

CLAY MINERALOGY OF HAVENSVILLE SHALE

by

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INTRODUCTION

Purpose of Study

In order to understand the possible geologic factors which have affected the distribution of clay minerals in ancient sedimentary rocks, a stratigraphic unit from the Lower Permian Series in Kansas was selected as a study unit.

The stratigraphy of the Havensville Shale Member of the Wreford Limestone Formation has been described in detail by Hattin (1957). Although the physical characteristics of the source area are not certain, the Havensville Shale crops out more than 200 miles along the Prairie Plains Homocline in Kansas and Oklahoma with a definite trend of thickening toward northern Kansas. It was hoped that the effects of unknown and poorly defined variables, such as different source areas, climate, and topography, could be held to a minimum by choosing one stratigraphic unit.

The principal objectives and steps of this study are as follows:

1. Identification of the vertical and lateral clay mineral assemblages for samples from selected localities, using X-ray diffraction.
2. Recognition of possible significant trends in the clay mineral assemblage from qualitative and semi-quantitative interpretation of the X-ray data.
3. Measurement of the K/Rb ratios for samples from selected localities.

4. Determination of the polytypes of the phyllosilicates.
5. Measurement of the Rb/Sr age of the clay minerals.

The above considerations may allow some constraints to be set upon the factors responsible for the total clay mineral assemblage of the Havensville Shale.

Review of the Literature

Considerable discussions have accumulated on the origin of clays and the factors affecting the distribution of clays both in Recent and ancient sediments. These discussions have been particularly concerned with:

1. whether there occurs any structural change in clay minerals when they pass from the fluvial to the marine environment, and
2. the reasons for such a change,
3. the extent of diagenetic effects on the mineral composition, and
4. the relative importance of authigenesis or neoformation in a particular environment.

Examples of the modification of clay minerals in the marine environment can be found in the early papers. Grim, Dietz, and Bradley (1949) found, in their study of clay minerals in sediments off the Pacific Coast, that samples taken near the coast were richer in kaolinite than montmorillonite and illite. They suggested that there was a transformation of the clay minerals into illite and chlorite by adsorption of potassium and magnesium ions in the ocean water. Similar results were also found for sediments in

the Gulf of Mexico and the Mississippi River delta (Grim and Johns, 1954; Johns and Grim, 1958).

Milne and Early (1958) explained that the clay mineral assemblage in an area of active deposition is dependent largely on the character of the source area, whereas alteration of clay minerals can be expected where the sedimentation rate is low and sufficient time is available for chemical equilibrium between the sea water and the clay minerals. This conclusion was based on the clay mineral study in the sediments between the Mississippi delta and the Mobile River in southern Alabama.

Powers (1954, 1959) found interesting results at Chesapeake Bay where illite was dominant. Mixed layers, vermiculite and chlorite were formed within the estuary. With the increasing salinity of the environment, the stability of the chloritic minerals upon heating also increased. He suggested that there could be an evolution of the disordered micaceous lattices, inherited from the land, toward chlorite.

Contrasting results indicating little modification of clay minerals in the marine environment can also be found. Murray and Sayyab (1955), in their study of the sediments off the North Atlantic coast, found that the basic clay minerals did not change with distance offshore or with depth, but improved crystallinity was found with corresponding decrease in the amount of mixed-layers. Likewise, Taggart and Kaiser (1960) did not find any modification in clay minerals of the Mississippi deltaic sediments.

Diagenetic evolution of clay minerals can also be evaluated if one

considers a thick sequence of sediments with a known source. Powers (1959, 1967) and Burst (1959, 1969), respectively, have studied the evolution of clay minerals in the Tertiary Series off the Gulf Coast. They observed a decrease in montmorillonite as a function of depth. Montmorillonite seemed to be converted to illite by a substitution of magnesium for aluminum in the silicate structure with consequent fixation of inter layer potassium. Mixed-layer illite was found at intermediate depth.

Quite different interpretation of this subject was discussed by Weaver (1958b). He considered that variations in clay mineral assemblages are mainly due to the changes in the source of the sediments or in the distance from the shore. Weaver (1958a, 1958b) contended that most of the clays in sediments were detrital and only slight modifications could occur in the depositional environment, in the form of cation adsorption or reconstitution of weathered illites and chlorites back to original form. He believed that none of the major clay mineral types are restricted to particular environments and no basic structural change occurs in different environments, whereas some other investigators (Millot, 1952, 1970; Grim, 1958) favor the concept that certain clay minerals are more common in certain environments than in others.

Whitehouse, Jeffrey and Debrecht (1960) made important contribution with their work on differential settling of clay minerals. Their study of settling velocity in marine and brackish water with 1500 samples of clay from all kinds of sources showed that chlorite settles slightly faster than

kaolinite, and vermiculite faster than illite.

It is obvious that very different opinions have been viewed by different investigators on the origin and distribution of clay minerals in Recent and ancient sediments. It seems particularly problematic whether transformations and diagenesis may occur to a large extent in clay mineral assemblages.

In the past 15 years several master's theses and research papers at Kansas State University have dealt with the clay minerals in the Kansas stratigraphic column. These studies showed that the clay mineral suites in the vicinity of Manhattan generally consist of a monotonous sequence with little vertical and lateral changes.

Mc Pherron (1956) studied clay minerals in most of the shale units in the Council Grove Group and Chase Group near Manhattan. He found illite, chlorite, and mixed-layer chlorite-vermiculite as major clay minerals in all units. The presence of montmorillonite as a mixed-layer was attributed to an alteration product of volcanic ash.

Studying five Pennsylvanian and six Permian limestones, Watkins (1957) observed illite, chlorite and illite-montmorillonite as the dominant clay minerals. Mixed-layer chlorite-vermiculite were in subordinate amounts. The chlorite was iron-rich and poorly crystalline in all cases.

Asmussen (1958) studied limestones and shales from the Council Grove Group near Manhattan. Montmorillonite as well as volcanic ash was noted in the Neva Limestone. He also reported that the chlorite was degraded

iron-rich variety. All possible variations in interstratification were presumed.

Hargardine (1959) investigated the effect of weathering on the clay mineralogy of the Grenola Limestone, and found a possible correlation between the iron content, the crystallinity of the clay minerals, and the degree of weathering to which the rock was subjected. More iron-rich and poorly crystalline chlorite was found in weathered rocks. Regularly interstratified chlorite-montmorillonite was common in fresh samples. He noticed that chlorite was abundant where dolomite is present.

Bryson (1959) related the clay mineral assemblage to the environmental conditions which were imposed by regional structures at the time of deposition. He covered a wider geographic range than other investigators, studying limestones, dolomites, and shales of the upper Chase and lower Sumner Groups in North and Central Kansas. Illite and chlorite were consistently dominant in the basin and mixed-layer chlorite was found parallel to anticlinal structures.

Dominant illite and interlayers of chlorite and vermiculite were noted in Huber's study (1965) of Crouse Limestone. Further detailed study of the clay mineralogy of the Crouse Limestone is being carried out and preliminary investigations reveal that illite is dominant and random layers of chlorite and vermiculite also occur. Discrete chlorite was also found with an abrupt increase toward upper units of each section (Twiss and Lee, 1972).

Valuable data and information were obtained by Stindl (1966) in his

investigation of the clay mineralogy of the Cottonwood Limestone. Two types of clay mineral assemblages were reported; a northern facies containing illite and mixed-layer chlorite-vermiculite and a southern part with illite, randomly interlayered illite-montmorillonite, and chlorite. He concluded that the clay mineral assemblages of the Cottonwood Limestone were mainly the product of different source areas and different environments of deposition. It is interesting to note that kaolinite was found at only one locality in the southern part of the Cottonwood Limestone outcrop belts.

Dowling (1967), in his petrographic and geochemical study of the Eiss Limestone, indicated two types of clay mineral assemblage and attributed them to two different sources.

Brookins, Chaudhuri, and Dulekoz (1969) investigated the Eskridge Shale for Rb-Sr whole-rock isotopic age determination and clay mineral composition. They found illite, with the 2M polytype dominant, as the most common clay mineral, followed by chlorite and expandable mixed-layer clay minerals. Using isotopic data they reported that the maximum age of formation for the Eskridge Shale is 300 ± 4 million years on the basis that principal Rb-bearing phase is allogenic 2M illite.

These published results have provided valuable knowledge in the understanding of clay mineral suites in Late Paleozoic rocks in Kansas, although the investigations were, in many instances, carried out over small geographic areas.

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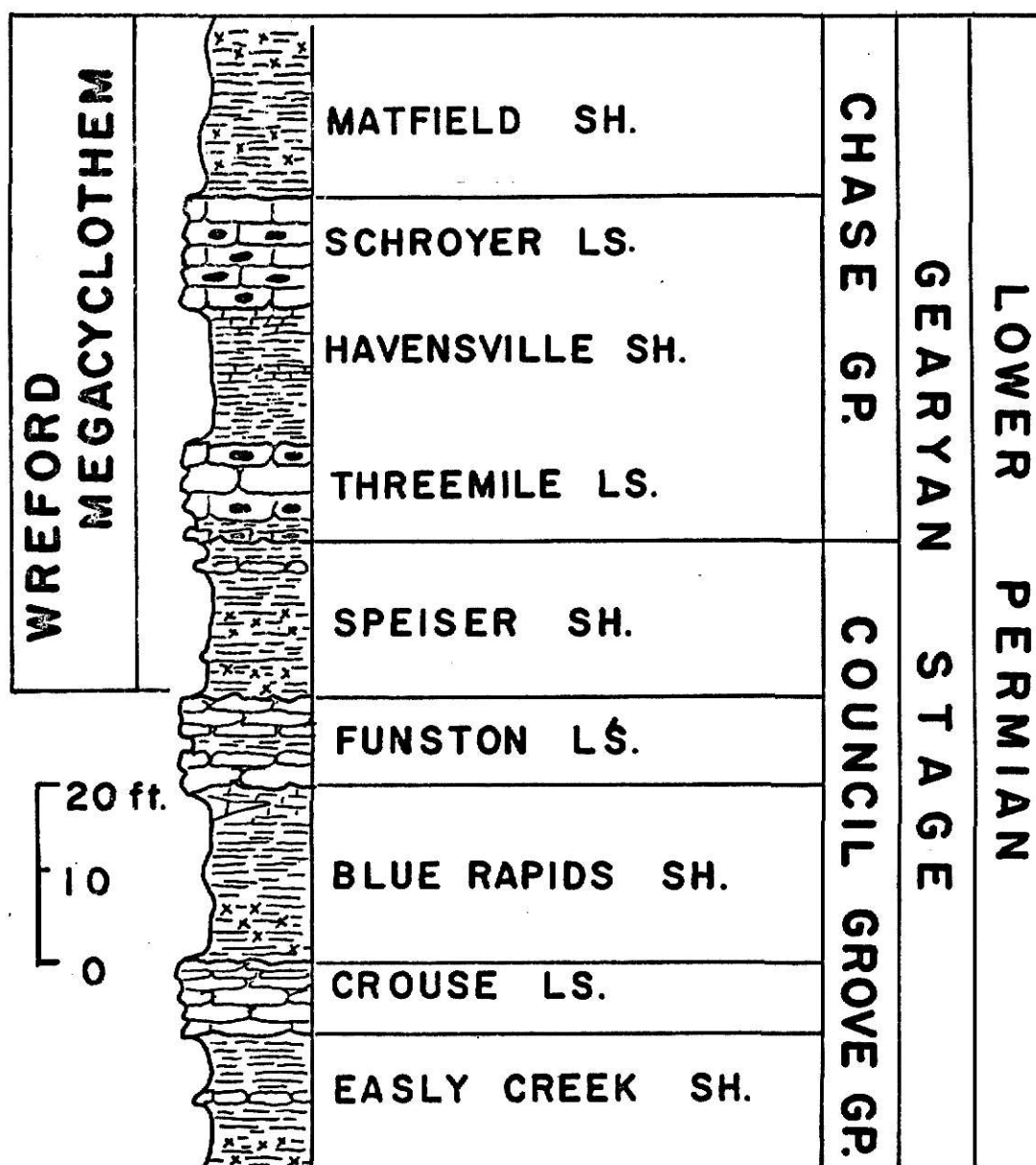
EXPLANATION OF PLATE I

Stratigraphic column, showing portion of Chase and Council Grove Group, Gearyan Stage, Permian System. Havensville Shale is a part of the Wreford Megacyclothem.

PLATE I

WREFORD MEGACYCLOTHEM

(AFTER HATTIN, 1957)



STRATIGRAPHY OF THE HAVENSVILLE SHALE

Schroyer Limestone, Havensville Shale, and Threemile Limestone comprises, in descending order, the Wreford Limestone Formation of the Chase Group, Lower Permian Series. The Wreford Limestone extends from southeastern Nebraska across Kansas into northcentral Oklahoma, (Twenhofel, 1919; Hattin, 1957; Greig, 1959) and is the oldest of the Permian formations of Kansas to contain an abundance of chert. It is the basal formation of the Chase Group, underlying the Matfield Shale and overlying the Speiser Shale (Garrison Shale in Oklahoma) and ranges 30 to 40 feet thick in Kansas (Zeller, 1968); a maximum of seven feet is assigned to the Wreford in Pawnee County, Oklahoma. Subdivisions of the formation are identifiable across Kansas but have not been defined in northern Oklahoma.

The middle member of the Wreford Limestone was named the Havensville Shale by Condra and Upp (1931) from exposures near Havensville in Pottawatomie County, Kansas who reported a thickness at the type locality of from 18 to 19 feet. Later work by Hattin (1957) corrected it to 27 feet. Across Kansas and Oklahoma a great range in thickness of the member has been observed. Throughout northern Kansas in Riley, Geary and Pottawatomie Counties, the thickness ranges from 14 to 20 feet and consists dominantly of shale and a few beds of argillaceous limestone. The minimum thickness is 1.6 feet in Chase County where the Threemile Limestone Member contains a thick reef limestone. In southern Kansas and Oklahoma the unit averages 6 to 7 feet with a dominance of thick-bedded limestones.

Fisher (1956) described the unit in Osage County, Oklahoma, as alternating, gray, fine crystalline, thin-bedded, non-fossiliferous limestones, and gray shales ranging from 2 to 12 feet thick. The Wreford Formation thins to a featheredge in the southern part of Pawnee County and no detectable horizon, separating Council Grove and Chase Groups, can be found (Greig, 1959). The Wreford in this region consists of thin interbedded, fossiliferous limestones and red shale in the lower part and highly leached sandstones and sandy limestones in the upper part. The sandstones are stained dark red by ferric oxide from adjacent shales, with pitted surface and well-developed bedding. Due to poor exposures at northern Oklahoma, correlation was very difficult and it was only assumed that abrupt facies changes occur in this region with persistent limestones becoming more sandy toward the south.

Complete exposures of Wreford Formation are rare throughout Kansas due to easy erosion of the overlying chert-bearing Schroyer Limestone and slope-forming habit of Havensville Shale. In most cases, the Havensville Shale member is partly or wholly covered even in complete sections, and as in central Kansas where the Wreford outcrop is broad, exposures are only in the sides of gullies.

Hattin (1957) observed a repetitive sequence of sedimentary rock types in the Wreford Limestone and adjacent shales. Based on the recurrence of lithologic types with characteristic fossils, he suggested two complete cyclothems in the Wreford, each with distinctive transgressive and regressive

phases. The term "Wreford Megacyclothem" was proposed for this assemblage of rocks which includes the Speiser Shale, Wreford Limestone, and overlying Wymore Shale. The cyclic system is most nearly complete in northern Kansas, although some local changes exist. In central Kansas, however, significant deviation occurred from cyclic sedimentation due to the reefs in Threemile Limestone which cropout in Chase and Morris Counties.

The algal-molluscan beds in Cowley County are probably the product of an environment that may have been restricted by reefs in central Kansas. The reefs seem to be connected and Hattin (1957) presumed them to be offshore barriers.

