composes about 10% of the clay fraction.

Kaolinite is supposed to be detrital. According to Keller (1964, p. 17) kaolinite may indicate a source area in which aluminum silicate parent material is altered under extensive leaching conditions. The area would therefore be well drained which would indicate high relief of the land, steep slopes, and high permeability of the soil. Montmorillonite could also be formed in the same general area as observed by Mohr and Van Baren (1954). However it would be restricted to water-logged sites where silica and metal ions are concentrated.

Vertical Variations in Clay Mineralogy.--The clay mineral assemblage in the southern facies changes vertically much more than that in the northern facies. Within the southern facies the extent of vertical variations increases southward. This might be the result of periodic changes in sedimentation patterns and indicate a small distance to the

source area in the south. The lack of significant vertical changes in the northern facies and also the small total clay fraction may indicate little influence of the source area in the north as well as the one in the south.

Environment of Deposition

The environment of deposition depends largely on the morphology of a sedimentary basin. The shape of the Cottonwood sea is roughly indicated on the paleogeographic map (Plate XII). More details are obtained by the isopachous data of the Florena Shale (Imbrie, Laporte, and Merriam, 1959) and by thickness measurements of the Cottonwood Limestone along its outcrop (Laporte, 1962). The isopachous map of the Florena Shale seems to indicate relationships between regional variations in the thickness of the shale and structural features proposed by Merriam (1963, p. 178) for pre-Desmoinesian post-Mississippian time. The forces, which caused the formation of these structures, may still have been active to a small extent in Permian time, and thus may have controlled the morphology of the basin. Due to different rates of subsidence some parts of the basin were morphologically lower than others, and therefore may have accumulated more sedimentary material. Although the Cottonwood Limestone displays an extremely constant thickness along its outcrop, slight variations in thickness at some places may be related to the proposed morphology of the basin.

Additional information for the Manhattan area is obtained from Parish's data on insoluble residue. The weight percentages of the fine fraction of the insoluble residues, which are given for several levels within the Cottonwood, are plotted on maps (Plate XIII). Thereby differentiated east-west running patterns are revealed, in agreement with the main structure of the Irving Syncline. Units of low percentages probably represent areas where the clays were winnowed by turbulent water.

Two parameters, which are related to the basin morphology, strongly control the alterations of clay minerals. These are: (1) salinity of the sea-water and (2) time of reaction between clay minerals and sea-water. The latter point depends on sedimentation rate and distance of source area.

Northern Facies.--The northern facies (bioclastic-fusuline) is characterized by a low sedimentation rate and probably a moderate distance to source area. The salinity seems to be high, as indicated by the restricted fauna (Laporte, 1962, p. 538). Bottom currents, which are indicated by scour and fill structures in the bioclastic facies (Laporte, 1962) and also by the occurrence of detrital heavy minerals (Wilbur, 1956), have probably reworked the sediment many times. By all these factors the time for an interaction between sea-water and clay minerals is increased.

The observed clay mineral assemblage seems to confirm these assumptions. An almost constant ratio of illite to chlorite-vermiculite or illite to chlorite-montmorillonite is reported for all samples in the Manhattan area. In Chase County this ratio is somewhat higher. Only

EXPLANATION OF PLATE XIII

Weight percentages of the fine fraction of the insoluble residues of the Cottonwood Limestone are given by Parish (1952). The percentages of zone A, B, C, and D, distinct levels within the Cottonwood in descending order, are represented on Figures 1, 2, 3, and 4, respectively. Points of approximately equal weight percentages are connected by lines.

