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CLAY MINERALOGY OF SOME PERMIAN AND PENNSYLVANIAN LIMESTONES

by

K. N. Watkins

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CLAY MINERALOGY OF SOME PERMIAN AND PENNSYLVANIAN LIMESTONES

by

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INTRODUCTION

Purpose of Investigation

The purpose of this investigation was to determine the non-carbonate mineralogy of representative samples of limestone screenings from eastern Kansas quarries. The carbonate mineralogy was determined in some cases if the sample contained a relative abundance of magnesium. The non-carbonate minerals of limestones, which are normally present in minor amounts, are very significant in determining the suitability of the limestone for engineering and industrial uses.

Secondly, the author has attempted to determine the significance of the clay mineral associations found in the limestone samples. Although the non-carbonate minerals in limestones are present in minor amounts, valuable information may be obtained by a study of the mineral association. Because of the lack of information concerning the clay mineralogy of limestones, particular emphasis was placed on the association of these minerals in the limestone samples.

Methods Used

In this study the non-carbonate mineralogy was determined by petrographic analysis, binocular microscope study, and X-ray diffraction. The portion of the insoluble residue used for petrographic analysis was divided into the heavy and light mineral fractions and the mineral frequencies were determined for each

sample. The coarser material was examined with a binocular microscope. X-ray diffraction analysis was used to determine the mineralogy of the clay-size fraction. In the high magnesium limestones the carbonate mineralogy was determined by stain test and X-ray diffraction.

REVIEW OF LITERATURE

Limestones

The term limestone, originally a lay word for any rock that may be burned to produce lime, has been adopted by geologists and redefined to make it of greater scientific usefulness. Rodgers (1954) stated that in its geologic use limestone has had, in general, two distinct meanings:

a. all rocks in which the mineral calcite and/or dolomite are the dominant constituents,
b. those rocks within group (a) in which calcite predominated over dolomite.

The latter meaning has been in more common useage.

Rodgers (1954) made a survey of the opinions of several geologists to standardize the terminology of rocks composed of calcite and dolomite. As a result of this survey, he arrived at the following definition of limestone:

> A sedimentary rock containing 50 percent of the minerals calcite (plus aragonite) and dolomite (including ankerite) in which calcite (plus aragonite) is more abundant than dolomite.

This survey also revealed that the term dolomite was generally accepted as the term applied to rocks dominated by the

mineral dolomite. Dolostone was preferred by some authors while others preferred dolomitic limestone or dolomite rock. The definition of dolomite according to Rodgers (1954) was as follows:

> Dolomite (the rock) or dolostone--a sedimentary rock containing more than 50 percent of minerals calcite (plus aragonite) and dolomite (including ankerite) in which the mineral dolomite is more abundant than calcite.

Further subdivisions of limestone and dolomite may be made on the basis of the relative percentages of calcite and dolomite in the carbonate fraction (Rodgers, 1954; Pettijohn, 1957; Heinrich, 1956).

Genetic Classification

Limestones may be formed by physical or chemical processes and, after deposition, they may be profoundly modified by diagenesis. They may be classified according to the method of accumulation of calcareous material. The method of accumulation and the classification according to Twenhofel (1950), p. 356, and Pettijohn (1957), pp. 393-411 is as follows:

Method of accumulation	Twenhofel	Pettijohn
Accumulation of calcareous shells and skeletal structures formed in place.	Chemical organic	Autochthonous A. Biohermal B. Biostromal C. Pelagic
Photosynthesis Bacterial activity of denitrifying bacteria.	Chemical organic	Miscellaneous chemical limestones
Evaporation Loss of carbon-dioxide	Chemical inorganic	Miscellaneous chemical limestones

Method of accumulation	Twenhofel	Pettijohn
Clastic limestones including transported and sorted shell fragments.	Mechanical	Allochthonous A. Calcirudite B. Calcarenite C. Calcilutite
Limestones formed or modified by replacement and alteration.	Dolomitic limestones	Metasomatic limestones

Twenhofel (1950), p. 357, stated that most calcitic limestones (limestones in which calcite is the principle carbonate) are of organic origin. The precipitation of calcium carbonate by organic methods does not require a saturated solution.

Because of contrasting opinions concerning the origin of dolomitic limestones (metasomatic limestones) further mention should be made. The literature concerning this subject is extensive (Pettijohn, 1957, p. 421).

The replacement origin of dolomite is quite widely held. It is believed that the replacement is a metasomatic process in which the dolomite replaces the calcite volume for volume. If the replacement were molecule for molecule, there would be a 12 percent decrease in volume. Ramberg (1952), p. 230, in a discussion of metasomatism, stated that "there are no known possibilities for forming a primary sediment with the 50 percent of $MgCO_3$ needed to give dolomite".