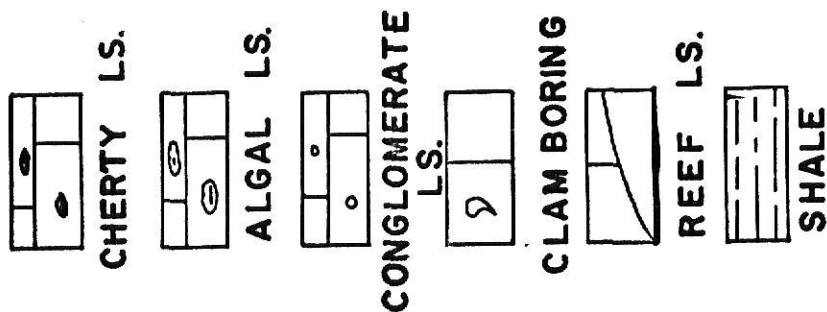
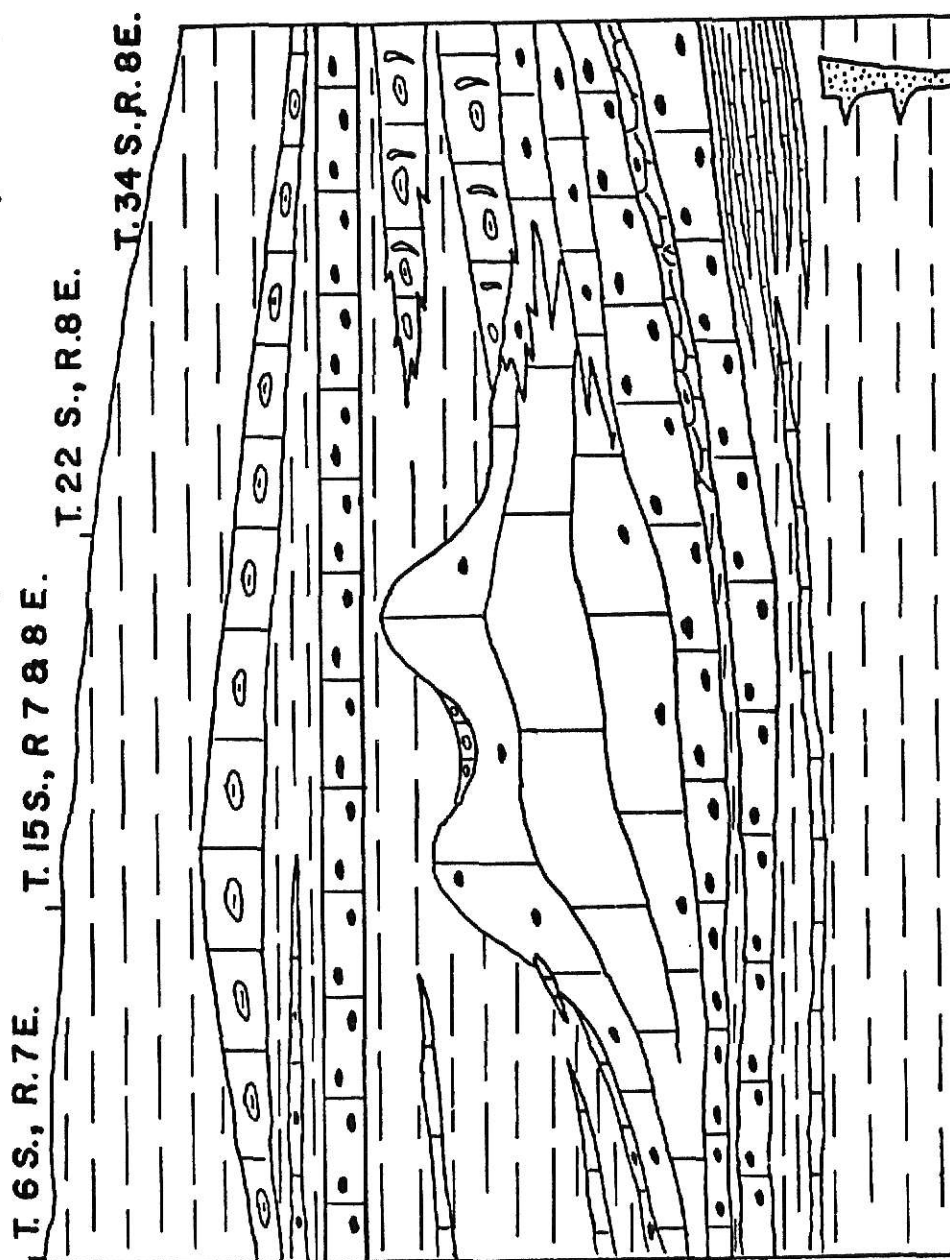
The Source area or areas which affected deposition of Havensville Shale is not clearly known. Paleogeography during Permian time shows highland areas in the south, including the Arbuckle and Oklahoma Mountains and low-lying land in the north. It was hoped that the study of lateral clay mineral assemblage might be helpful in understanding the effect of provenance.

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PLATE II

FACIES IN WRETFORD MEGACYCLOTHEM (after HATTIN, 1957)



PRELIMINARY INVESTIGATION

In order to establish the minimum number of samples necessary to define the clay mineral assemblages of the Havensville Shale, one thick section was chosen for detailed preliminary study. Samples were taken at one foot intervals from the road-cut on I-70, about 14 miles west of the junction of K-177 and I-70.

Oriented slides were made from ten random samples for three fractions of particle sizes: less than 0.5, 2, and 10 microns. Clay minerals were identified by X-ray diffraction and a planimeter was used for semi-quantitative measurements. Detailed laboratory procedures will be discussed later.

The data were first tested for homogeneity of variance by Hartley's method (Fryer, 1966, p. 246) and then analyses of variance were done to obtain significant tendencies. Table 1 shows the results.

The following results were obtained from this preliminary study:

1. Regularly interstratified chlorite-vermiculite or chlorite-montmorillonite, illite, and small amounts of discrete chlorite were found in all samples with minor amounts of calcite, dolomite, and quartz except in less than 0.5 micron fraction.
2. Illite was more abundant in the finer fractions, whereas mixed-layer chlorite was abundant in the coarser fractions.
3. The relative amount of illite seemed to increase toward the middle part of the section, whereas mixed-layer chlorite increased toward the top

TABLE I

Two-way analyses of variance after Hartley's test.

Illite

	Sum of Square	D. F.	Mean Square	F-test	L. S. D.	0.05
Size	463	2	231.5	7.47**	5.2	
Sample	2045	9	227.2	7.33**	9.6	
Error	<u>558</u>	<u>18</u>	<u>31.0</u>			
Total	3066	29	105.7			

Mixed-layer Chlorite

	Sum of Square	D. F.	Mean Square	F-test	L. S. D.	0.05
Size	130	2	84.2	4.22**	4.1	
Sample	2033	9	65.0	14.7 **	6.74	
Error	<u>278</u>	<u>18</u>	<u>225.9</u>			
Total	2441	29	15.4			

Chlorite

	Sum of Square	D. F.	Mean Square	F-test	L. S. D.	0.05
Size	35	2	17.5	1.06	Not significant	
Sample	167.9	9	18.7	1.13	at 0.10, 0.05 level	
Error	<u>297.3</u>	<u>17</u>	<u>16.5</u>			
Total	500.2	28				

** Significant at 5% level.

and bottom of the unit.

4. No significant trend was found with the analysis of variance on discrete chlorite.

5. No differences could be found in the type and amount of clay minerals between limestones and shales in the section.

6. No relationship could be inferred between mixed-layer chlorite and absolute amount of dolomite.

7. Although there is a difference in the amount of clay and non-clay mineral contents among different size fractions, for practical purposes, less than two micron size was adapted for later investigation.

EXPLANATION OF PLATE III

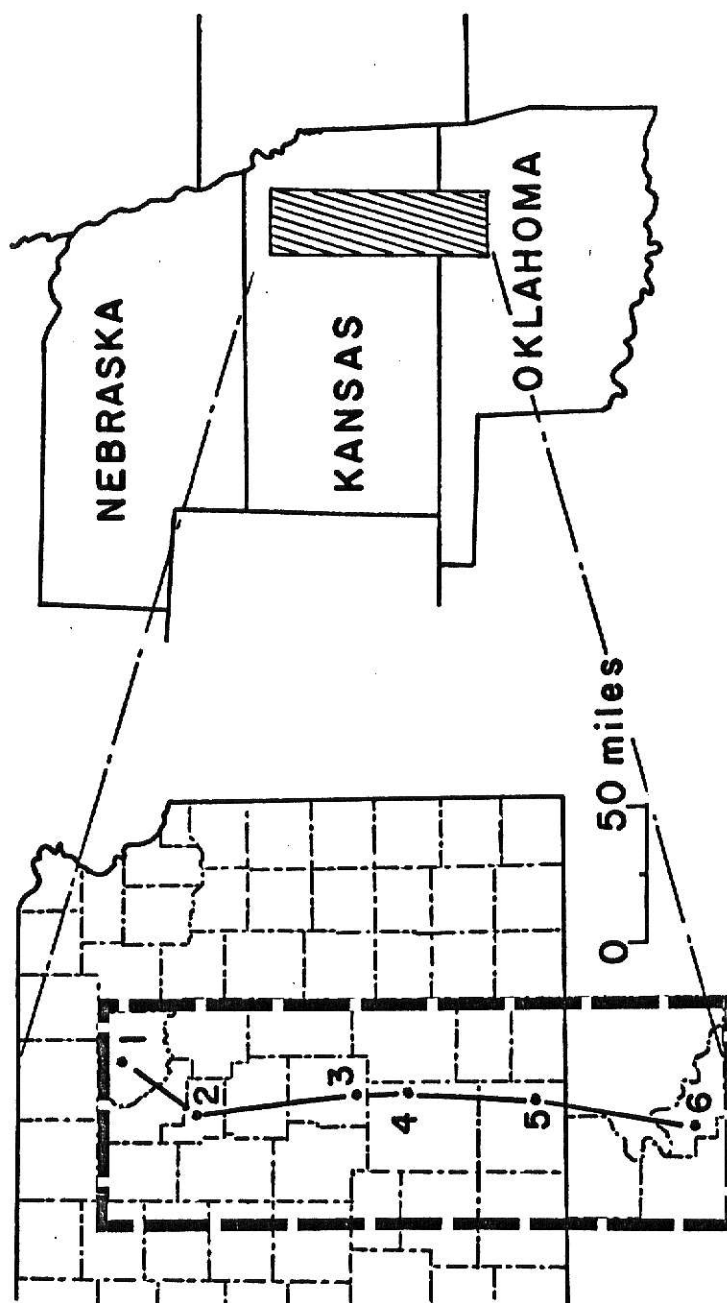
Map indicating locations of samples. Sample localities cover more than 200 miles from northern Oklahoma to northern Kansas.

Sample locations and designations are as follows:

1. HP, Pottawatomie Co., Kansas
2. HG, Geary Co., Kansas
3. HCh, Chase Co., Kansas
4. HB, Butler Co., Kansas
5. HC, Cowley Co., Kansas
6. W, Pawnee Co., Oklahoma

PLATE III

AREA OF INVESTIGATION



FIELD PROCEDURE

Samples of the Havensville Shale were collected from the following locations:

1. Geary County, Kansas (SW 1/4, Sec. 34, T. 11S., R. 6 E.) Road-cut on I-70, 14 miles east from K-177 junction. Havensville Shale 21 feet exposed, partly covered.
2. Pottawatomie County, Kansas (SW 1/4, Sec. 3, T. 7S., R. 9E.) Road-cut on K-99, 5 miles north of Westmoreland. Havensville Shale 15 feet exposed.
3. Morris County, Kansas (SW 1/4, SE 1/4, Sec. 2, T. 16 S., R. 8 E.) Road-cut on K-177, 1.6 miles north of Council Grove.
4. Chase County, Kansas (SW 1/4, NW 1/4, Sec. 19, T. 22 S., R. 8 E.) Abandoned quarry on the east side of intersection, K-177 and Atchison-Topeka Railroad, 2.8 miles southwest of Matfield Green. Havensville Shale 1.6 feet assigned.
5. Butler County, Kansas (SE 1/4, Sec. 19, T. 25 S., R. 8 E.) Gully in the ranch, 4.5 miles northeast of Rosalia. Havensville Shale 10 feet exposed.
6. Cowley County, Kansas (SW 1/4, Sec. 19, NW 1/4, Sec. 30, T. 33 S., R. 7 E.) Road-cut on K-15, 2 miles south of Dexter. Havensville Shale 7 feet exposed.
7. Pawnee County, Oklahoma (South line of Sec. 4, T. 22 N., R. 4 E.) Road-cuts along Oklahoma Hwy. 15. Wreford 6 feet exposed.

The number of samples taken at a given locality was judged by lithologic changes and correlation with other outcrops. For a thick sequence of rocks, samples were taken at one-foot intervals. In order to minimize the effect of weathered portion, samples were collected from freshly dug small trenches.

EXPLANATION OF PLATE IV

General laboratory procedures adapted in this study.

FLOW SHEET

RAW SAMPLE

DISAGGREGATION

WET SIEVING ----- <62 u

WASHING & DECONTANTATION

SETTLING

SILT (2-62 u)

ORIENTED SLIDES

UNTREATED HEATED

GLYCOLATED 450°C

RANDOM POWDER

HCL

600°C

RANDOM POWDER

X-RAY DIFFRAC.

CATION SATURATION

Mg

GLYCOL

GLYCEROL

Ca

K

DRYING

QIN HCL

FUSION
(La_2O_3
 $\text{Li}_2\text{B}_4\text{O}_7$)

Rb-Sr

MASS SPEC.

X-RAY SPEC.

CLAY (2 u)

LABORATORY PROCEDURE FOR CLAY MINERAL ANALYSES

General procedure for the X-ray analyses is shown in the flow sheet. For clay mineral analyses, the procedures used by Hathaway (1955) were adapted.

Fractionation of Clay Minerals

About 300 grams of air-dried sample were put in a beaker and covered with distilled water for 48 hours. Then the disaggregated sample was transferred to a Waring Blender and stirred for 10 minutes. The material was wet-sieved through a 230-mesh screen with about 800 ml. of distilled water and repeated centrifugation and decantation were followed until dispersion could be effected. No dispersing agent was used in this study. In case of hard, dense limestone, the sample was crushed by a jaw crusher and 0.3 M Acetic Acid was used to obtain enough clay-sized material. The method is similar to that described by Ostrom (1961). Separation of clay from sandstone was based on the technique proposed by Folk (1968).

The washed slurry was stirred again and 1,000 ml. cylinders were used for gravity settling. The length of time necessary for settling was calculated from the equation given by Folk (1968, p. 40). Fractions finer than two microns were siphoned off after proper length of settling time and the slurry was used for oriented slides, random powder acid treatment, and cation saturation. A portion of the slurry was dried for Rb-Sr isotopic analyses and X-ray spectrographic analyses.

Oriented Slides and Random Powder

Several papers have discussed the methods for proper clay mineral mounting and orientation. Conventional pipette or dropper-on-glass slide technique is still widely used, while some favored a suction-on-ceramic tile technique (Kinter and Diamond, 1960) or smear-on-glass slide method (Gibbs, 1965, 1968).

In this study, oriented slides were made by the drop-on-glass method but care was taken not to drop too much slurry on the slide. A portion of less than two micron slurry was acid treated, dried, and ground for X-ray diffraction of the powdered sample. Non-clay mineral identification was supplemented by random powder mounts of the silt fraction.

X-ray Diffraction

In this study, identification of clay minerals was solely based on X-ray diffraction, using a Norelco Wide Range Diffractometer. Untreated slides and random powders were scanned from 1 to 62 degrees two theta with Ni filtered Cu K-alpha radiation. Additional diffractograms for glycolated and heated samples were mostly run from 1 to 30 degrees two theta. Other mechanical settings were as follows: Scanning speed of 1° /min., chart speed 30 inch/hr., and time constant of two seconds; a proportional counter detector and pulse height analyzer were used.

The goniometer slit system was composed of a divergent and anti-scatter slits of one degree, and a 0.003 inch receiving slit.

Organic Liquid Treatment

Ethylene Glycol $\left[\text{C}_2\text{H}_4(\text{OH})_2 \right]$ and Glycerol $\left[\text{C}_3\text{H}_5(\text{OH})_3 \right]$ were used in the clay mineral identification. These organic liquids enter the inter-layer sites of the expandable 2:1 clay structures of such clay minerals as montmorillonites, mixed-layer illites, and some varieties of chlorite and vermiculite, and thus cause expansion of the structure along c-direction.

Brunton (1955) discussed the glycolation technique which uses vapor pressure for solvation. For present study oriented slides were allowed to stand in desiccators containing ethylene glycol or glycerol for 48 hours. Direct spraying of the liquids on slides was found to destroy proper orientation.

The purpose of using both ethylene glycol and glycerol was that they could be useful in differentiating expandable vermiculites from montmorillonites (Walker, 1961). Mg-saturated montmorillonite expands by forming organic complexes with both liquids due to its low layer charge. Mg-vermiculite does not expand upon glycerol treatment, although expansion may occur under certain conditions if ions such as Ca, Sr, or Ba occupy the interlayer positions.

Heat Treatment

The changes in structure due to dehydration and transformation that occur on heating different clay minerals can be used for more accurate identification, although other properties such as particle size, crystallinity,

and composition of the clay minerals involved should be considered.

The polymorphic varieties of kaolinite lose structural water and completely decompose at about 550°C (Brindley, 1961a, p. 84). All montmorillonites lose interlayer water in the range of 100 to 200°C , resulting in collapsed structure which depends on the type of interlayer cations. Heating at 500°C causes dehydroxylation of the members of the Smectite group (MacEwan, 1961, p. 188). Vermiculite shows progressive removal of interlayer water upon heating as shown by Walker (1961, p. 304), although rehydration occurs quickly at low temperature. Chlorite is not affected by heating up to 600°C , but poorly crystalline types decompose at temperatures as low as 450°C (Brindley, 1961b, p. 263). Illite is not affected significantly below 600°C except in some anhydrous modifications (Brindley and Grim, 1961, p. 232). For the present investigation oriented slides were heated at 450 and 600°C respectively, in a muffle furnace. The heated samples were scanned immediately.

Acid Treatments

In order to determine the stability of clay minerals in concentrated acid treatment, a few standard clay minerals were treated with 6N HCl for 10 hours at 60 to 70°C . Fithian illite and Mc Namee kaolinite retained their characteristic diffraction pattern, whereas Bayard montmorillonite showed only a weak diffuse band in the 14 \AA region. It was believed that montmorillonite minerals are more or less soluble upon warm acid treatment (Mac Ewan,

1961, p. 186). It was also found that chlorite and vermiculite are not resistant upon acid treatment.

About 25 ml of slurry was put in a beaker and the sample was warmed at 60° to 70° C with 20 ml of 6N HCl for ten hours. Treated slurry was thoroughly washed until a pH of nearly 7 was regained. Oriented slides were made after mixing with 5 to 10 ml of alcohol with the slurry to prevent curling of the oriented specimen.

Cation Saturation

The significant role of interlayer cations on structural parameters has been known (Radoslovich and Norrish, 1962; Leonard and Weed, 1966). Basal spacings of montmorillonite minerals and vermiculite are significantly different due to different water uptake by exchangeable cations in the interlayer site (see Brown, 1961, p. 195 and p. 370).

The cation exchange property of clay minerals depends on several factors: magnitude of interlayer charge, particle size, time of treatment, nature of replacing cation (size and valence), temperature, presence of exchangeable H^+ , solution concentration and pH effect (Sawhney, 1966; Scott and Smith, 1966; Dolcater and others, 1968; Barshad, 1954). The exchange property of clay minerals may be applicable for genetic differentiation as explained by Weaver (1958).

In this study, the samples were saturated with K^+ , Mg^{+2} , Ca^{+2} , and Ba^{+2} solutions to obtain characteristic X-ray diffractograms. The samples were treated with 1N chloride or nitrate salt solutions for 48 hours, and,

for a few representative samples, a period of nearly 2 weeks. Each sample was then washed thoroughly for removal of excess salts.

X-RAY SPECTROGRAPHIC ANALYSES

The ratio K/Rb was earlier interpreted as being relatively constant in igneous rocks and meteorites by Ahrens and others (1952), although some anomalous ratios were reported (Taylor and others, 1956). Similarities in their ionic radii ($K^+ = 1.33 \text{ \AA}$, $Rb^+ = 1.47 \text{ \AA}$) would account for their close association in igneous, metamorphic and sedimentary environments.