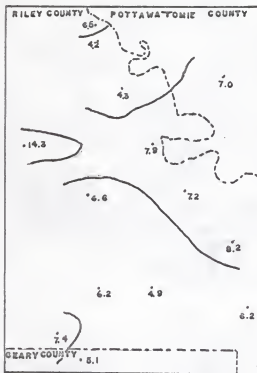


Fig. 1

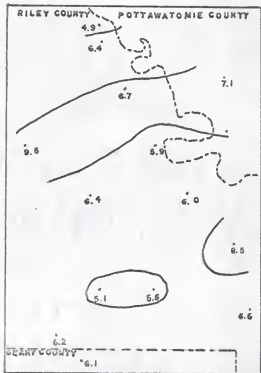


Fig. 2

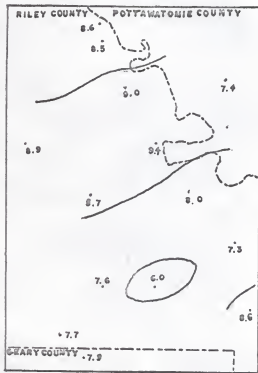


Fig. 3

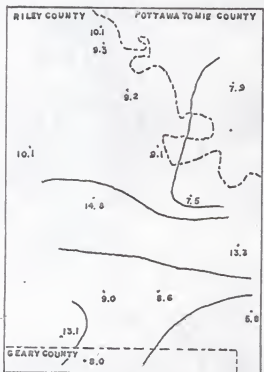


Fig. 4

SCALE 0 1 2 3 4 5 6 7 8 MILES

REGIONAL DISTRIBUTION OF WEIGHT PERCENTAGES OF THE FINE INSOLUBLE RESIDUES OF COTTONWOOD LIMESTONE

small amounts of free montmorillonite and traces of superlattice minerals are observed in the northern facies. The Stearns Shale and Eskridge Shale, on the other hand, show a considerable concentration of inter-layered minerals.

Because the activation energy for conversion is lowest for interlayered minerals (Keller, 1964, p. 52), these minerals are most easily involved in a reaction which might explain their instability in certain environments. It is assumed that, if superlattice minerals ever occurred in abundance in the northern facies, they would have had time to change to other phases. Also any degraded illite or chlorite that was transported into the basin would have had enough time to adsorb Potassium or Magnesium in order to fill the vacancies in the structure.

It is believed that the described mechanisms are responsible for the formation of the monotonous illite and chlorite-vermiculite inter-layer assemblage in the northern facies.

Southern Facies.--The southern facies is quite different from the northern one. It is a product of a different source area, shorter distance to source, and higher sedimentation rate. The two latter factors prevented the clay minerals from adjusting thoroughly to the environment. This might explain why an abundance of mixed-layer clays occurs in this facies. Normal salinity is suggested by the diversity of the fossil assemblage (Laporte, 1962).

Illite-Montmorillonite Interlayer.--The occurrence of randomly interlayered illite-montmorillonite can be explained in following ways:

(1) soil material containing illite-montmorillonite interlayer was transported to the sea and deposited without any significant change in the structure of the clay minerals.

(2) montmorillonite was transported to the sea and flocculated when entering the alkaline and saline environment. By picking up Potassium it collapses to a mixed-layer illite-montmorillonite. The reason it does not collapse completely to an illite may be due to (a) a high sedimentation rate which does not give enough time for full adsorption of Potassium, or (b) a low interlayer charge on the montmorillonite which is satisfied by partial adsorption of Potassium.

Because the interlayer illite-montmorillonite in this study did not collapse to 10 A.U. after the KOH treatment, it is assumed that this mixed-layered mineral was formed from a bentonitic montmorillonite. This assumption agrees with observations of Weaver (1959, p. 164) who also noted that interlayered illite-montmorillonite appears to have a 1M or 1M₁ structure which would indicate a low temperature environment of formation.

Montmorillonite.--The occurrence of montmorillonite in the outcrop of Greenwood County seems to be contradictory. In a marine environment it should have collapsed to illite, it collapsed to illite when treated with KOH in the laboratory. Maybe it was carried from the southern source area as very light fraction in the top water zone of the sea where the salinity was reduced, and became trapped by the algae of the Greenwood Shoal.

Also weathering may have caused the formation of montmorillonite in the Cottonwood Limestone. However, in this case it seems strange

that montmorillonite occurs also in the Eskridge Shale where weathering effects should be small.

Chlorite-Montmorillonite Interlayer.--In the outcrops in Cowley County interlayered chlorite-montmorillonite and swelling chlorite-montmorillonite interlayers were observed. Similar minerals are described in the literature. Corrensite, a regular interlayer of swelling chlorite and chlorite, is reported from the red-bed and evaporite sequences of the Triassic of Europe (Lippmann, 1954 and 1956), and from the Permian Stassfurthsalz in Germany (Braitsch, 1960). Regularly interstratified chlorite-montmorillonite is also known from the Permian in west Texas (Earley et al, 1956). The high crystallinity of these minerals, which is generally observed, suggested an authigenic origin. They are typical of hypersaline conditions.