Horstman (1957) reported statistically constant K/Rb ratios in all igneous rocks. The ratio differed for different magmatic suites, but showed little variation in a given rock series. According to him, K/Rb ratio decreases during weathering and Rb is retained by clay minerals having a structural position for the ion. Horstman also suggested that adsorption on clay mineral surface may play an important role in the enrichment of Rb relative to K in the late stages of weathering and during sedimentation.

It is hoped, therefore, that measurement of the K/Rb ratios in the present investigation would be useful in distinguishing the provenances of the sediments.

The principal K and Rb bearing clay mineral is believed to be illite. Samples were pretreated with 0.1 N HCl, followed by washing and decantations, in order to remove carbonate minerals and loosely adsorbed Rb ions from the clay mineral surfaces. With this process much of the Rb in clay minerals other than illite was believed to be removed (Chaudhuri and others, 1970). It has to be emphasized, therefore, that the results of the K/Rb analyses are limited only to the interpretation of illite clay minerals.

Grim (1968) summarized chemical analyses of the major clay mineral groups. Illites contain K_2O ranging from 3.25 percent up to 8 percent, mostly less than 0.5 percent in montmorillonites, and average 0.7 percent in kaolinite. Evidently, the main source of potassium is illite clay minerals.

The K_2O and Rb content in the acid treated samples were determined by using X-ray spectrography. Prior to the analyses, the samples were fused in order to minimize the absorption effects as shown by Rose and others (1963). The fused material consisted of a mixture of 0.25 gr. of powdered sample, 0.13 gr. of La_2O_3 and 1 gr. $Li_2B_4O_7$. The fusion was achieved for 20 minutes at about $1,000^{\circ}C$ using graphite crucible and meker type burner. The cooled bead was then ground in a mortar and boric acid powder was added to each sample to bring the total weight to 1.50 gr. The samples were then put in Spex caps and pellets were made with a hydraulic press maintained at 12 tons for 20 seconds.

The instrumental settings of the X-ray spectrograph and the standard calibration curve for K_2O analyses are given in Plate V.

For measurements of Rb content, a standard sample was analyzed by isotope dilution (Chaudhuri, personal communication) and the X-ray intensities of unknown samples were compared to the standard sample.

EXPLANATION OF PLATE V

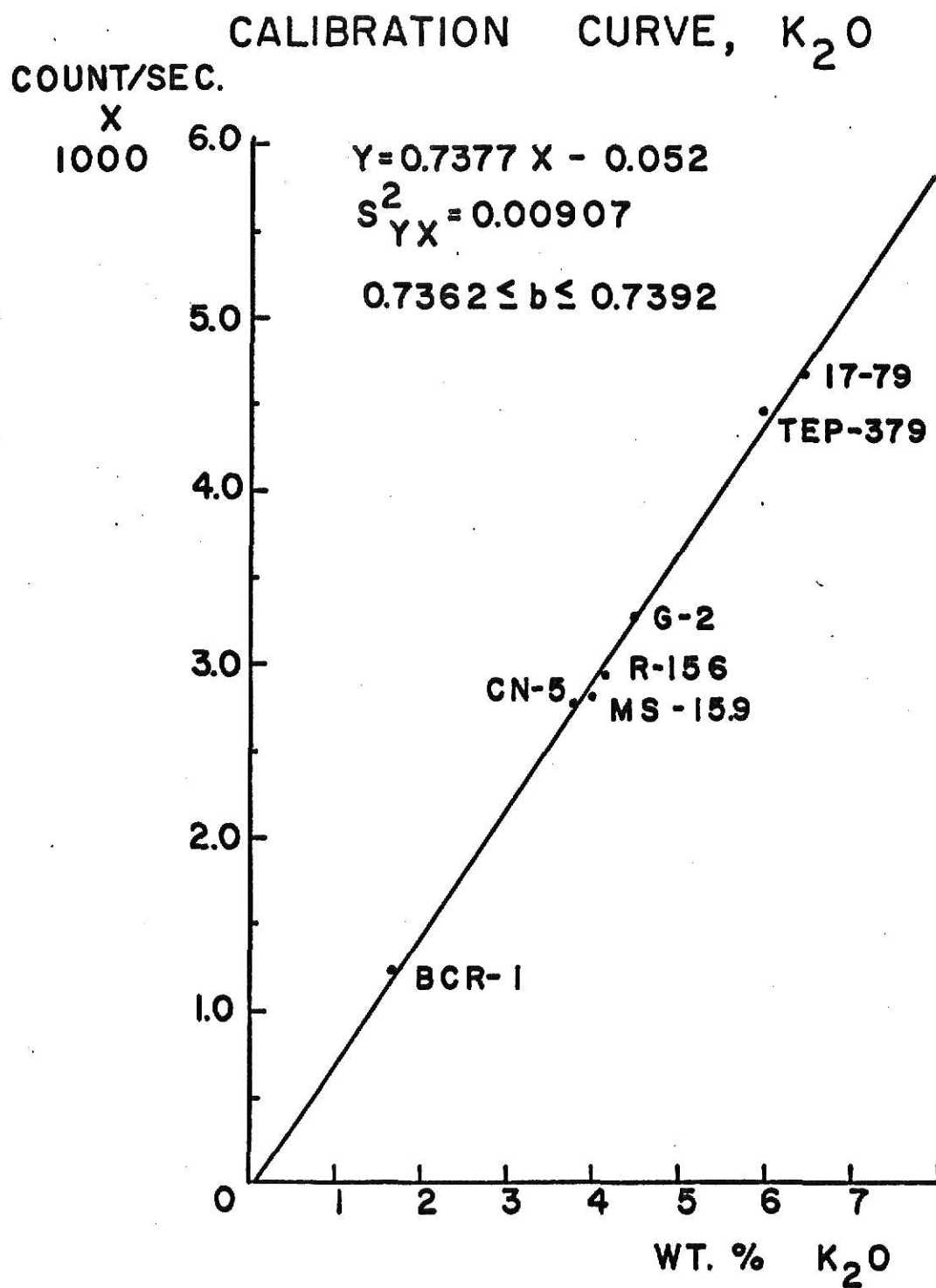
Standard Calibration Curve for K_2O Measurements. Linear regression equation was drawn using 7 standard samples. Variance due to deviation from the regression was 0.00907. Confidence interval for the slope at 95 percent level is also shown.

A Norelco Vacuum Spectrograph, equipped with gas-flow proportional counter, was used for analyses. The instrumental settings were as follows:

Cr tube at 45 KVP and 24 MA, Detector Voltage 1.46 KV
Level 2.8 Volts, Window 3.2 Volts, EDDT Analyzing crystal

For background and peak intensity counting, a teletype was used with 10 seconds of fixed counting interval. X-ray counting standard deviation was 1.0 to 1.3 percent at 95 percent or 2 standard deviation level.

PLATE V



Rb-Sr ISOTOPIC AGE DETERMINATION

The strontium isotopic analyses on clay minerals have been found useful in determining their origin (Dasch, 1969). Illite is the most important carrier of radiogenic strontium if derived from older rocks, and, if some authigenic illite was formed in marine environment, it may show the isotopic composition that is the result of equilibration with dissolved sea-water strontium. In most cases, however, the masking effect by detrital composition will make it hard to prove this evidence.

Rb-Sr isotopic analyses were performed on the samples of less than two micron fraction. All samples were treated in 0.1 N HCl prior to the isotopic analyses. The acid treatments were designed to remove the normal strontium from the carbonate bearing phases and to remove the strontium from all clay minerals other than illite. The strontium isotopic composition of montmorillonites may approach that of sea-water by ion exchange (Dasch, 1968) but up to 80 percent of the composition is leached out during the process of carbonate removal (Chaudhuri and others, 1970). Kaolinite and chlorite minerals generally contain little strontium, which is largely removed by the acid treatment. Hence, the acid treatment makes it possible to determine the radiometric ages for essentially a monomineralic phase. As in K/Rb analyses, the results of the isotopic analyses are thus limited to illites.

Preliminary Rb/Sr ratios were determined by X-ray fluorescence using a Mo target at 45 KVP, 40 MA with scintillation counter and LiF analyzing crystal. The acid-treated powdered samples were packed into a holder

with spatula and three runs were made after repacking each time in order to check the reproducibility. Rb/Sr ratios were calculated by measuring peak heights.

The mass-spectrometric analyses were done by Dr. S. Chaudhuri in the Department of Geology, Kansas State University. Detailed theory in Rb-Sr geochronology and laboratory procedures are in Chaudhuri (1966) and Dulekoz (1969).

INTERPRETATION OF X-RAY DIFFRACTOGRAMS

Identification of Clay Minerals

Routine schemes for X-ray identification of clay minerals were based on analyses of oriented samples for enhanced intensity. X-ray diffractograms were obtained from air-dried, glycolated, heated, and acid-treated samples. Random powders were X-rayed mainly for the differentiation of polytypes and identification of non-clay minerals. The basic criteria for identifications are discussed.

Illite. A series of basal peaks at 10 \AA , 3.3 \AA , and others, characterized by variable peak intensities and peak resolutions, were noted. The basal peaks were not significantly affected by either glycol or heat treatment up to 625° C . Poor crystallinity and extremely small crystallites are known to cause less intense, broad, and diffuse reflections (Murray and Sayyab, 1954). Peak broadening in illite may also be caused by replacement of potassium ions by H_3O^+ , resulting in an inter-layer hydration state which may be called degraded illite by further hydration. The ion content of illites in their octahedral position strongly affects 002 peak height, such that iron-rich illites or glauconites have low 002 peak intensity (Weaver, 1958a).

Measurements of 001 and 002 peak heights were done in this study to compare with potassium contents which were obtained by X-ray spectrographic analyses.

Cation treatments of Mg^{+2} , Ca^{+2} , and K^+ did not change the basal

spacings, but heating at 450°C and 600°C for one hour usually caused the sharpening of 001 reflection and a slight decrease in spacing (less than 0.5\AA). X-ray diffractograms of powdered samples indicate that the illites in the Havensville Shale are mostly dioctahedral, although some uncertainties were commonly present because of interference of quartz peaks at 1.54\AA (311) and 1.50\AA (302).

Illite - Montmorillonite. Mixed-layer illite-montmorillonite was indicated in all samples on the low angle side of the 10\AA illite reflection as a diffuse and broad peak. In some samples, a prominent reflection with 11\AA basal spacing appeared on untreated diffractometer patterns. Glycolation shifted the peak to nearly 14\AA , the expanded position depending upon the relative amount of montmorillonite in the interstratification. The interstratifications were random judging from the absence of higher order reflections and by the diffused reflections. Both heating at 450°C and potassium treatment caused the structural contraction to 10\AA , which strongly suggests that most of this mixed-layer exists as a degraded form of illite. Ca- and Mg-saturated samples showed broad and diffuse peaks at the 11\AA region, which indicates a disorder in c-axis stacking sequence of the random interstratification with a different magnitude of cation exchange capacity in each unit layer.

In this study, the relative abundance of each component could not be determined because of the diffuse nature of the reflections and small amount of the mixed-layer present.

Montmorillonite. Montmorillonite was identified by its characteristic structural expansion upon saturation with organic liquid vapor. The strong 001 reflection at 14.9 \AA was readily expanded to 17 \AA ; higher order reflections were either weak or absent.

When heated to 450°C the first order spacing contracted to 10 \AA by losing absorbed water layers. Upon potassium treatment, $d(001)$ decreased to 12 \AA , possibly due to low layer charge of the montmorillonite. The contracted spacing of K-treated sample was further expandable upon glycolation. A broad peak of about 11.6 \AA remained after acid treatment. This suggests irregular interstratification of highly aluminous montmorillonite with only hydrogen ions remaining in its interlayer after treatment with hydrochloric acid (Mac Ewan, 1961, p. 186).

At room temperatures, montmorillonite having Na as exchange cation has one water molecule with basal spacing of about 12 \AA , whereas montmorillonites with Ca or Mg in exchange sites have two water molecules, resulting in d spacing 15 \AA (Grim, 1968). Similarities between Ca-saturated and untreated patterns indicate that the exchangeable cations were mostly calcium in the samples analyzed.

Differentiation of montmorillonite from vermiculite was achieved by magnesium saturation and glycerol solvation (Walker, 1961, p. 316).

Chlorite. Untreated slides showed 14 \AA , 7 \AA , 4.7 \AA and 3.5 \AA reflections which could be attributed to chlorite, vermiculite or interstratification between them. Glycolation usually revealed an unexpandable 002 chlorite

reflection at 7.1 \AA . First order reflection was usually masked by the strong mixed-layer chlorite peak. When heated to 450°C , the 001 and 002 intensities decreased drastically, but at 600°C the 14 \AA intensity increased with higher orders destroyed.

A few varieties of chlorite were observed. For example, in some samples the first order reflection at 14 \AA decreased to 13.5 \AA upon initial heating at 450°C ; no higher orders were observed. The decreased spacing remained unchanged on further heating.

The measurements of basal intensities could not be done satisfactorily because of generally small quantities present.

Mixed-layer Chlorite. A strong and sharp reflection in the range of 14.0 to 14.5 \AA was observed in most of the samples with weaker higher order reflections at 7.2 \AA , 4.7 \AA , and 3.5 \AA . Two kinds of interstratifications were identified based on untreated, glycolated, and heated sample analyses: (1) partially random with alternation and (2) regular alternation between chlorite and vermiculite-like or montmorillonite-like expandable layers.

The second order reflections of the regularly interstratified mixed-layers usually appeared at about 14.7 \AA on untreated patterns. Basal spacings are compared with other published data in Table 2. The data fit the description of regularly interstratified chlorite-vermiculite (Bradley and Weaver, 1956), montmorillonite-chlorite (Early and others, 1956), and also of corrensite (Lippmann, 1956).

Whether the regular interstratification occurred between chlorite and

TABLE 2

Comparison of X-ray data in Å for swelling chlorites.

hkl	Bradley & Weaver(1958)			Early et al. (1956)			Lippmann(1956)		Present study			
	Untreated	Ethylene Glycol	550° C	Untreated	Glycerol	600° C	Untreated	Ethylene Glycerol	Untreated	Ethylene Glycerol	450° C	600° C
001	29.00	31.00	23.00	30.5	32.7	22.1	29.00	31.00	-	-	-	23.00
002	14.60	15.5	12.0	14.5	16.1	12.0	14.5	15.5	14.71	15.71	12.09	11.77
003	9.70	10.2	8.0	9.7	9.9	7.97			9.70	10.0	8.0	7.87
004	7.30	7.7	6.0	7.25	8.01	5.91	7.2	7.75	7.30	7.75	-	-
005	5.90	6.2	4.77	-	-	4.77			-	-	-	-
006	4.90	5.12	4.0	4.85	5.34	-	4.79	5.15	4.92	5.12	-	-
007	4.17	4.40	3.40	-	4.60	3.38	-		-	-	-	-
008	3.63	3.84	2.97	3.64	-	2.96	3.57		3.63	-	-	-

montmorillonite, or between chlorite and vermiculite is somewhat problematic because gradations may exist between montmorillonite and vermiculite in terms of layer charge and other properties. Mg-saturated samples usually had higher peak intensities without shifting peak positions and subsequent glycerol solvation did not expand the structure. Calcium treated samples revealed slightly increased basal spacings at 14.9 \AA which expanded to 16 \AA upon glycerol treatment. The results imply the presence of low charged vermiculite-like layer in the regular interstratification. However, the X-ray diffractograms of potassium saturated samples revealed characteristics which are common to the high-charge montmorillonite-like layers.

The basal reflections of the partially random mixed-layers examined in this study showed some changes in d-spacings upon glycol solvation and heating. The strong reflection in the range of 14.0 to 14.5 \AA expanded to the range of 14.7 \AA to 15.2 \AA upon glycolation. Some of the samples from southern localities showed weak resistance to heating, resulting in complete disappearance of 14 \AA reflection at 450° C with only a trace of broad peak at 11 to 13 \AA region. However, a broad peak at 12 \AA usually appeared after heating at 600° C . Higher order reflections were generally weak or absent. These features were believed to be due to the differences in relative amount of chlorite and other expandable components in the partial random interstratification, and the degree of order and disorder in c-axis stacking sequence.

A specific name, such as chlorite-vermiculite or chlorite-montmorillonite was not assigned to the regular and random interstratification solely

on the basis of swelling and thermal behaviors, because the exact nature of the expandable layers was not clearly known. Judging from Mg^{+2} - and K^{+} - saturated diffractometer patterns, it was believed that the expandable layers both in regular and partially random interstratifications were mostly vermiculite-like layers.

Kaolinite. Diffractograms of untreated samples from Pawnee County showed strong and sharp 001 and 002 reflections at 7.15 \AA and 3.58 \AA . The intensity of higher order reflections, 003 and 004, was less than one-tenth of the 001. The peak positions were not shifted upon glycolation, and heating at 450°C caused some decrease in the peak intensity. Upon heating to 600°C all basal reflections disappeared, indicating complete structural decomposition. Warm acid treatment did not affect the kaolinite structure.

Differentiations of kaolinite in the presence of chlorite minerals were obtained by the 003 chlorite peak at about 4.7 \AA . Where the third order chlorite peak was absent or weak, as in iron-rich chlorite, acid treatment and slow scanning ($1/4^{\circ} 2 \text{ theta/min.}$) were sufficient for the identification.

The kaolinite was more abundant in the less than 2 micron than in the 0.5 micron fraction. The kaolinite was judged to be well crystallized because diffraction peaks were intense and sharp and remained unchanged after heat treatment to 450°C .

Quantification of Clay Mineral Mixtures

In dealing with large number of samples, some kind of quantitative

technique is needed for comparative purposes. In the determination of the relative amounts from X-ray diagrams, difficulties arise because of differences in mass absorption coefficients of the component minerals (Carroll, 1970), variations in structural and chemical composition, sample preparation, orientation, crystallinity, and even the differences in the methods used. Various techniques for the quantitative estimation have been reported.

Johns and others (1954) provided the basis for many of the semi-quantitative methods reported later. Their method depends on peak height intensities on glycolated, untreated, and heated (450°C) samples. The relative values of montmorillonite and illite were obtained by comparing 17 \AA peak intensity and multiplying the 10 \AA intensity by a factor of 4. The amount of chlorite was estimated by subtracting heated 7 \AA intensity from that of untreated sample on the basis that no kaolinite loses its diffraction by heating at 450°C for 45 minutes while sedimentary chlorite may lose 7 \AA reflection depending on the composition and crystallinity.

Keller and Richard (1967) adopted a factor of 3 for comparing montmorillonite and illite, using the peak area method. Biscaye (1965), using a method similar to that of Johns and others (1954), weighted the peak area for quantitative estimation. He assigned the area of the 17 \AA glycolated peak for montmorillonite, four times the 10 \AA peak for illite and twice the 7 \AA area for chlorite and kaolinite.

Recently, Neiheisel and Weaver (1967) discussed their method in which the number of chart paper squares under 17 \AA , 10 \AA , and 7 \AA peak

EXPLANATION OF PLATE VI

Untreated X-ray diagrams showing major lateral clay mineral assemblages in Havensville Shale. Samples from Pawnee and Cowley Counties are rich in mixed-layer illite, montmorillonite, and kaolinite, while more illite, swelling chlorite, and discrete chlorite were found in northern part of Kansas.

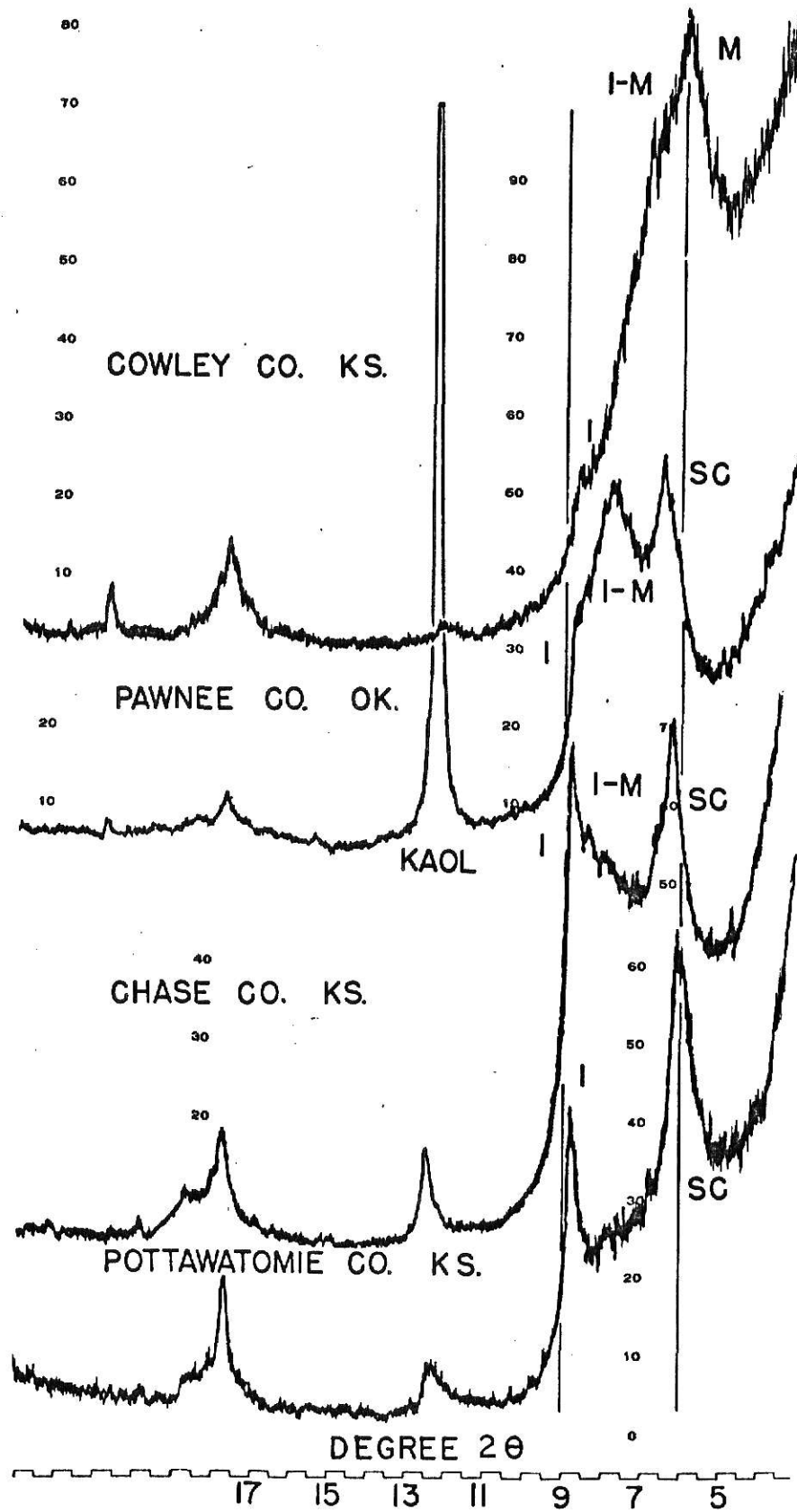
SC: Mixed-layer swelling chlorite

M: Montmorillonite

I-M: Illite-montmorillonite

I: Illite

PLATE VI



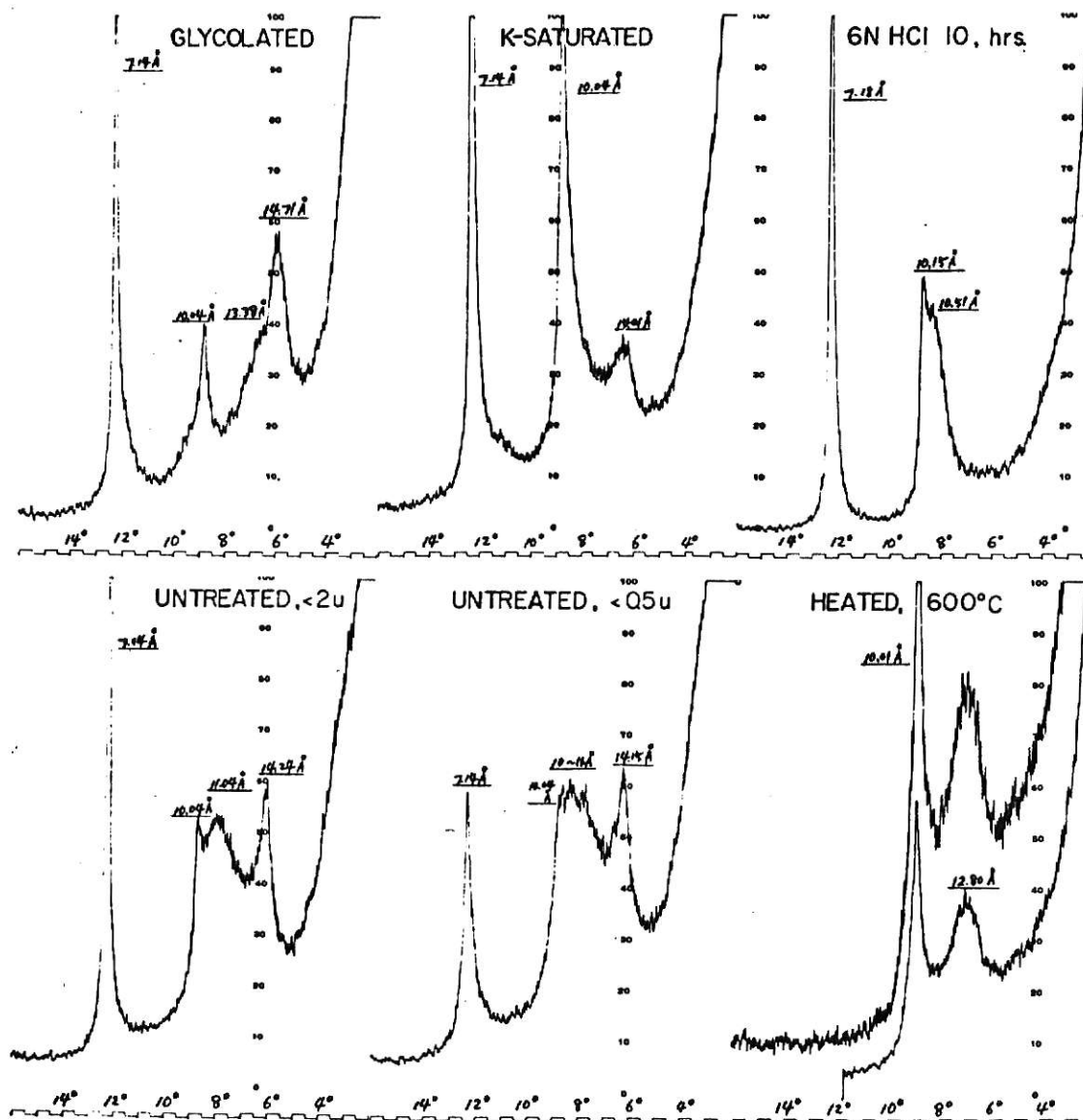
UNTREATED X-RAY DIAGRAMS

EXPLANATION OF PLATE VII

X-ray diffraction patterns of sample WGC from Pawnee County, Oklahoma. Presence of kaolinite, illite, illite-montmorillonite, and swelling chlorite was confirmed.

The coarse-sized nature of kaolinite can be seen by comparing $<2M$ and $<0.5M$ fraction. Illite-montmorillonite is somewhat more abundant in $<0.5 M$ size.

PLATE VII



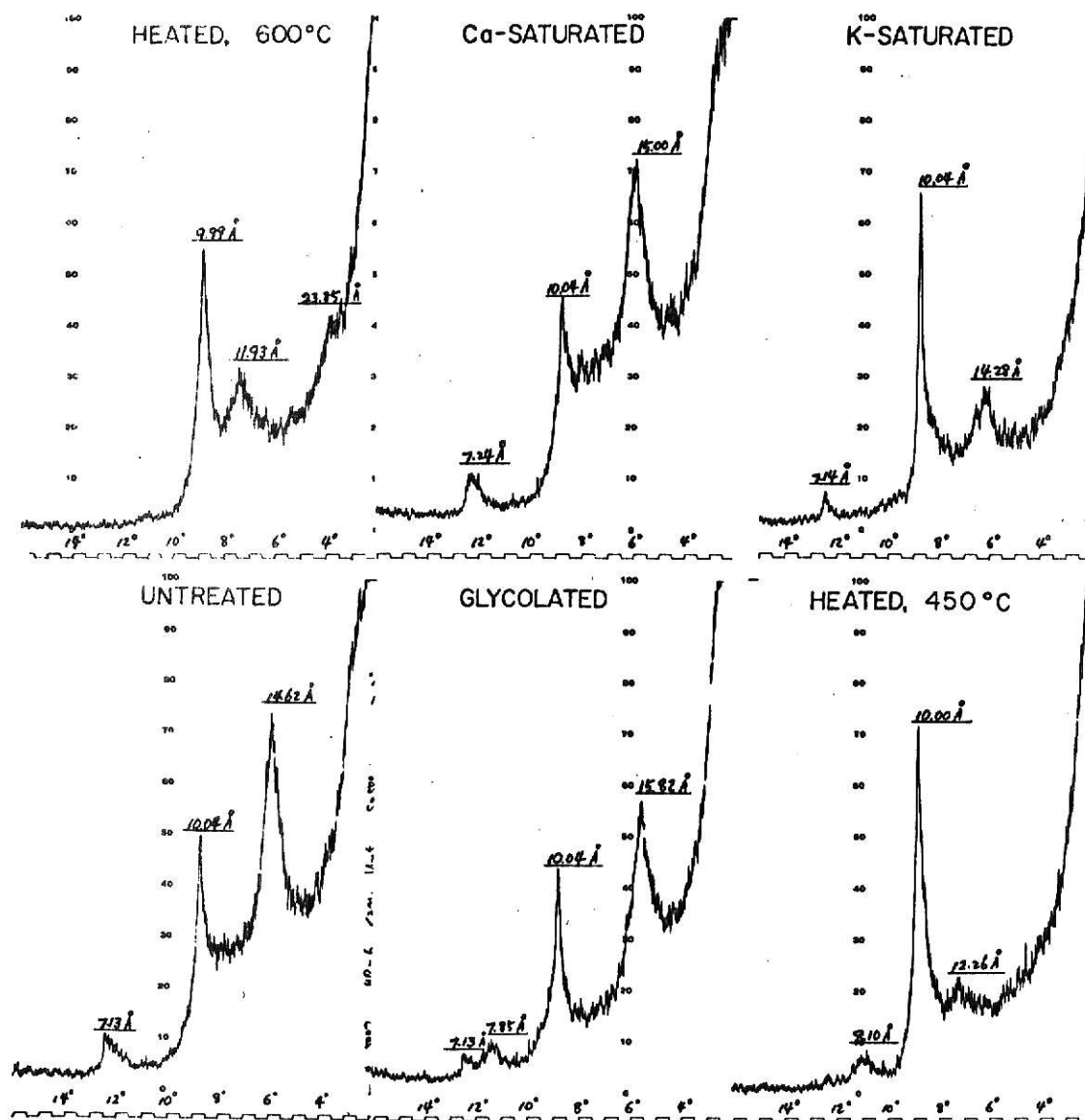
X-RAY DIFFRACTOGRAMS OF SAMPLE WGC

EXPLANATION OF PLATE VIII

X-ray diffraction patterns of sample Hp-6 from Pottawatomie County, Kansas. Illite, mixed-layer chlorite and small amount of chlorite were present. Ca-saturation confirmed the presence of vermiculite-like expandable layer in the mixed-layer chlorite. Heating at 600^o C revealed the first order reflection at 23.8 Å.

Potassium saturation contracted more than half of 002 reflection, leaving chlorite layers at 14 Å. Regular interstratification was assumed for the mixed-layer chlorite.

PLATE VIII



X-RAY DIFFRACTOGRAMS OF SAMPLE HP-6

**THIS BOOK
CONTAINS
NUMEROUS PAGES
WITH MULTIPLE
PENCIL AND/OR
PEN MARKS
THROUGHOUT THE
TEXT.**

**THIS IS THE BEST
IMAGE AVAILABLE.**

were used for relative percentages of montmorillonite, illite, and kaolinite. They used the 10 \AA measurement as a direct proportion, whereas the 17 \AA measure was divided by two for montmorillonite and 7 \AA divided by 2 for kaolinite. Dividing factor of 2 was used on the ground that kaolinite had poor crystallinity and most montmorillonite contained minor amount of montmorillonite.

It was shown by Pierce and Siegel (1969) that the use of peak height intensities greatly lowers the relative amount of montmorillonite and the peak area method was recommended for this reason. It was also noted that, although currently used methods differ from one another and give significantly different results, internally consistent results can be obtained for comparative purposes if the same laboratory techniques and the same diffraction methods were used.

For the present study, peak areas of 17 \AA , 15 \AA , 10 \AA , and 7 \AA (multiplied by 2) were measured from the glycolated pattern as a direct measure due to the uncertainties in the diffraction potential of mixed-layer clay minerals. Area of illite-montmorillonite was measured by superimposing glycolated and untreated diffractograms.

Many variables, affecting the quantitative estimation of clay minerals, were reduced to a minimum by adhering to the same method in preparation of the samples, slide mounting, and the techniques of obtaining X-ray diffractograms. For comparison of a large number of samples, any suitable method, although at best semi-quantitative, may be used after proper identifications of clay mineral components are obtained.

Polytypism of Clay Minerals

One-dimensional polytypism in layer silicates occurs because the atomic arrangement in the subcell has monoclinic or triclinic symmetry, whereas symmetry of the surface of the subcell is hexagonal or pseudo-hexagonal formed by basal oxygens in the tetrahedral sheet (Smith and Yoder, 1956).

Smith and Yoder (1956) configured six possible polymorphs of mica on the basis of different ways of stacking two adjacent layers. Only the 1M, 2M, 2M₂, and 3T polytypes are observed in nature. Detailed mechanism of polymorphic formation was also described by Bailey (1967).

Polytypism in mica minerals bears special importance in clay mineralogy. Earlier, Yoder and Eugster (1955) synthesized one-layer monoclinic disordered (1 Md), one-layer monoclinic (1 M), and two-layer monoclinic (2 M) muscovite polytypes from K₂O-Al₂O₃-SiO₂-H₂O system and found the conversion of 1 Md → 1M → 2M during progressive increase of temperature. They believed that 1 Md and 1M polymorphs are metastable or stable only at low temperatures (below 250° C) and transformation to 2M polymorph occurs at higher temperature. Their experiments were later confirmed by Velde (1965) who found the sequence of polymorphic transformation with an increase of either time, temperature, or pressure. He also concluded that 2M is the only stable polymorph of ideal muscovite and 1 Md or 1M are, if present, either metastable muscovite or other micas with a composition differing from muscovite, i. e., glauconite, celadonite, illite.

There is now considerable interest among sedimentary petrologists and mineralogists in determining the polymorphic forms of micaceous minerals as a basis for differentiating between the low-temperature, diagenetic, and high-temperature, detrital minerals (Weaver, 1958a; Velde and Hower, 1963; Hower and Mowatt, 1966). However, the temperature range, in which the polytypes are metastable or stable, are so wide that their use as a geothermometer is questionable.

Identification of illite polytypes depends solely on the random powder method. Yoder and Eugster (1955) gave X-ray powder data for different polymorphic forms of mica. According to their data, although many overlaps in peak positions commonly occur among the polymorphs, the critical region for differentiation lies in the range of 20 degrees to 36 degrees 2θ with Ca K alpha radiation. Characteristic 2M peaks with no other interfering reflections are 4.29 \AA° (111), 3.89 \AA° (113), 3.74 \AA° (023), and 3.50 \AA° (114); 1M has 3.66 \AA° (112) and 3.07 \AA° (112); 1Md also has characteristic peaks but all of them interfere with other reflections.