The crystallinity of the similar Cottonwood minerals is low. From this and from paleontological evidence hypersaline conditions can be excluded.

Eryson (1959, p. 91) stated that the chlorite-montmorillonite and vermiculite-montmorillonite assemblage could be visualized as a composite concentrated deposit of reworked sediments which are intimately associated with the immediate source area in a brackish environment.

This description seems to fit the occurrence of chlorite-montmorillonite in the Cottonwood, although, as mentioned, normal salinity is suggested by the diversity of the fauna.

Diagenesis

Chemical reactions, which may take place in a sediment, are governed by Gibb's phase rule:

$$f = c - p + 2$$

where f = degrees of freedom or variance, c = number of components, p = number of phases. Considering mobile components c' (i.e., their chemical activities are fixed independently of the bulk composition of the sediment) the variance is reduced to:

$$f' = c - p + 2 - c'$$

(Korzhinskii, 1950, p. 52; Thompson, 1955, p. 80). For arbitrary values of temperature and pressure ($f' = 2$) the maximum number of phases is:

$$p = c - c'$$

Equilibrium reactions within a system are represented on phase diagrams. Zen (1959) in his study of modern sediments off the coast of Peru and Chile used such diagrams to interpret the assemblages he found (Fig. 1, Plate XIV). Seven components were considered: CaO, MgO, FeO, Al₂O₃, SiO₂, CO₂, and H₂O. The CO₂ and H₂O are mobile components and SiO₂ is assumed to be in excess; thus, only CaO, Al₂O₃, MgO, and FeO are left for representation on the phase diagram. MgO and FeO are treated together as one component because they substitute for each other. The formation of illite was not considered because this would involve an additional phase, K₂O.

EXPLANATION OF PLATE XIV

Fig. 1: The diagrams were given by Zen (1959) in his study on alterations of modern sediments. They are useful when dealing with clay mineral-carbonate relations, such as occurring in limestones during diagenesis. Three possible equilibrium assemblages are shown. They are related by following schematic equations:

From (a) to (b): montmorillonite + calcite + carbon dioxide
= kaolinite + dolomite + quartz + albite + water

From (b) to (c): montmorillonite + dolomite
= calcite + chlorite + albite + quartz + water
+ carbon dioxide

The phase assemblages of dolomite-kaolinite-chlorite or chlorite-kaolinite-calcite, for example, would be incompatible according to these diagrams.

Fig. 2: The 5 mineral assemblages represented on the diagram were found in buried limestones (Peterson, 1961 and 1962) thus proving the efficiency of the phase rule. The assemblages are:

1. dolomite, corrensite
2. calcite, dolomite, corrensite
3. calcite, corrensite
4. calcite, chlorite-vermiculite
5. calcite, chlorite-vermiculite, montmorillonite (containing some mixed 10 A.U. layers)

No kaolinite has been found; its possible formation is indicated by the dotted lines.

PLATE XIV

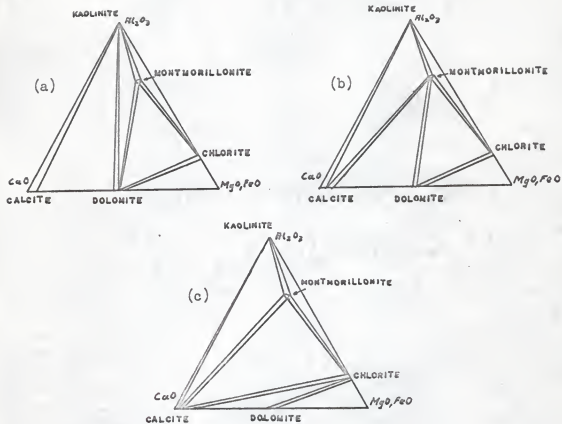


Fig. 1

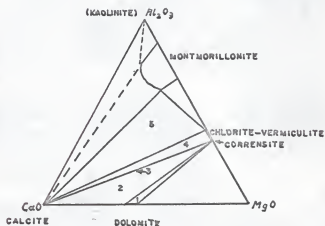


Fig. 2

TERNARY DIAGRAMS REPRESENTING CLAY MINERAL AND CARBONATE
EQUILIBRIA IN SEDIMENTS

Peterson (1961 and 1962), who investigated the Mississippian carbonate rocks in Tennessee, found the mineral assemblages to obey the phase rule. The sediments were buried at least 4500 feet deep. The assemblages he discovered are represented on Fig. 2 of Plate XIV.