A semi-quantitative method for estimation of the relative abundances of the polymorphs is possible only when interference from other clay and non-clay minerals is eliminated by proper acid treatment. Velde and Hower (1963) observed that amount of 2M increased as the intensity ratio of 3.74 \AA° (023) and 2.58 \AA° (130) (200) increased. Reynolds (1963) also reported that the area ratio between 3.00 \AA° and 2.58 \AA° peak reasonably approximates the abundance of 2M in the absence of other interfering reflections, although absolute significance is lacking.

In the present study, for practical purposes, powdered samples were pretreated with 6N HCl in order to eliminate chloritic minerals and carbonates. The intensities of 2.58 \AA° and 3.00 \AA° were measured directly from diffractograms. The latter reflection was attributed solely to 2M, while 2.58 \AA° was assigned to combined 1 Md, 1M, and 2M. Then the presence of 1M polytype was checked by 3.66 \AA° reflection.

Crystallinity Index

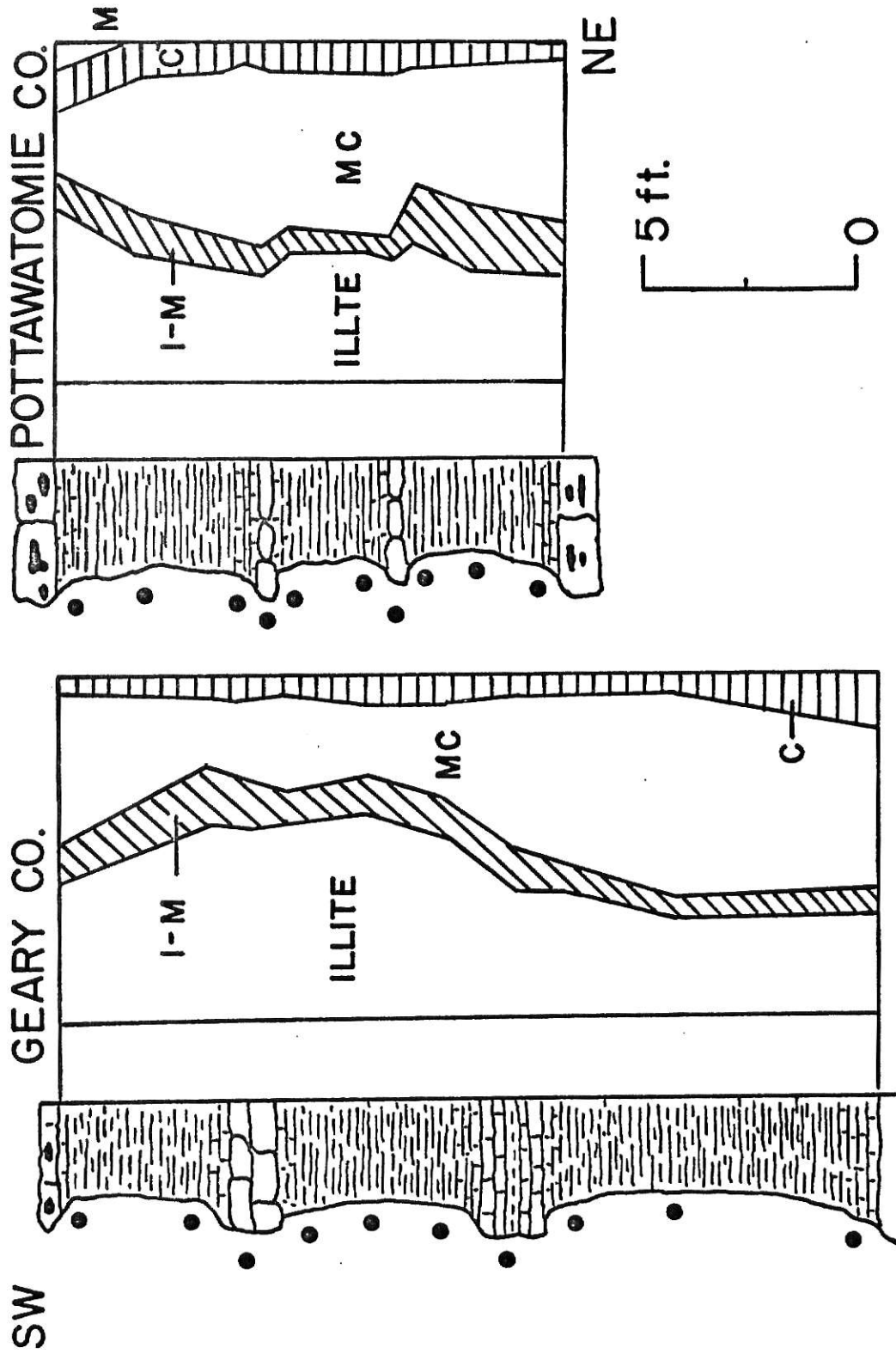
A measure of crystallinity was found to be a useful parameter to characterize illites in different localities. The half-peak-width/peak-height ratio of the illite 001 reflection was not suitable to measure because some of the samples had superimposed peak of montmorillonite 002 reflection at high-angle side of illite 001 on glycolated diffractograms, thus broadening the width of the illite reflection. Instead, the height of the peak above the background and the depth of the valley on the low-angle side of the illite 001 reflection were measured from the glycolated diffractograms, and the ratio was calculated for an approximation of crystallinity (Biscaye, 1965).

EXPLANATION OF PLATE IX

Vertical variations in clay minerals of the Havensville Shale in Geary and Pottawatomie Counties, Kansas. Samples show monotonous sequence of illite, mixed-layer chlorite, with minor amount of chlorite. Mixed-layer chlorite has some regularity in interstratification.

- I: Illite
- I-M: Illite-montmorillonite
- MC: Mixed-layer chlorite
- C: Chlorite
- M: Montmorillonite

PLATE IX

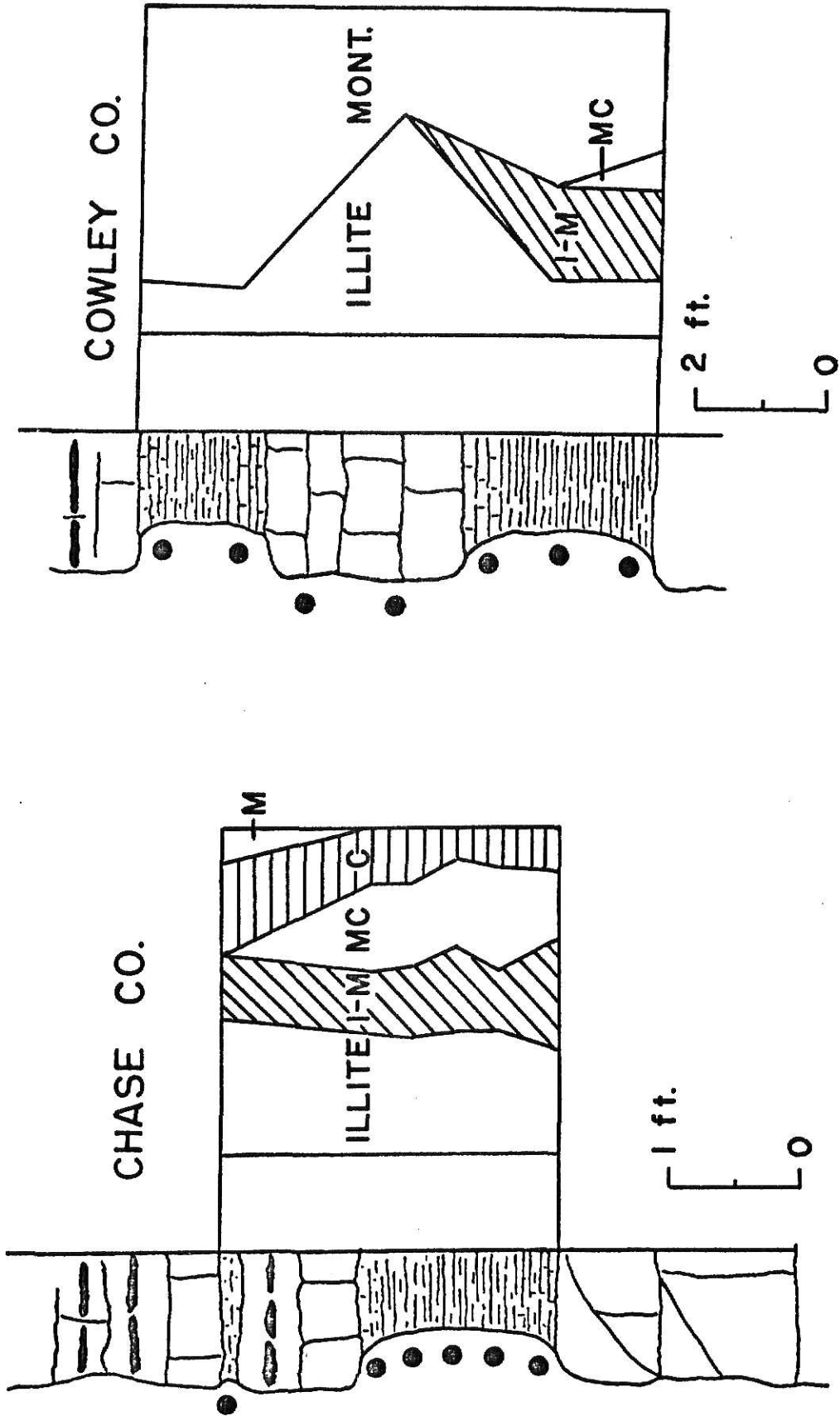


EXPLANATION OF PLATE X

Vertical variations in clay mineralogy of the Havensville Shale in Chase and Cowley Counties, Kansas.

An abrupt increase of chlorite is seen in the upper part of the Havensville Shale and in the Schroyer Limestone. Relative amount of montmorillonite is significantly less in algal limestones at Cowley County, compared to adjacent shale units.

PLATE X

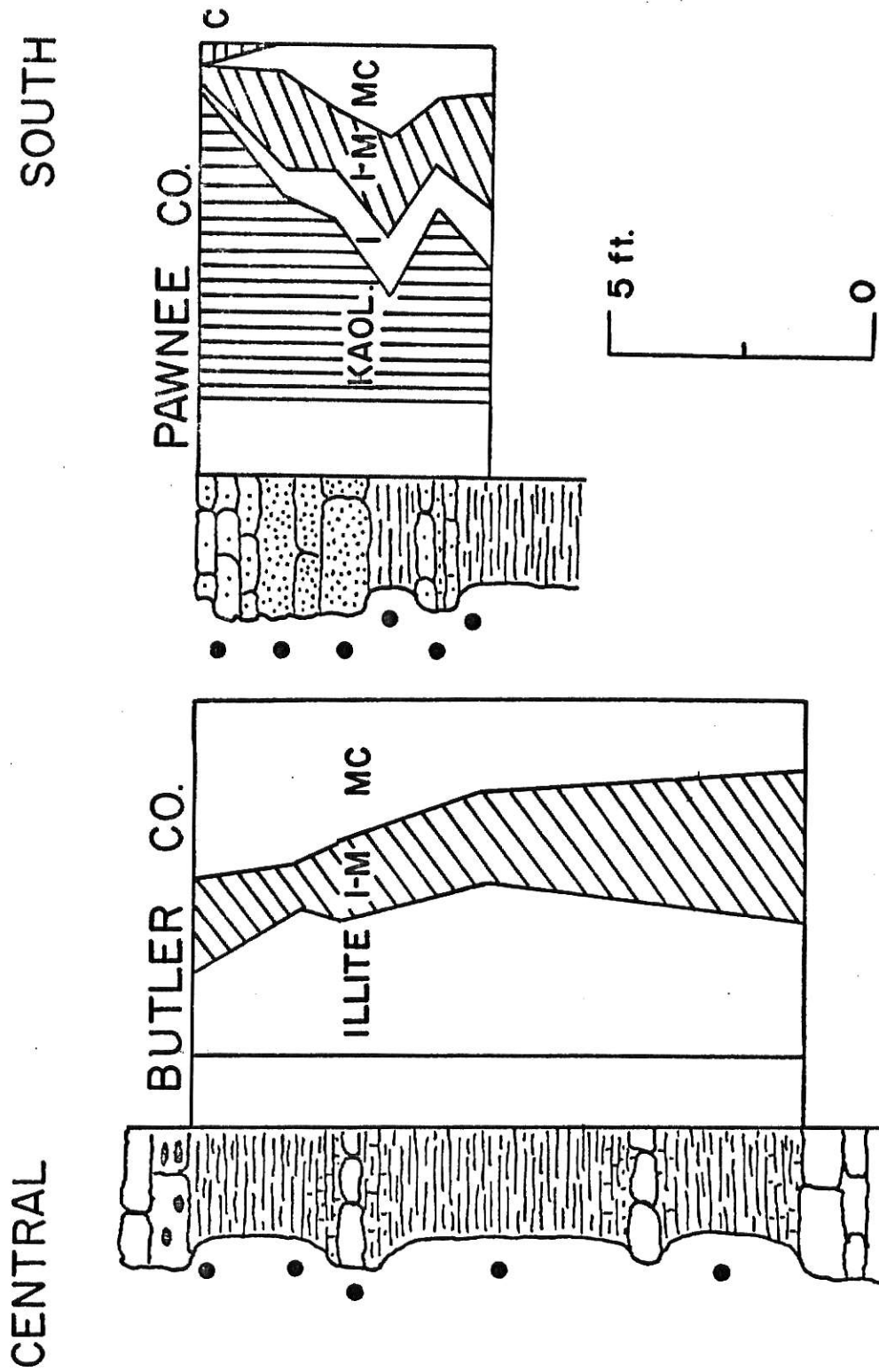


EXPLANATION OF PLATE XI

Vertical variations in clay minerals of the Havensville Shale in Butler and Pawnee Counties, Kansas.

Kaolinite tends to be more abundant in sandstones and sandy limestones. Where cyclic sedimentation is evident, variations are observed only in relative amounts.

PLATE XI



RESULTS AND DISCUSSIONS OF X-RAY DIFFRACTION DATA

Vertical Distribution of Clay Minerals

Pawnee Co., Oklahoma. The clay mineralogy of the Wreford Formation at Pawnee County was characterized by an abundance of kaolinite. Red shale, fine argillaceous sandstone, and arenaceous limestone, in ascending order, are the common rock types in this area. Average clay mineral contents were 54 percent kaolinite, 21 percent illite-montmorillonite, 13 percent mixed-layer chlorite, 11 percent illite, and a trace amount of chlorite. Plate XI shows this vertical distribution of clay minerals and their relations to lithology.

Kaolinite in the sandy limestone averaged 70 percent while underlying sandstone contained 54 percent. Least amount of kaolinite was in the lower red shale, averaging 36 percent. The trend was reversed with the amount of illite-montmorillonite: more porous sandstone units, containing more kaolinite, contained lesser amount of illite-montmorillonite than in compact shale. There was no apparent control of lithology on the distribution of illite and mixed-layer chlorite.

The mean 001/002 intensity ratio of illites in this area was 2.0 and their crystallinity index 1.2. Illite polytype was dominantly 1 Md, averaging 85 percent.

Cowley Co., Kansas. Abundant montmorillonite was at this locality where calcareous shale and algal limestone comprise the major lithology.

Average montmorillonite content was 60 percent followed by 27 percent illite and 11 percent illite-montmorillonite. Only a trace of mixed-layer chlorite was present. In most cases, the prominent first order montmorillonite peak masked the illite-montmorillonite and mixed-layer chlorite.

The hard algal limestone in the middle of the section contained significantly more illite than the underlying and overlying calcareous shales. The abundance ratio was about 3:1. Montmorillonite had a reversed trend accordingly, averaging 30 percent in the limestone and 67 percent in shale units. Illite-montmorillonites, being totally absent in the upper shale unit, were primarily in the lower shale unit with a trace in the overlying middle limestone unit. Mixed-layer chlorite is only in the lower shales.

The illite polytype was dominantly 1 Md, averaging 78 percent. The 001/002 ratio of illite ranged from 1.7 to 2.4. The high proportion of 1 Md and low 001/002 ratio may have resulted from interfering, since montmorillonite was not destroyed completely by 6N acid treatment. However, judging from its low mean crystallinity index of 1.5, illite was believed to be highly disordered and contains considerable amount of expanded layers.

Butler Co., Kansas. Illite and mixed-layer chlorite averaged 40 and 34 percent, respectively, with a significant quantity of illite-montmorillonite in the lower part of the section. Lithologic associations of major clay minerals was not found between the dominant shales and interbedded argillaceous limestones. The crystallinity and 001/002 ratio, averaging 2.6, increased somewhat as compared to two southern localities. The dominant illite polytype was 1 Md with mean content of 75 percent.

Mixed-layer chlorite showed weak resistance to heating, especially the samples from basal units of the section where are minor amounts of montmorillonite.

Chase Co., Kansas. The Havensville Shale in Chase County is the thinnest of all the localities investigated. Only 18 inches of thickness was assigned to Havensville Shale with no interbedded limestones.

Nevertheless, some vertical variation was observed mainly due to different percentages of discrete chlorite. The overlying Schroyer Limestone and upper part of the Havensville Shale contained more discrete chlorite, ranging from 17 to 28 percent, than the lower part of the Havensville Shale where mean chlorite content was 11 percent. This type of chlorite could not be defined well because the first order reflection was usually masked by an adjacent mixed-layer chlorite peak. By comparing the second and third order intensities after glycolation and by acid treatment, this species was identified as a common Fe-chlorite.

Illite content averaged 37 percent with mean 001/002 ratio 3.1 and a mean crystallinity index 1.12. At this locality, the increase in the crystallinity index was paralleled by the increase in 2 M content, ranging from 30 to 60 percent.

Mixed-layer chlorite showed uniform vertical distribution, ranging from 25 to 31 percent, but only a trace was observed in the overlying Schroyer Limestone. The mixed-layer chlorite was fairly resistant to heating at 450°C.

Geary Co., Kansas. A maximum thickness of 21 feet was assigned

to Havensville Shale at Geary County where gray shale and mudstone are the major lithology with a few interbedded argillaceous limestones.

Major clay minerals and their mean proportions are: Illite 46 percent regularly interstratified chlorite-vermiculite 37 percent, and illite-montmorillonite 10 percent. Small amount of chlorite, generally less than 10 percent, were present in most samples of the section. The relative amount of illite increased toward the middle part of the section without any lithologic preference. The vertical trend is shown in Plate IX.