Clay mineral assemblages observed in the Cottonwood Limestone did neither confirm nor disprove the results of the above mentioned studies. Some of the samples seemed to obey the phase rule and others did not. This is probably due to the methods applied or to limitations of the theories as exact criteria for distinguishing between the theoretical models are lacking. The clay fraction is generally less than 10% of the Cottonwood Limestone. The clays are finely distributed within the carbonate material which suggests at least local equilibrium. The 200-500 g samples, which were commonly used in this study, are probably too big to show local equilibrium relationships. Peterson (1961 and 1962), for comparison, used one gram rock samples in his investigation. In addition, detailed textural studies are needed in order to say anything definite about phase relations.

There might also be the possibility that equilibrium has not yet been attained because of too low reaction rates at near-surface temperatures and pressures (Garrels, 1959).

Weathering

Although the clay minerals are generally thought to be the end product of weathered non-clay minerals they too are altered by weathering. Murray

and Leininger (1956) and Droste (1956) studied such processes. They reported that illite and chlorite would form illite-montmorillonite and vermiculite respectively. According to Rich (1958) the first stages in the weathering of micas are characterized chemically by removal of K and Mg by dissolution and Fe by oxidation, and structurally by loosening and expanding of the crystal structure to form illite-montmorillonite and vermiculite. Bryson (1959) investigated weathered and unweathered parts of the same outcrop. He reported that illite was changed to montmorillonite and chlorite to vermiculite. An assemblage of chlorite and calcite changes, according to Bryson, to poorly crystalline Fe-rich chlorite-montmorillonite and dolomite. Weathering of clay minerals is more severe in limestone than in shale because of higher permeability (Milne and Earley, 1958, p. 338).

Some of the above mentioned alterations were observed in this investigation. Chlorite-vermiculite and chlorite-montmorillonite in the limestone of the northern facies are considered to be formed by weathering. Locations like Stagg Hill, Mc Dowell Creek, and Intersection K 177 - K 13 show relatively more chlorite-montmorillonite and chlorite-vermiculite than outcrops at Deep Creek (Interstate 70) and Spillway, which have been exposed to atmospheric conditions only in recent years. The change from the brucite layer in the chlorite to the hydrated interlayer cations in the vermiculite involves a partial removal of Magnesium. This process is probably caused by acidic leaching. However, because the pH of a limestone in equilibrium with water and atmospheric CO₂ is slightly alkaline (Garrels, 1960) some mechanism has to be involved in which the

alkalinity is lowered. Leaching by humic acids derived from soil may have been the mechanism for this process.

It is assumed that weathering did not play an important role in changing the clay mineralogy of the southern facies because of the lower permeability of the shales in this facies.

Correlation Problem

During the study of the southern facies the problem arose as to whether the Cottonwood in Pawnee County, Oklahoma, and the Cottonwood in Cowley County, Kansas, represented the same stratum. Greig (1959), who mapped the outcrops of Pawnee County, described the Cottonwood as a limestone that is 2.2 feet thick. Laporte (1962), on the other hand, reported that the Cottonwood thins southward into Oklahoma and he described an outcrop in Osage County, Oklahoma, north of Greig's area, where the Cottonwood (silty Osagia facies) is represented by 6 inch thick beds of limestone with shaly interbeds. The outcrops of Greig's Cottonwood and Laporte's Cottonwood are less than 10 miles apart. The clay mineralogy of the limestone in Pawnee County was similar to the clay mineralogy of the Morrill Limestone of Cowley County, Kansas (see Plates VI and VII). Even the proportions of the distinct clay mineral types agreed with each other (see Table 2 and Plate X). In addition, the algal pellets reported from the Morrill of Cowley County could also be observed in the "Cottonwood" of Pawnee County. Based on lithology, paleontology, and clay mineralogy

it is concluded that the correlation of the Cottonwood is not assured for the area of Pawnee and Cowley County. It is thought that the Cottonwood in Pawnee County and the Morrill in Cowley County represent an identical stratum.