Relative proportion of 2M illite ranged 38 to 68 percent. The average 001/002 ratio and crystallinity index were 2.9 and 1.18, respectively. These parameters were not particularly related to vertical lithologic change.

Pottawatomie Co., Kansas. Variety and quantity of clay minerals at this locality were very similar to that of adjacent Geary County samples.

Illite had a homogeneous distribution throughout the section without significant lithologic control and averaging 42 percent. Regularly interstratified chlorite-vermiculite ranged from 40 to 50 percent, but, at the contact with the overlying Schroyer Limestone, only 18 percent was present. Instead of reduced chlorite-vermiculite, somewhat increased quantities of discrete chlorite as well as small quantities of montmorillonite were present.

Illite-montmorillonite averaged 12 percent and is more abundant in the lower part of the section than in the middle and upper part. As in Geary County samples, no correlation between lithology and the clay mineral assemblage was observed, except for the small amount of montmorillonite at the

top of the section where deeply weathered yellowish shale was exposed.

Illite 001/002 ratio and crystallinity index were also similar to Geary County's averaging 2.8 and 1.16, respectively. The 2M polytype contents ranged from 33 to 55 percent.

Analyses of Variance

The results of analyses of variance and calculation of Least Significant Differences (Fryer, 1968) are given in Table 4.

Two-way analyses of variance showed significantly different quantities of illite, illite-montmorillonite and mixed-layer chlorite in their lateral assemblages. Vertical variations for combined sample localities were not significant at 5 percent critical level. Fisher's L.S.D. indicated that illite content in Pottawatomie, Chase, Geary, and Butler Counties were more or less the same whereas Cowley and Pawnee Counties contained significantly lesser amounts. Geary and Pottawatomie samples contained considerably smaller amounts of illite-montmorillonite compared to the rest of the localities.

The real value of statistical analyses on these clay mineral data cannot be fully assessed, since an investigator frequently deals with biased geologic samples and there always exist possible errors by different investigators.

Lateral Distribution of Clay Minerals

Illite. The relative quantity of illite increased northward from 13 percent in Pawnee County, Oklahoma to 40 percent in Butler County, Kansas. The northern localities of the area of investigation, which include Chase,

TABLE 3

Relative percentages of clay minerals based on peak area measurements from glycolated patterns.

Sample Locality and Number	Kaolinite	Illite	Illite- Mont.	Mixed-layer Chlorite	Chlorite	Montmor- illonite
Pawnee Co., Okla.						
W-5	88	7	tr.	tr.	5	-
W-4	58	7	27	7	tr.	-
W-3	51	15	17	18	tr.	-
W-2	30	16	29	25	tr.	-
W-1	53	16	17	15	-	-
WGC	42	11	33	14	-	-
Cowley Co., Kans.						
HC-7	-	16	tr.	tr.	-	84
HC-6	-	14	tr.	-	-	86
HC-4	-	69	tr.	-	-	31
HC-2	-	17	29	-	-	54
HC-1	-	17	26	12	-	45
Butler Co., Kans.						
HB-7	-	26	25	49	-	-
HB-6	-	41	13	46	-	-
HB-5	-	38	23	39	-	-
HB-4	-	49	25	26	-	tr.
HB-1	-	47	20	21	-	11
Chase Co., Kans.						
Sch	-	41	20	-	28	11
HCH-5	-	37	19	27	17	-
HCH-4	-	35	23	25	17	-
HCH-3	-	38	25	26	10	-
HCH-2	-	33	29	26	12	-
HCH-1	1	38	19	31	12	-
Geary Co., Kans.						
HG-21	-	41	10	44	5	-
HG-18	-	57	17	21	5	-
HG-17	-	54	7	34	5	-
HG-15	-	56	11	26	7	-
HG-12	-	58	13	23	6	-
HG-11	-	51	13	26	10	-
HG-6	-	38	11	42	9	-
HG-4	-	37	7	50	6	-
HG-3	-	31	4	60	5	-
HG-1	-	32	6	48	14	-

TABLE 3 (Continued)

Sample Locality and Number	Kaolinite	Illite	Illite- Mont.	Mixed-layer Chlorite	Chlorite	Montmor- illonite
Pottawatomie Co., Kans.						
HP-14	-	51	10	18	12	9
HP-12	-	38	9	40	10	3
HP-10	-	40	8	43	9	tr.
HP-9	-	33	7	52	8	-
HP-8	-	37	8	46	9	-
HP-6	-	39	4	48	9	-
HP-5	-	37	6	48	9	-
HP-4	-	42	17	33	8	-
HP-3	-	33	19	40	8	-
HP-1	-	32	18	44	6	-

TABLE 4

Analyses of variance tables for component clay minerals.

	Sum of Square	D. F.	Mean Square	F - Test
<u>Illite:</u>				
Total	5,553	24		
Locality	2,697	4	674	4.55*
Position	490	4	123	0.8
Error	2,366	16	148	
Locality L. S. D. 0.05 = 13.4%				
<u>Illite-Montmorillonite:</u>				
Total	995	19		
Locality	494	3	165	6.3*
Position	194	4	49	1.9
Error	307	12	26	
Locality L. S. D. 0.05 = 5.7%				
<u>Mixed-layer Chlorite:</u>				
Total	2,509	19		
Locality	1,292	3	427	5.3*
Position	246	4	62	0.8
Error	971	12	81	
Locality L. S. D. 0.05 = 10.13%				

* Equality of variance was tested by Hartley's method (Fryer, 1966).

TABLE 5

Relative amounts of illite polytypes in less than 2 micron fraction.

Sample Number	2M Percent	1 Md Percent
W-2	17	83
WGC	13	87
HC-7	12	88
HC-6	13	87
HC-4	33	67
HC-2	34	66
HC-1	15	85
HB-7	27	73
HB-6	25	75
HB-5	26	74
HB-4	23	77
HB-1	30	70
HCH-5	36	64
HCH-4	33	67
HCH-3	63	37
HCH-2	40	60
HCH-1	39	61
HG-21	38	62
HG-15	68	32
HG-12	54	46
HP-14	55	45
HP-12	33	67
HP-10	48	52
HP-8	33	67
HP-6	38	62
HP-4	38	62
HP-3	38	62
HP-1	47	53

TABLE 6

Intensity ratios of 001/002 and crystallinity indices,
measured from glycolated pattern.

Sample Number	Illite		Mixed-layer Chlorite	
	001/002	Crystallinity	001/002	Crystallinity
W-5	2.6	1.1	-	-
W-4	2.0	1.2	-	2.6
W-3	1.5	1.2	-	1.4
W-2	2.1	1.2	-	1.1
W-1	2.3	1.1	-	1.3
WGC	2.0	1.1	-	1.25
HC-7	2.0	1.3	-	-
HC-6	1.9	1.4	-	-
HC-4	1.7	2.0	-	-
HC-2	1.8	1.3	-	-
HC-1	2.4	1.3	-	-
HB-7	2.4	1.3	6.4	1.2
HB-6	2.3	1.4	6.3	1.2
HB-5	2.9	1.2	5.7	1.3
HB-4	2.7	1.2	4.0	1.5
HB-1	2.8	1.2	6.1	3.1
SCH	3.6	1.1	1.1	2.2
HCH-5	3.4	1.2	2.3	1.3
HCH-4	3.0	1.1	5.7	1.5
HCH-3	3.1	1.1	2.5	1.4
HCH-2	2.7	1.1	6.5	1.4
HCH-1	3.0	1.1	4.3	1.3
HG-21	3.0	1.4	3.6	1.2
HG-18	2.6	1.2	2.7	1.4
HG-17	3.5	1.1	4.4	1.4
HG-15	3.8	1.1	3.0	1.4
HG-12	3.1	1.1	3.6	1.6
HG-11	3.4	1.2	3.3	1.5
HG-6	2.7	1.3	5.5	1.3
HG-4	2.3	1.2	3.6	1.2
HG-3	2.7	1.1	4.1	1.2
HG-1	2.3	1.1	3.2	1.1

TABLE 6. (Continued)

Sample Number	Illite		Mixed-layer Chlorite	
	001/002	Crystallinity	001/002	Crystallinity
HP-14	2.6	1.2	-	2.9
HP-12	3.2	1.2	4.9	1.8
HP-10	3.0	1.2	6.1	1.5
HP-9	2.2	1.1	4.4	1.4
HP-8	2.8	1.2	4.7	1.4
HP-6	2.7	1.1	5.8	1.2
HP-5	2.7	1.1	5.7	1.2
HP-4	3.0	1.2	3.0	1.4
HP-3	3.2	1.2	5.0	1.3
HP-1	2.8	1.1	6.6	1.5

TABLE 7

Relative amount of non-clay minerals in 62 micron fraction.
(By peak height measurements)

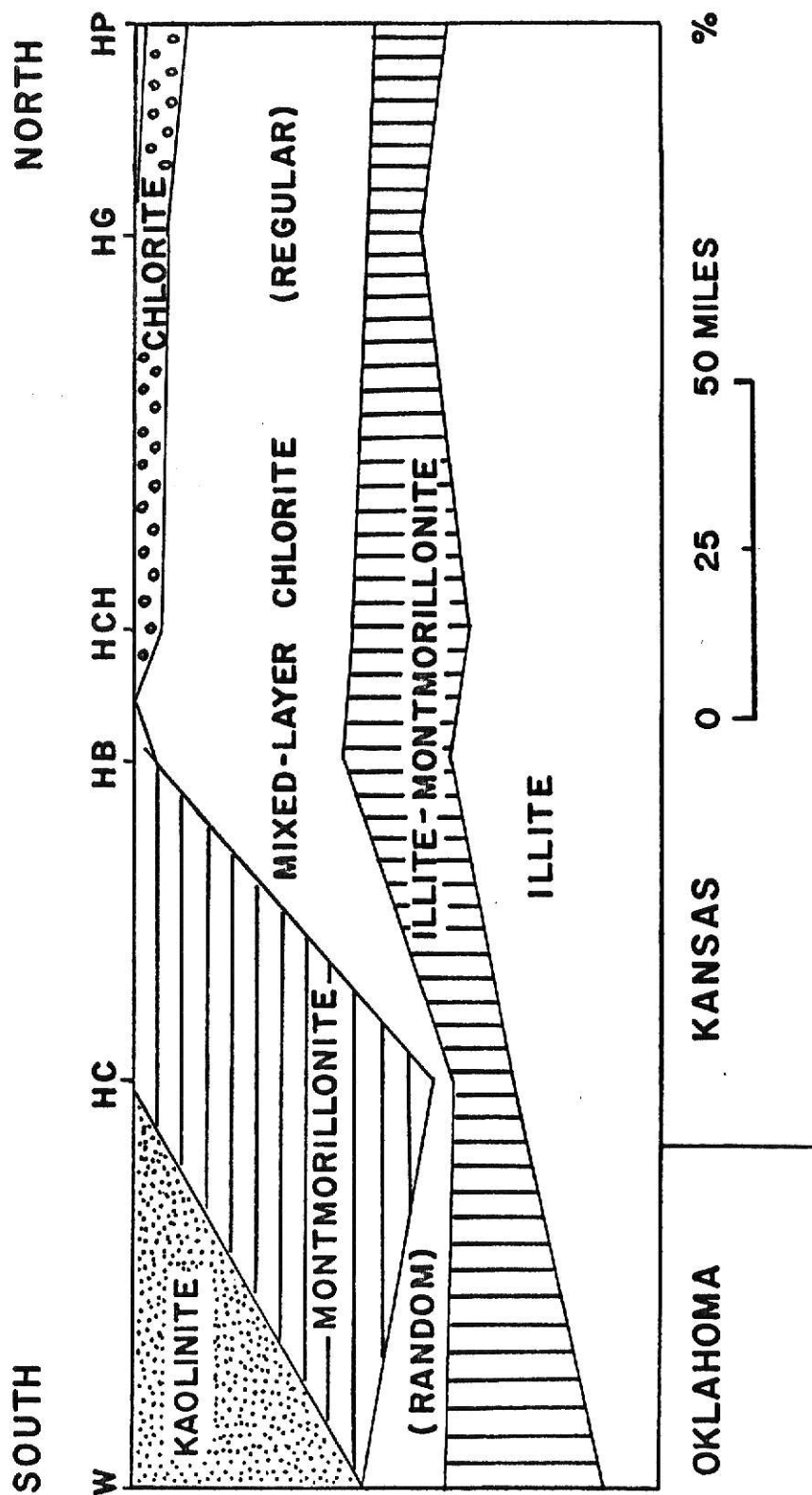
Sample Number	Calcite	Dolomite	Quartz	Feldspar
W-4	7	-	83	10
W-3	-	-	86	14
WGC	6	-	81	13
HC-7	87	-	13	-
HC-6	89	-	11	-
HC-4	87	-	13	-
HC-2	87	-	12	-
HC-1	87	-	11	2
HB-7	91	tr.	8	1
HB-6	91	-	8	1
HB-5	94	-	6	tr.
HB-4	88	1	10	2
HB-1	88	-	10	2
SCH	36	58	5	1
HCH-5	33	59	7	1
HCH-4	10	78	9	3
HCH-3	9	78	10	3
HCH-2	1	86	10	3
HCH-1	13	77	8	2
HP-14	11	9	61	19
HP-12	9	53	30	8
HP-10	4	27	64	5
HP-8	11	7	77	5
HP-6	32	13	39	17
HP-5	85	tr.	10	5
HP-3	36	2	54	8
HP-1	48	tr.	40	11

EXPLANATION OF PLATE XII

Lateral variations of clay mineral assemblage in Havensville Shale from northern Oklahoma to northern Kansas. Inferred distribution of clay minerals are expressed in relative amount.

PLATE XII

CLAY MINERAL PHASES IN HAVENSVILLE SHALE



Geary, and Pottawatomie Counties contained a higher illite content than the southern provinces. Plate XII shows the relative distribution of illites for the area investigated.

It is shown in the Plates IX, X, and XI that there is no apparent control of lithologic association in determining the relative distribution of illites. Nevertheless, it is significant that the two localities in the southern province has considerably smaller quantities of illite in comparison to the areas to the north. Whether the relative distribution of illites is a result of the strong influence of source area or areas or the strong influence of the environments of deposition, including diagenesis, cannot be known fully until all parameters are considered.

Polytypism of illite is a commonly used criterion in the genetic consideration of clay minerals. The analytical data for the illites are given in Table 5. The illites of Pawnee and Cowley Counties were primarily 1 Md with a small amount of 2M, the average content of 2M being 21 percent.

More abundant illite-montmorillonite and montmorillonite may have caused an apparent increase in 1 Md illite because they were present in acid-treated random powders and they have structures similar to 1 Md illite. However, a low 2M content of illites was evident as many of the samples indicated no X-ray reflections in the range of 20 to 25 degrees two theta, a characteristic used in their identification. The 2M illites, averaging 26 percent, increased slightly in Butler County, whereas to the north in Chase, Geary, and Pottawatomie Counties, the quantities of 2M illite were as high as 40 to 50 percent.

The apparent increase in 2M content northward can be explained as either due to a possible conversion of 1 Md to 2M or due to a higher influx of 2M illite from other source area(s). It has been suggested that low-temperature metamorphism and/or deep-burial could facilitate the conversion of 1 Md to 2M (Velde and Hower, 1963; Hower and Mowatt, 1966; Maxwell and Hower, 1967; Segonzac, 1970).

Due to lack of any discernible evidences for differences in metamorphism and burial for the two extreme areas in the north and south, it can be suggested that such mechanisms were inoperative. Adsorption of K^+ in degraded micas may also account for the conversion of 1 Md to 2M (Weaver, 1958b; Velde and Hower, 1963). Whether this process was responsible for the apparent increase in 2M content cannot be evaluated properly. It seems unlikely that the presumed differences in the environments of deposition, with shallow water to the south becoming deep water northward (Hattin, 1957), could account for the different K^+ -uptake of the 1 Md illites, causing an increase in 2M content.

The K^+ -fixation during diagenesis is possible if there could be a release of K^+ from K^+ -bearing phases such as feldspars (Reynolds, 1963). However, there is no evidence to substantiate this mechanism.

Should the distribution of 2M content be controlled by the influence of the source area, then, at least, these 2M components should be regarded as detrital in origin. Therefore, a chemical and mineralogical investigation of the illites would be of great importance in the evaluation of the effect of source

area(s) for the resultant assemblages. In the discussion to be followed, there appears to be significant quantities of evidence in favor of the influence of the source area(s). The relative amount of 2M polytype has a good linear relation with that of illite-montmorillonite as shown in Fig. 1 of Plate XIII. The trend will be discussed later with combined K/Rb data.

Other properties measured in illites are 001/002 X-ray intensity ratios and crystallinity indices. The result of 001/002 measurements showed the ratio of 1.9 to 2.0 in Pawnee and Cowley Counties and 2.7 to 3.1 in the rest of the localities to the north. The value of this ratio may be useful to distinguish between aluminous and magnesian illites, because the intensities of X-ray reflections are related to the atomic scattering factors of the ions in the mineral structure. Fine-grained muscovite has a strong 002 reflection, whereas fine-grained biotite shows a weak 002 intensity (Weaver, 1958a), thus giving distinguishable 001/002 ratios. Therefore, Mg or Fe substitutions in the illite octahedra may result in different X-ray intensities for 001 and 002 reflections. Then the differences observed in 001/002 ratios in this study are either an indication of different source areas in terms of illite composition or an indication of transformation in which substitution of Mg^{+2} for Al^{+3} gradually occurred with consequent fixation of inter-layer potassium in different environments of deposition.

It has to be emphasized, however, that the possible effect of different source areas was more important for illite than minor structural changes in depositional environments, considering the consistent differences in relative

amount, 2M proportion, and again 001/002 ratios between the two sample groups in the north and south. The boundary for the different source areas may be drawn between Butler and Cowley Counties, where the shallow Greenwood Shoal (Imbrie and others, 1959) possibly existed during the Early Permian.