As was observed in the northern facies, clay minerals in beds of limestone stay constant in their relative proportions over an extended area. This property was used to correlate the limestone of the southern facies. It seems that quantitative clay mineral determination can serve as a supplementary means in correlation studies, although there are simpler ways such as paleontologic and lithologic features.

SUMMARY

The clay mineralogy of the Cottonwood Limestone Member of the Beattie Limestone is mainly a product of source area and environment of deposition; diagenetic and weathering effects have caused only minor changes. Based on the general composition of the clay mineral assemblages in the two facies and on variations of single minerals, such as illite type 1 and type 2, it is concluded that the two facies are a product of different source areas and different environments.

High salinity, considerable distance to source area, and a low sedimentation rate favored the possibility of alteration of detrital clay minerals in the northern basin that resulted in a significantly monotonous clay assemblage of illite and interlayered chlorite-vermiculite. Even the ratio of illite to chlorite-vermiculite is constant in the Manhattan area and is only slightly higher in Chase County.

A higher sedimentation rate, shorter distance to source area, and normal salinity in the southern basin controlled the formation of the clay mineral assemblage there which consists of illite, illite-montmorillonite, chlorite, and regularly interstratified clay. Especially, the regularly interstratified minerals seem to indicate an immature stage of alteration. Randomly interlayered illite-montmorillonite, however, has almost reached its full capacity for Potassium fixation thus indicating origin from a low charged montmorillonite. This montmorillonite may have been formed by alteration of volcanic ash.

Diagenetic effects, both in the southern and in the northern facies, have not been confirmed. It is assumed that if present they have worked according to the phase rule to remove disequilibria.

Weathering had a stronger influence on the limestone of the northern facies than on the shale of the southern facies because of higher permeability. It caused the formation of chlorite-vermiculite, vermiculite-chlorite, and chlorite-montmorillonite from chlorite and of montmorillonite from chlorite and/or illite.

As an incidental result of the clay mineral investigation it was found that the "Cottonwood" Limestone in Pawnee County, Oklahoma and the Morrill Limestone in Cowley County, Kansas, represent an identical stratum. Quantitative clay mineralogy may thus be used as a supplementary means for correlation studies. This is also supported by the constant illite and chlorite-vermiculite assemblage in the limestone of the northern facies.

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REFERENCES

- Asmussen, L. E., 1958, Clay mineralogy of some Permian shales and limestones: Kans. St. Univ. M. S. Thesis, 73 p.
- Barshad, I., 1954, Cation exchange in micaceous minerals, Part II: Soil Sci., v. 78, p. 57 - 76.
- Bass, N. W., 1929, The geology of Cowley County, Kansas, with special reference to the occurrence of oil and gas: Kans. Geol. Survey Bull., v. 12, 203 p.
- Bradley, W. F., and Weaver, C. E., 1956, A regularly interstratified chlorite-vermiculite clay mineral: Am. Mineralogist, v. 41, p. 497-504.
- Braitsch, O., 1960, Mineral Paragenese und Petrologie des Stassfurthsalzes in Reyershausen: Kali u. Steinsalz, p. 1-14.
- Brindley, G. W., 1961, Chlorite minerals, in the X-ray Identification and Crystal Structures of Clay Minerals: Mineralogical Society, London, Jarrold and Sons Ltd., p. 242-296.
- Brown, G., 1961, (editor), The X-ray identification and crystal structures of clay minerals: Mineralogical Society, London, Jarrold and Sons Ltd., 544 p.
- , and Mac Ewan, D. M. C., 1950, The interpretation of X-ray diagrams of soil clays, Part II: Jour. Soil Sci., v. 1, p. 234-253.
- Bryson, W. R., 1959, Clay mineralogy and clay paragenesis of the upper Chase and lower Sumner limestones and shales in north and east central Kansas: Kans. St. Univ. M. S. Thesis, 120 p.
- Cullity, B. D., 1956, Elements of X-ray diffraction: Reading, Addison-Wesley Publishing Company, Inc., 514 p.
- Degens, E. T., Williams, E. G., and Keith, M. L., 1957, Environmental studies of carboniferous sediments, Part I: Geochemical criteria for differentiating marine from fresh-water shales: Am. Assoc. Petroleum Geologists Bull., v. 41, p. 2427-2455.
- Droste, J. B., 1956, Alteration of clay minerals by weathering in Wisconsin tills: Geol. Soc. America Bull., v. 67, p. 911-915.
- Earley, J. W., Brindley, G. W., Mc Veagh, W. J., and Vanden Hende, R. G., 1956, A regularly interstratified montmorillonite-chlorite: Am. Mineralogist, v. 41, p. 258-267.

- Garrels, R. M., 1959, Rates of geochemical reactions at low temperatures and pressures, in *Researches in geochemistry*: New York, John Wiley and Sons, Inc., p. 25-37.
- Garrels, R. M., 1960, Mineral equilibria at low temperature and pressure: New York, Harpers and Brothers, 254 p.
- Greig, P. B., 1959, Geology of Pawnee County, Oklahoma: Oklahoma Geol. Survey Bull. 83, 183 p.
- Griffin, M. G., 1962, Regional clay mineral facies - products of weathering intensity and current distribution in the northeastern Gulf of Mexico: Geol. Soc. America Bull., v. 73, p. 737-768.
- Grim, R. E., Lamar, J. E., and Bradley, W. F., 1937, The clay minerals in Illinois limestones and dolomites: Jour. Geol., v. 45, p. 829-843.
- 1953, Clay mineralogy: New York, Mc Graw-Hill, 384 p.
- and Johns, W. D., 1954, Clay minerals in the northern Gulf of Mexico: Clays and Clay Minerals, 2nd Conf., New York, Pergamon Press, p. 81-103.
- 1958, Concept of diagenesis in argillaceous sediments: Am. Assoc. Petroleum Geologists Bull., v. 42, p. 246-253.
- Hargadine, G. D., 1959, Clay mineralogy and other petrologic aspects of the Grenola Limestone Formation of the Manhattan, Kansas, area: Kans. St. Univ. M. S. Thesis, 76 p.
- Huber, D. D., 1965, Petrology of the Crouse Limestone in the vicinity of Manhattan, Kansas: Kans. St. Univ. M. S. Thesis, 133 p.
- Hurley, P. M., Brookins, D. G., Pinson, W. H., Hart, S. R., and Fairbairn, H. W., 1961, K-Ar age studies of Mississippi and other river sediments: Geol. Soc. America Bull., v. 72, p. 1807-1816.
- Imbric, J., Laporte, L., and Merriam, D., 1959, Beattie Limestone facies and their bearing on cyclical sedimentation theory: Kans. Geol. Soc. Guidebook, 24th Field Conf., p. 69-78.
- Johns, W. D., Grim, R. E., and Bradley, W. F., 1954, Quantitative estimation of clay minerals by diffraction methods: Jour. Sed. Petrology, v. 24, p. 242-251.
- Jonas, E. C., and Brown, T. E., 1959, Analysis of interlayer mixtures of three clay mineral types by X-ray diffraction: Jour. Sed. Petrology, v. 29, p. 77-86.