A possibility of structural change is inferred from Fig. 2 of Plate XIII where a good relationship between crystallinity and 001/002 ratio is shown. Crystallinity in illite is related to expanded layers and 001/002 ratio is related to substitutions in octahedral layer and also to inter-layer potassium. Then the relation shown in the Figure 2, although drawn with only 5 average values, implies that structural changes other than cation adsorption may have happened in the clay structure with the formation of better crystalline illite.

Illite-Montmorillonite. Illite-montmorillonite occurs as a random interstratification in most of the samples. For air-dried, untreated samples, the diffractometer patterns showed at least two different modes of occurrence: a rather strong peak at 11 \AA for the Pawnee County samples, and a diffuse and broad peak at the low angle side of 10 \AA illite reflection for other areas. The relative amount of the mixed-layer in Pawnee, Cowley, Butler, and Chase samples was nearly uniform, averaging 20 percent, whereas samples from Geary and Pottawatomie Counties contained only 10 percent.

Illite-montmorillonite in sedimentary rocks may be interpreted in two possible ways: first, a weathered and potassium-deprived illite which was

EXPLANATION OF PLATE XIII

Fig. 1. A plot of percent 2M illite vs. percent of illite-montmorillonite. Increase of 2M amount is inferred with the decrease of illite-montmorillonite.

Fig. 2. A plot of illite crystallinity indices vs. 001/002 ratios. Average values are plotted for the two variables. The trend may indicate some structural changes in the structure during the formation of better crystalline illite.

PLATE XIII

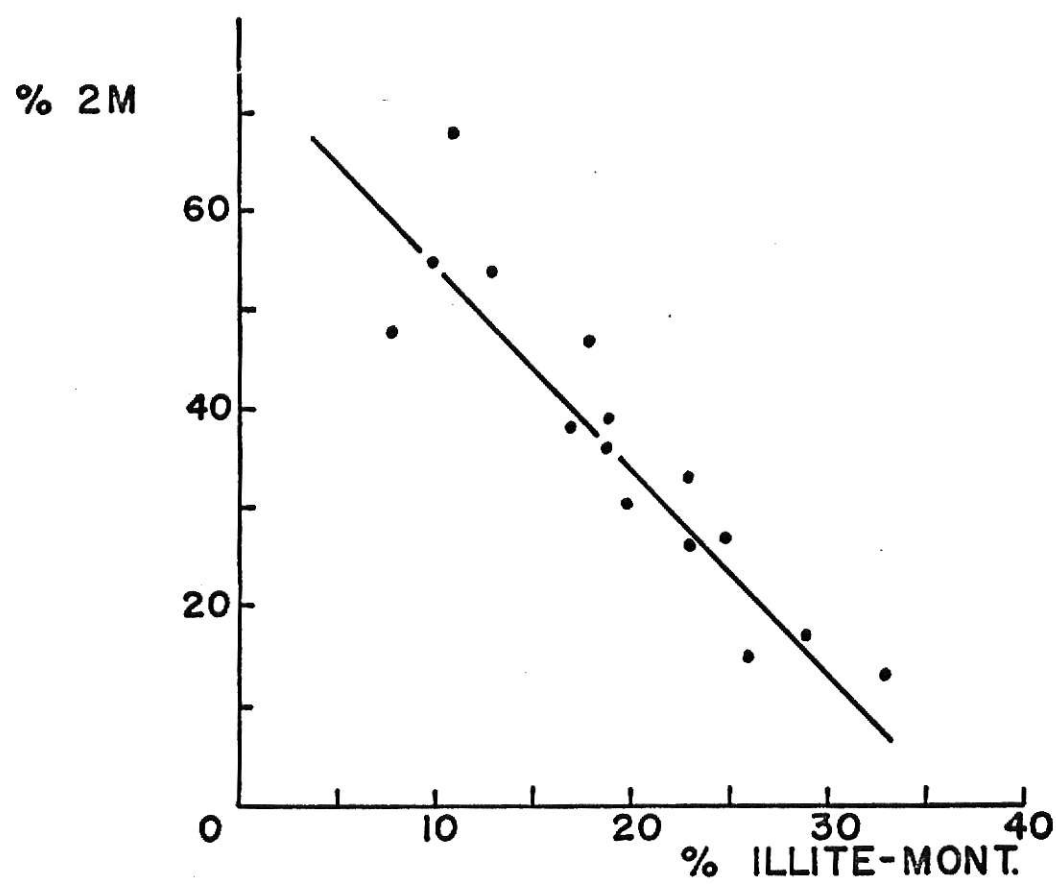


Fig. 1.

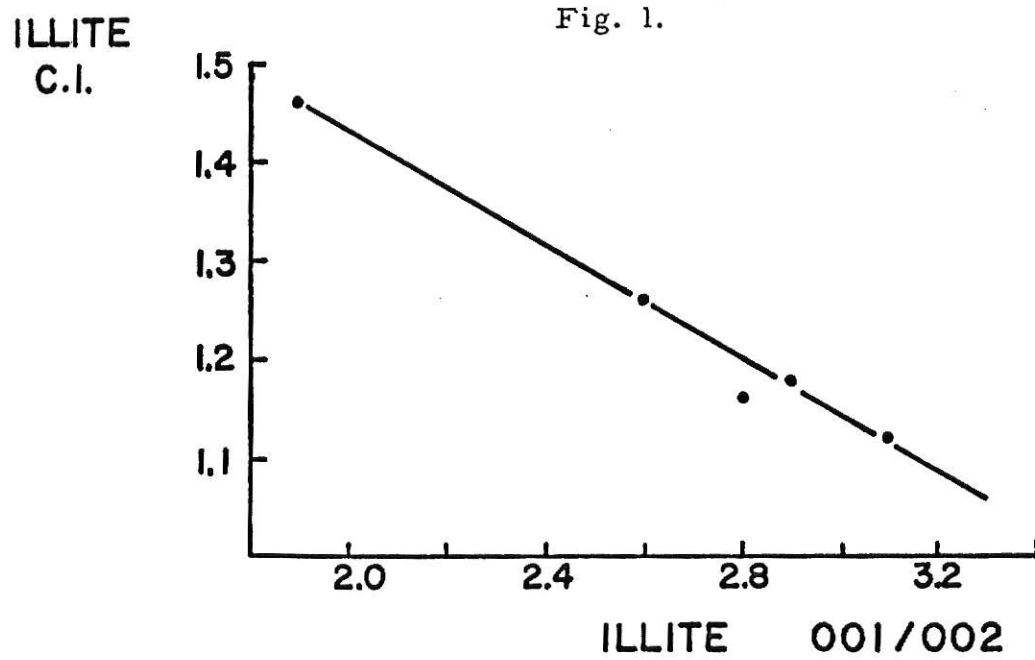


Fig. 2.

derived either from continental sources or from post-depositional weathering of the sediment (this group contracts to original illite structure by potassium adsorption (Weaver, 1958b)); the other is an authigenic formation of low-temperature 1 Md type illite-montmorillonite which could be formed in the stages of sedimentation and lithification. The disordered and expandable layer may be transformed into more stable 2M illite in the sedimentary environment by potassium fixation by increases in temperature and pressure and during diagenesis (Velde and Hower, 1963).

The relative abundance of illite-montmorillonite seemed to be controlled by lithology in Pawnee County area, where the mixed-layer clay was more abundant in shales than in the porous and permeable sandstones and sandy limestones.

Recent studies on the alteration of micas have shown that the illite-montmorillonite in marine sediments had originated from the muscovites of igneous and metamorphic rocks. Hower and Mowatt (1966), however, reported that illite-montmorillonites do not appear to be degraded, high-temperature, dioctahedral micas, unless a drastic chemical alteration occurred in basic structure during weathering. One common characteristic of the illite-montmorillonites was that the structures contracted to 10 \AA° upon potassium saturation. Thus, most are a degraded form of illite, which were derived from micas as suggested by Weaver (1958b).

A near constancy in the distribution of the illite-montmorillonite mixed-layers and their general independence of lithology would prohibit an

assumption that the environment played an important role in determining their total assemblage. On the other hand, the structural contraction to 10 \AA by potassium treatment would suggest that most illite-montmorillonites were essentially degraded forms of illite, which were derived from the weathering profile, and many seemingly were rejuvenated to illite in a normal marine environment. The lithologic associations of the mixed-layer clay in the Pawnee County samples may have resulted from relatively close distance to the source area and rapid sedimentation rate.

Montmorillonite. The trend indicates the abundance of montmorillonite only in the Cowley County samples which are composed of very calcareous shales and algal limestones. The average content was 60 percent at this location, with the greatest quantity being in the shale. A very small amount of montmorillonite, less than 10 percent, was also in the lower shale unit in Butler County and at the top of the Havensville Shale in Chase and Pottawatomie Counties. The overlying Schroyer Limestone in northern Kansas seemed to contain even more montmorillonite. An abundance of montmorillonite was also reported in the Florena Shale (Imbrie and others, 1959) and the Cottonwood Limestone (Stindl, 1966) in southern Kansas where the paleogeography suggests the shallow Greenwood Shoal.

The highest montmorillonite content was in a locality which is also considered to be an area of shallow marine environment. Montmorillonites, when brought from a fresh water environment, are known to flocculate in a marine environment. As the montmorillonites in the Havensville Shale have

a small geographic distribution, being very much more abundant in the shallow marine facies of southern Kansas, it may be tempting to suggest that a differential settling through flocculation occurred as the clays were brought from a different source area than those from adjacent localities.

A few weathered sections in the upper part of the Havensville Shale contained considerable amount of montmorillonite. The effect of weathering, then, might have been an important factor in producing montmorillonite.

The diagenetic effect on montmorillonite has been discussed by some clay mineralogists (Burst, 1959, 1969; Muffler and White, 1969; Perry and Hower, 1971). Their results generally showed progressive illitization by a decrease in expandable layers through intermediate phases of illite-montmorillonites, although Weaver (1967b) interpreted this type of transformation as a mere rejuvenation of the original phase.

Whether or not such a process was operative for the Havensville Shale would be difficult to explain from the viewpoint of their distribution. It is highly unlikely that the diagenetic environments were so greatly different, in regard to burial, for the southern and northern areas that could account for the nearly complete absence of montmorillonites in the northern areas. However, there remains a possibility that some montmorillonites were transformed into mixed-layer illite-montmorillonite upon potassium adsorption and into mixed-layer chlorite upon magnesium adsorption during diagenesis.

The low-charge of the montmorillonites, as revealed by potassium treatment, may indicate that they were an alteration product of volcanic ash. However, judging from their limited geographic occurrence, it seems unlikely

that devitrification occurred during Havensville or post-Havensville time.

Mixed-layer Chlorite. Samples from Geary and Pottawatomie Counties contained dominantly regularly interstratified 1:1 chlorite-vermiculite clay minerals, ranging from 30 to 40 percent, with traces of random mixed-layers. All other localities contained random mixed-layers with the relative amount being greater in Chase and Butler Counties than in southern Cowley and Pawnee Counties. There were no distinct lithologic preferences of the regular and random mixed-layers both in near-shore and off-shore facies. However, the random mixed-layers from near-shore deposits generally showed very weak resistance to thermal treatment, whereas the random mixed-layers of the off-shore facies in Chase and Butler Counties were fairly resistant.

The regularly interstratified phases may be formed in a high temperature and pressure hydrothermal environments (Iiyama and Roy, 1961) or as a result of low-temperature mineral paragenesis in the depositional environment or very shortly after deposition (Peterson, 1962).

Because lithologies were not clearly related to the abundance of regular mixed-layer phases in the Havensville Shale, the chemical composition of the sediments and/or the chemical factors in the depositional environment could not have been important in the formation of the regular mixed-layers in a equilibrium state, although dolomites were frequently associated with the mixed-layers. Also, due to lack of evidence for either metamorphism or deep burial, it cannot be suggested that the regular mixed-layer chlorites were the products of either diagenesis or any post-depositional thermal events.

It is presumed that the primary phases of the regular mixed-layers were introduced as detrital minerals, possibly of hydrothermal or of metamorphic origin.

The randomly mixed-layer chlorites could have been formed as the result of weathering of chlorites (Weaver, 1958a; Whiting and Jackson, 1955) or as the structural transformation of montmorillonites (Whitehouse and Mc Carter, 1958; Powers, 1954, 1959; Russel, 1970). It is also possible that the random mixed-layers were formed as equilibrium products in the depositional environment (Peterson, 1962).

The possibility that the random mixed-layers are equilibrium products in a particular environment is ruled out because the mixed-layers were in every locality, although different in relative amount, both in the near-shore and the off-shore facies and because they were not related to any particular lithology. Considering the dioctahedral structure of the montmorillonites and trioctahedral structure of the random mixed-layer chlorites, the possibility of structural transformation is also exempted. Then the only possible mechanism for the formation of the random mixed-layers is the degradation effects on discrete chlorites by weathering at the source area(s) and/or at the depositional sites due to subaerial exposure. The random mixed-layer chlorites apparently received minor structural modifications in different environments of deposition, possibly as a form of Mg adsorption, as shown by their increased thermal stability in the samples of Chase and Butler Counties as compared to other southern samples. Powers (1954, 1959) also reported an

increased thermal stability of the mixed-layer chlorites with an increase in salinity of the depositional environment.

It is suggested, therefore, that the effect of different source areas had an important role on the distribution of the two different types of mixed-layer chlorites. On the other hand, the effects of weathering and different environments of deposition affected the distribution of the random mixed-layers.

Chlorite. Discrete chlorite was a minor constituent, mostly less than 10 percent, in the samples of Geary, Pottawatomie, and Chase Counties. Samples from the southern localities contained either a trace or no chlorite at all. The chlorites were not resistant to moderate heat treatment. There were no specific lithologic control on their distribution.

Chlorite is more abundant in the upper part of the Havensville Shale and in the overlying Schroyer Limestone. The same trend was also found in Crouse Limestone which is about 50 feet below the Havensville Shale. The chlorite seemed to be more abundant in the upper part of the Crouse Limestone than in the lower parts of the unit. The discrete chlorites in the Crouse Limestone and in the Havensville Shale generally revealed the same X-ray characteristics.

The chlorites could have been introduced as a discrete phase or as a result of rejuvenation by Mg adsorption on detrital mixed-layer chlorites. Because the chlorite was not in the southern localities where the mixed-layer chlorites do exist, the rejuvenation process could not have been so distinct as to form discrete chlorites in the northern area. Rather, it is presumed that

different amounts of detrital chlorites were introduced according to the postulated cyclic sedimentation patterns during the Early Permian (Moore, 1964).

Kaolinite. An abundance of kaolinite is in Pawnee County area, where the lithology represents a near-shore facies. Kaolinite was more common in sandstone and sandy limestone than in shale, indicating a certain dependence on the porosity and permeability of the host rock.

Kaolinite is characteristically common in fluvial, lacustrine, and near-shore environments (Grim, 1968). Its stability in normal open marine environment, except in a few examples, has been questioned based on the reported geological and geochemical evidence. Kaolinite is not a stable product in an environment where the pH is high and the activities of potassium and calcium are high (Grim, 1968; Millot, 1970). It is also known that kaolinite has a tendency to flocculate upon entry into saline water (Beavers and Marshall, 1951; Pryor and Glass, 1961; Whitehouse and others, 1960).

Whether the kaolinite in the Havensville Shale in Pawnee County is detrital has to be evaluated in terms of the small geographic distribution and lithologic preference. The Havensville kaolinite is associated with rocks of supposed near-shore facies. Thus, from the viewpoint of its proximity to the continent, it is possible that land derived kaolinite flocculated as it entered the marine environment. Such a process would account for the detrital origin of the kaolinite.

Because the kaolinite is far more abundant in the rocks of sandy texture than of silty to clayey textures, permeability and porosity might have been important in its genesis. The kaolinite in the sandy facies is well-crystallized

as is observed from the sharp and symmetrical (001) X-ray reflections. Furthermore, the area of high kaolinite content is also the area of high mixed-layer illite-montmorillonite to illite ratio, a situation where low potassium activity was maintained.

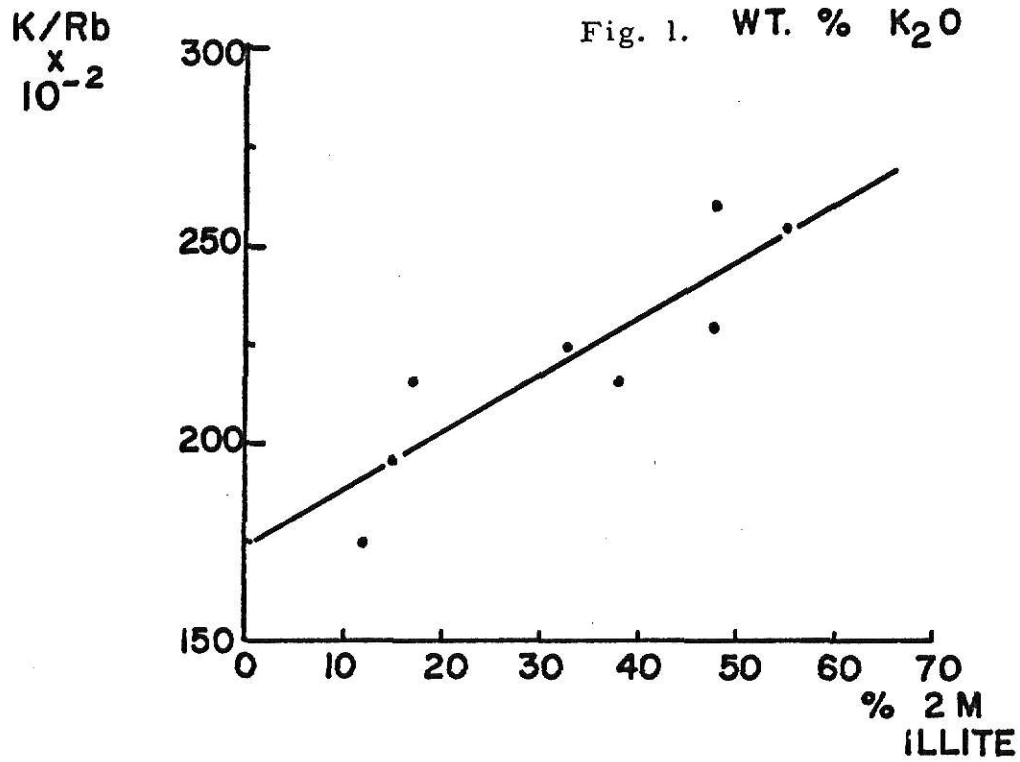
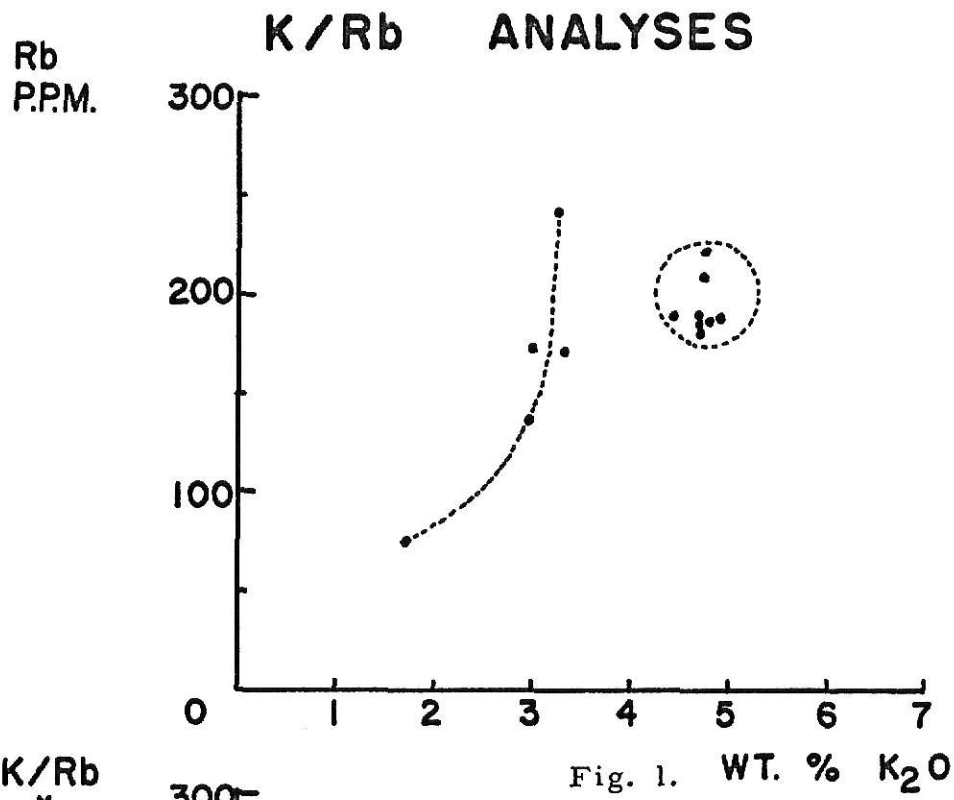
Considering the lithologic preference and association with minerals which have lost potassium, a non-detrital origin, possibly from a post-depositional alteration of potassium-bearing minerals, for the kaolinite is supported.

EXPLANATION OF PLATE XIV

Fig. 1. A plot of Rb vs. K_2O . Two distinct populations are seen; samples from Pottawatomie and Butler Counties fall in the circle, whereas samples from Cowley and Pawnee Counties revealed scattered distribution. This is attributed to different source effects of illite group.

Fig. 2. A plot showing relative increase of illite 2M polytype with the increase of K/Rb ratio. The plot is drawn for the representative samples of Pottawatomie, Butler, and Cowley Counties. This may indicate that disordered 1 Md structure was converted to 2M by potassium fixation.

PLATE XIV



RESULTS AND DISCUSSION OF K/Rb ANALYSES

Thirteen samples were analyzed for their K_2O and Rb concentrations, the data being presented in Table 8. The mean K_2O and Rb concentrations were 4.03 percent and 180 p.p.m., respectively, with a mean K/Rb ratio of 226. In a plot of K vs. Rb, as shown in the Fig. 1 of Plate XIV, two distinct assemblages were indicated. The samples from Butler and Pottawatomie Counties defined a very close K/Rb ratio and exhibited a cluster of points in the K vs. Rb plot, whereas the samples from southern localities were widely scattered.

It is suggested, from the viewpoint of K/Rb ratios, that the illite in the northern localities is unlike in origin from that of the southern localities. If the illite had been detrital in origin, then the differences in the K/Rb ratios could be ascribed to differences in the source areas.

Authigenic illite in equilibrium with sea water would be expected to have a uniform K/Rb value. The extent of diagenetic effects were possibly not so much different between the northern and southern regions as to account for the differences in the present K/Rb ratios.

The differences in the K/Rb ratios for the illite is also in agreement with the difference in 2M polytype, illite 001/002 ratios, and the relative percentages between the two regions. With this evidence in mind, it may be suggested that the present difference in the K/Rb ratios of the illite from the two separate regions in northern and southern Kansas is primarily the result of the difference in the type of land-derived illite, although the role of post-

depositional modifications cannot be totally ignored.

Fig. 2 of Plate XV shows that the relative amounts of 2M illite increased with an increase of K/Rb ratio, i. e., with the increase of potassium content. Although analytical data are not sufficient, the trend leaves a possibility, combined with the relation drawn in the Fig. 1 of Plate XIII, that by K^+ fixation, at least part of the 2M illite was transformed from illite-montmorillonite mixed-layers or from disordered detrital illite in the environment of deposition.

TABLE 8

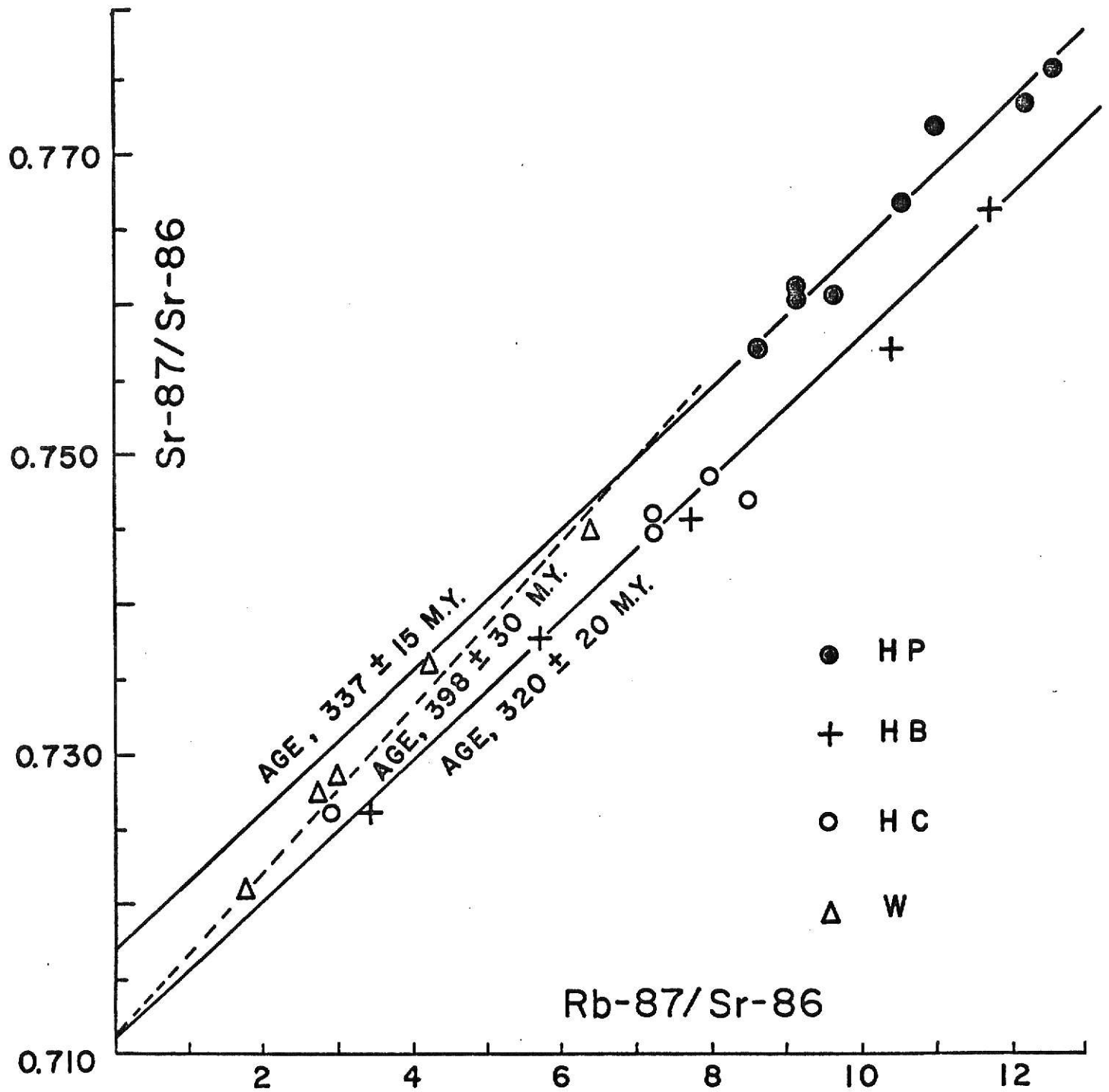
Results of potassium-rubidium analyses.

Sample No.	Wt. % K_2O	p. p. m. Rb	K/Rb
HP-14	4.71	185	255
HP-10	4.73	182	260
HP-5	4.91	188	262
HP-4	4.80	222	216
HP-1	4.77	208	229
HB-7	4.41	190	232
HB-4	4.83	177	273
HB-1	4.82	186	259
HC-7	3.06	174	176
HC-4	1.72	77	225
HC-1	3.37	171	197
WGC	3.25	242	135
W-2	2.99	137	218

EXPLANATION OF PLATE XV

Isochron diagrams for the four sample groups from Havensville Shale. The isochrons were drawn by the least squares method. Note that the two parallel isochrons are drawn for the HP samples and for the combined HB and HC samples. Although this is a statistical estimation of the regressions, significantly different initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratios are apparent.

PLATE XV



RESULTS AND DISCUSSION OF AGE DETERMINATION

Strontium isotopic measurements were made on 23 samples from four sections of the Havensville Shale. The analytical data are presented in Table 9.

All $\text{Sr}^{87}/\text{Sr}^{86}$ values reported were corrected for fractionation by assuming $\text{Sr}^{86}/\text{Sr}^{88} = 0.1194$. Isochron diagrams were drawn for four sample groups by plotting $\text{Rb}^{87}/\text{Sr}^{86}$ ratios against their corresponding $\text{Sr}^{87}/\text{Sr}^{86}$ ratios. The slopes and initial ratios were calculated by a least squares method. The ages were calculated from the slopes using the Rb^{87} decay constant of $1.39 \times 10^{-11} \text{ yr.}^{-1}$.

The calculated ages for the Pottawatomie and Butler samples were about 340 m.y. each with initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratios of 0.717 and 0.709, respectively, whereas the Pawnee County samples yielded an age of 390 m.y. with an initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of 0.711. Cowley samples had an isochron age of 300 m.y. with an initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of 0.714. As the Rb/Sr ratios of the Cowley samples had a very limited range, for all practical purposes, their individual age will not be considered in the discussion of the results.

The $\text{Rb}-\text{Sr}$ isotopic studies of the illites from the Havensville Shale thus define at least two different ages: an age of approximately 390 m.y. for the samples from the southernmost area of investigation and an age of 340 m.y. for the samples from the northern localities. These ages appear to be too high for the generally lower limit of 270 ± 10 m.y. for the Permian rocks. These ages then reflect events which are undoubtedly older than the time of

their sedimentation. In this regard, the illites should be considered detrital in origin.

In addition, the high initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratios of the samples, in comparison to the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of Permian sea with a value of approximately 0.7080 (Brookins and others, 1969), strongly suggest that the illites had inherited radiogenic strontium at the time of the sedimentation, and, therefore, they were detrital in origin. Furthermore, the differences in the two ages of the illites from the northern and southern localities can possibly be attributed to the differences in the source areas for these illites.

TABLE 9

Results of isotopic analyses on 23 samples from Havensville Shale.

Sample No.	Rb/Sr	$\text{Sr}^{87}/\text{Sr}^{86}$	$\text{Rb}^{87}/\text{Sr}^{86}$
WGC	2.2079	0.7445	6.414
W-4	1.0447	0.7283	3.028
W-3	0.6092	0.7209	1.765
W-2	1.4664	0.7358	4.257
W-1	0.9474	0.7269	2.747
HC-7	2.922	0.7466	8.491
HC-6	2.486	0.7457	7.224
HC-4	0.998	0.7257	2.894
HC-2	2.489	0.7444	7.231
HC-1	2.752	0.7482	7.998
HB-7	3.567	0.7565	10.376
HB-6	4.029	0.7659	11.733
HB-5	1.204	0.7252	3.450
HB-4	2.671	0.7455	7.761
HB-1	1.982	0.7376	5.755
HP-14	2.964	0.7568	8.622
HP-12	3.143	0.7600	9.144
HP-10	3.129	0.7606	9.104
HP-8	3.307	0.7600	9.623
HP-5	3.614	0.7664	10.523
HP-4	4.339	0.7753	12.641
HP-3	4.183	0.7728	12.186
HP-1	3.793	0.7713	11.050

SUMMARY AND CONCLUSION

1. Vertical variations in the clay mineralogy were not significant in the Havensville Shale except in the near-shore facies. The minor vertical changes in relative amounts of the same clay mineral suites were probably controlled by the factors of cyclic sedimentation. Kaolinite was more abundant in the porous and permeable sandstones than in associated shales, and occurs only in the southern locality.

2. Lateral variations were found both in mineralogy and in relative abundance. This was confirmed by a two-way analysis of variance.

Three major clay mineral assemblages were defined regionally: illite and mixed-layer chlorites in the northern shale facies, montmorillonite in the calcareous shale and the algal limestone facies, and kaolinite and mixed-layer illite in the southern sandy facies.

3. Consistent differences were observed among illites in the relative amount, 2M proportion, and 001/002 intensity ratios between the two sample groups in the north and south, the boundary is arbitrarily drawn between Butler and Cowley Counties. The differences are attributed to different source areas, although higher salinity and considerable distance to the source area could have affected degraded detrital illites to a greater degree in the north than in the southern regions.

4. Potassium-rubidium analyses revealed that illite in the Havensville Shale has two distinct populations in terms of K/Rb ratios. Samples from Butler and Pottawatomie Counties had nearly the same K/Rb ratios,

whereas Pawnee and Cowley samples showed marked differences. It is interpreted that illites in central and northern Kansas had come from different source area(s) with respect to the illites in Pawnee and Cowley Counties.

5. The detrital origin of the illites was also confirmed by Rb-Sr isotopic analyses. The radiometric ages ranged from 390 m. y. to 300 m. y. or from Devonian to Pennsylvanian time.

6. The dominant illite polytype was 1 Md in most samples. An increased amount of the 2M polytype was noticed with a relative decrease of mixed-layer illite and with the increase in the K/Rb ratios. Different environments of deposition may have partly caused the conversion of detrital 1 Md to 2M polytypes. Within the limit of present study, illite polytypism may not be a definite criterion for genetic differentiation.

7. Illite-montmorillonite inter-layers are believed to be degraded forms of illite as shown by potassium treatment. Based on X-ray diffraction patterns, lithologic associations in near-shore and off-shore facies, and also on relative amount, most of them seemingly were rejuvenated to illite in a normal marine environment.

8. The shallow depth at the Greenwood Shoal and the slightly alkaline marine water may have caused the flocculation and preservation of montmorillonite in southern Kansas. The post-depositional weathering effect of detrital illites is also postulated for montmorillonite.

9. Both regularly and randomly interstratified chlorite-vermiculite type clay minerals were found. The regular mixed-layers in northern Kansas were probably derived from a different source area in contrast to the random

mixed-layers in central and southern Kansas. The random mixed-layer chlorites probably received minor structural modifications, as a form of Mg adsorption, in a different environment of deposition, in view of their increased stability on heating in the samples from off-shore facies.

10. Minor percentages discrete chlorite were in the samples from northern Kansas. The chlorite tended to be more abundant in the upper part of the Havensville Shale and in the overlying Schroyer Limestone. Because the same trend was also in other stratigraphic units, it is believed that different amounts of detrital chlorites were introduced during the cyclic sedimentation of the Early Permian.

11. Kaolinite in Pawnee County is judged to be partly authigenic because of its well-crystalline and coarse-sized nature. Porous and permeable lithologies may have favored the crystal growth in a low pH environment.

12. It is concluded that most clay minerals in the Havensville Shale were detrital in origin, and minor structural modifications occurred in different environments of deposition, mainly as a form of cation adsorption or rejuvenation of degraded clay minerals. The role of diagenesis on the origin of the expandable clay minerals cannot be too significant because the clay mineral assemblage is independent of lithology and the geographic area is too small. Post-depositional weathering effects were seen in some of the Pottawatomie and Cowley samples. The lateral distribution of the detrital clay minerals was affected by the depositional environments.

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CLAY MINERALOGY OF HAVENSVILLE SHALE

by

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Samples of the Havensville Shale, collected from six localities in Kansas and northern Oklahoma, were analyzed for determining regional differences in the clay mineral assemblages.

The major clay mineral assemblages were: (1) illite, mixed-layer illite-montmorillonite, and mixed-layer chlorite in the shale facies of northern and central Kansas, (2) montmorillonite, illite, and mixed-layer illite-montmorillonite in the calcareous shale and algal limestone facies of southern Kansas, and (3) kaolinite, illite and mixed-layer illite-montmorillonite in the sandy facies of northern Oklahoma.

Regional differences were noted for the illite in terms of the relative content, abundance of 2M polytype, and 001/002 intensity ratio. The differences were especially striking between the samples of northern and southern localities. Two distinct populations of the illite were further confirmed by K/Rb data and Rb/Sr ages. These differences were attributed to detrital origin of illite being derived from different sources.

It was concluded that most of the clay minerals in the Havensville Shale were detrital in origin, and minor structural modifications occurred in different environments of deposition, mainly as a form of cation adsorption or rejuvenation of degraded clay minerals. The depositional environments of the Havensville Shale influenced the lateral distribution of the detrital clay minerals.