- Keller, W. D., 1964, Processes of origin and alteration of clay minerals, in *Soil Clay Mineralogy, A symposium*: The University of North Carolina Press, Chapel Hill, p. 3-76.
- Klug, P. K., and Alexander, L. E., 1954, *X-ray diffraction procedures*: New York, John Wiley & Sons, Inc., 716 p.
- Korzhinskii, D. S., 1950, Phase rule and geochemical mobility of elements: 18th Internat. Geol. Cong. Proc., Section A, Problems of Geochemistry, p. 50-57.
- Laporte, L. F., 1962, Paleocology of the Cottonwood Limestone (Permian), northern midcontinent: *Geol. Soc. America Bull.*, v. 73, p. 521-544.
- Lippmann, F., 1954, Ueber einen Keuperton von Zaisersweiher bei Maulbronn: *Heidelberg. Beitr. z. Petrog.*, v. 4, p. 130-134.
- 1956, Clay minerals from the Roet member of the Triassic near Goettingen, Germany: *Jour. Sed. Petrology*, v. 26, p. 125-139.
- Mac Ewan, D. M. C., 1949, Some notes on the recording and interpretation of X-ray diagrams of soil clays: *Jour. Soil Sci.*, v. 1, p. 90-103.
- 1961, Montmorillonite minerals, in *The X-ray Identification and Crystal Structures of Clay Minerals*: Mineralogical Society, London, Jarrold and Sons Ltd., p. 143-207.
- Mc Pherron, D. S., 1956, Clay mineralogy of some of the Permian shales: *Kans. St. Univ. M. S. Thesis*, 57 p.
- Merriam, D. F., 1963, The geologic history of Kansas: *Kansas Geol. Survey Bull.* 162, 317 p.
- Milne, I. H., and Earley, J. W., 1958, Effect of source and environment on clay minerals: *Am. Assoc. Petroleum Geologists Bull.*, v. 42, p. 328-339.
- Mohr, E. C. J., and Van Baren, J., 1954, *Tropical soils*: New York, Interscience, Publishers.
- Murray, H. H., and Leininger, R. K., 1956, Effect of weathering on clay minerals: *Clays and Clay Minerals*, 4th Conf., New York, Pergamon Press, p. 340-347.
- O'Connor, H. G., 1963, Changes in Kansas stratigraphic nomenclature: *Am. Assoc. Petroleum Geologists Bull.*, v. 47, p. 1873-1877.
- Ostrom, M. E., 1961, Separation of clay minerals from carbonate rocks by using acid: *Jour. Sed. Petrology*, v. 31, p. 123-129.

- Barish, K. L., 1952, A stratigraphic study of the insoluble residues of the Council Grove Group limestones of the Manhattan, Kansas, area: Kans. St. Univ. M. S. Thesis, 125 p.
- Peterson, M. N. A., 1961, Expandable chloritic clay minerals from upper Mississippian carbonate rocks of the Cumberland Plateau in Tennessee: Am. Mineralogist, v. 46, p. 1245-1269.
- 1962, The mineralogy and petrology of upper Mississippian carbonate rocks of the Cumberland Plateau in Tennessee: Jour. Geol., v. 70, p. 1-31.
- Ray, S., Gault, H. R., and Dodd, C. G., 1957, The separation of clay minerals from carbonate rocks: Am. Mineralogist, v. 42, p. 681-685.
- Rich, C. I., 1958, Muscovite weathering in a soil developed in the Virginia Piedmont: Clays and Clay Minerals, 5th Conf., New York, Pergamon Press, p. 203-212.
- Richardson, H. M., 1961, Phase changes which occur on heating kaolin clays, in The X-ray Identification and Crystal Structures of Clay Minerals: Mineralogical Society, London: Jarrold and Sons Ltd., p. 132-142.
- Shimane, H., and Sudo, T., 1956, Clay mineral associated with vermiculite: Clay Min. Bull., v. 3, p. 297-306.
- Smith, J. V., and Yoder, H. S., 1956, Experimental and theoretical studies of the mica polymorphs: Mineralogical Magazine, v. 31, p. 209-235.
- Suggestions to Authors of the Reports of the United States Geological Survey, 1958: Washington, U. S. Govt. Printing Office, 255 p.
- Swineford, A., 1955, Petrography of upper Permian rocks in south-central Kansas: Kansas Geol. Survey Bull. 111, 179 p.
- Tables for Conversion of X-ray Diffraction Angles to Interplanar Spacing, 1950: Washington, U. S. Govt. Printing Office, 159 p.
- Thompson, J. B., Jr., 1955, The thermodynamic basis for the mineral facies concept: Am. Jour. Sci., v. 42, p. 842-858.
- Vivaldi, J. L. M., and Mac Ewan, D. M. C., 1960, Corrensite and swelling chlorite: Clay Min. Bull., v. 4, p. 173-181.
- Walker, G. F., 1961, Vermiculine minerals, in The X-ray Identification and Crystal Structures of Clay Minerals: Mineralogical Society, London, Jarrold and Sons Ltd., p. 297-324.

- Watkins, K. N., 1957, Clay mineralogy of some Permian and Pennsylvanian limestones: Kans. St. Univ. M. S. Thesis, 64 p.
- Weaver, C. E., 1956, The distribution and identification of mixed layer clay minerals in sedimentary rocks: Am. Mineralogist, v. 41, p. 212-221.
- 1958a, A discussion on the origin of clay minerals in sedimentary rocks: Clays and Clay Minerals, 5th Conf., New York, Pergamon Press, p. 159-173.
- 1958b, The effects and geological significance of potassium fixation by expandable clay minerals derived from muscovite, biotite, chlorite, and volcanic material: Am. Mineralogist, v. 43, p. 839-864.
- 1958c, Geologic interpretation of argillaceous sediments: Am. Assoc. Petroleum Geologists Bull., v. 42, p. 254-309.
- 1959, The clay petrology of sediments: Clays and Clay Minerals, 6th Conf., New York, Pergamon Press, p. 154-187.
- Wilbur, R. O., 1956, Petrographic analysis of the insoluble residue of the Permian Chase and Council Grove limestones with regard to the origin of chert: Kans. St. Univ. M. S. Thesis, 88 p.
- Yoder, H. S., and Eugster, H. P., 1955, Synthetic and natural muscovites: Geochim. et Cosmochim. Acta, v. 8, p. 225-280.
- Zen, E-An, 1959, Clay mineral-carbonate relations in sedimentary rocks: Am. Jour. Sci., v. 257, p. 29-43.
- 1962, Problem of the thermodynamic status of the mixed-layer minerals: Geochim. et Cosmochim. Acta, v. 26, p. 1055-1067.

CLAY MINERALOGY OF COTTONWOOD LIMESTONE

by

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The clay mineralogy of the Cottonwood Limestone Member of the Beattie Limestone was investigated along an outcrop belt from northern Kansas to northern Oklahoma. Thirty-one samples from five locations were studied in the Manhattan area; twenty samples from an additional four locations, each 40 to 50 miles apart, were investigated from central Kansas to northern Oklahoma.

Each sample was divided into two parts; one part was used to determine the non-clay minerals, and the other part was treated with acetic acid to remove carbonates before identification of the clay minerals. Both oriented and powdered samples were X-rayed, and the type and percentage of clay-minerals and non-clay minerals were quantitatively determined. In some cases examination with a petrographic microscope supplemented the X-ray study.

Two distinct facies are recognized; a northern one encompassing the Manhattan area and Chase County, and a southern one extending southward from Greenwood County to northern Oklahoma. Both facies are separated by outcrops in Greenwood County which form a special facies (platy algal facies after Laporte, 1962). The northern facies province is characterized by a constant illite and mixed-layered chlorite-vermiculite assemblage; whereas, the southern one is characterized by illite, randomly interlayered illite-montmorillonite, chlorite, and regularly interstratified clay minerals. Types of single minerals, such as illite type 1 and type 2, are also associated with the facies. Type 1 of the north was distinguished from type 2 of the south by determining the peak height ratio of the first two basal spacings. It was concluded that the two facies were mainly the

product of different source areas and different environments of deposition. Diagenetic and weathering effects were assumed to be of minor influence.

High salinity, considerable distance to source area, and a low sedimentation rate favored the possibility of alteration of the detrital clay minerals in the northern basin, thus producing an illite and chlorite-vermiculite assemblage in constant proportions.

A higher sedimentation rate, shorter distance to source area, and normal salinity controlled the formation of illite, illite-montmorillonite, chlorite, and regularly interstratified minerals of the southern basin. Randomly interlayered illite-montmorillonite, forming the major phase in this facies, indicates a pre-existing montmorillonite of low interlayer charge, which may have been formed by alteration of volcanic ash.

Diagenetic effects were not definitely confirmed. Weathering had a stronger influence in the limestone of the northern facies than in the shale of the southern facies because of higher permeability. Weathering produced randomly interlayered chlorite-vermiculite, vermiculite-chlorite, and chlorite-montmorillonite from chlorite, and montmorillonite from chlorite and/or illite.

As an incidental result of the clay mineral investigation it was found that the "Cottonwood" Limestone in Pawnee County, Oklahoma, and the Morrill Limestone in Cowley County, Kansas, represent an identical stratum. Thus quantitative clay mineralogy combined with paleontologic and other lithologic features proved to be useful in correlation.