In contrast to this belief, Sloss (1953) and Chilingar (1956) presented the concept that some dolomites may be primary. Chilingar presented evidence that the mineral dolomite may be precipitated directly out of sea water upon evaporation at high

carbon dioxide pressure.

Other authors have presented evidence to support the replacement origin of dolomite (Fairbanks, 1957).

Environment of Deposition

Limestones may develop in many environments. Twenhofel (1950), p. 355, has written that calcareous sediments may be deposited in seas, lakes, rivers, and on the lands. The most widespread deposits occur on the bottom of the sea. Limestones may be produced and deposited in the same environment, or if detrital, may be produced in one environment and deposited in another. Factors which effect the deposition of calcareous material are temperature, circulation, and the entrance of argillaceous, arenaceous, and ferruginous materials from the lands (Twenhofel, 1950, p. 355). Sloss (1947), p. 109, divided the limestones into three categories on the basis of their depositional environment: (1) platform, (2) basin, and (3) geosynclinal.

Chemical Composition of Limestones

The limestones are primarily calcite, therefore, the content of CaO and CO_2 is high. Another constituent which may be high is MgO. If the amount of MgO exceeds one to two percent, there is a good possibility that the mineral dolomite is present (Pettijohn, 1957, p. 383).

The magnesium in limestones is a function of both the magnesium content of skeletal material of fossils and postdepositional

chemical changes. Clarke (Pettijohn, 1957, p. 383) found that the average limestone contains 7.90 percent MgO, equivalent of 16.5 percent $MgCO_3$. Analyses have shown that most limestones contain less than four percent $MgCO_3$ or more than 40 percent $MgCO_3$. Most limestones are, therefore, very calcitic or very dolomitic.

An excess of silica indicates the presence of considerable amounts of detrital quartz or chert. Pettijohn (1957), p. 384, listed 2.55 and 7.41 percent as representative percentages.

If both alumina and silica are abnormally high, argillaceous material would be a probable contaminating constituent. If argillaceous material is present, the amount of potash and combined water may also be abnormally high due to such minerals as illite.

Limestones may also be rich in other constituents such as phosphorous, iron oxide, or sulfide.

Pettijohn (1957), p. 384, lists the chemical analyses of several types of limestones. Runnels and Schleicher (1956) presented the chemical analyses of several eastern Kansas limestones.

Mineralogy of Limestones

Minerals in sedimentary rocks may belong to one of two main groups: detrital or chemical (Pettijohn, 1957, p. 108). The detrital minerals are those which have been weathered from the source rock, transported, and deposited. The chemical minerals are those which have been precipitated by physical or organic

methods.

Pettijohn (1949) had previously used allogenic and authigenic to describe the two main classes of minerals. Allogenic minerals originate outside of the sediment and are transported to the place of deposition. Authigenic minerals, on the other hand, originate in the place where they are now found.

Detrital and Chemical Minerals Other Than Clays. In Table 1 the author has attempted to list and classify the more common minerals found in limestones according to Pettijohn (1957). The list of detrital minerals is not complete. Complete lists and descriptions of common detrital minerals have been compiled by Milner (1952) and Krumbein and Pettijohn (1938). The clay minerals have been purposely omitted from this table for separate discussion.

Clay Minerals in Limestones. Clay materials form one of the most common contaminates of carbonate rocks and are represented by material less than one-two hundredth of a millimeter (.005 mm) in size (size classification of United States Bureau of Soils). This clay material may include colloidal sized quartz, feldspar, and other minerals plus the clay minerals.

The clay minerals consist of extremely small particles of a limited number of crystalline minerals (Grim, 1953, p. 16). It was not until 1920 to 1925 that adequate research tools became available to positively identify the clay minerals. Several investigators have contributed to the fundamental work on the clay mineral groups. Fundamental work on the kaolinite group has been

Table 1. Detrital and chemical minerals of limestones other than clays.

	Detrital	Chemical Precipitate	Remarks
Carbonates			
Calcite $CaCO_3$	X	XXX	Forms the bulk of limestones. May be detrital (calcarenites). May also be an authigenic modification of aragonite.
Dolomite $CaMg(CO_3)_2$		XXX	Intimately associated with calcite in limestones. Product of postdepositional replacement. (Refer to discussion of origin of dolomitic limestones.)
Aragonite $CaCO_3$	X	XXX	Unstable form of $CaCO_3$. Occurs in pelecypod and gastropod shells and some corals. Also occurs as minute needles. May be detrital in both cases. Alters to calcite in a short period of time.
Siderite FeCO		XXX	Not common in limestones unless they have been "sideritized".
Ankerite $Ca(Mg.Fe)(CO_3)_2$		XXX	Often referred to as ferriferous dolomite. Rarely reported in limestones.
Noncarbonates			
Quartz SiO_2	XX	X	Detrital quartz is usually rare in limestones except in arenaceous limestones. Chemically precipitated quartz may occur as secondary overgrowths on detrital quartz, as doubly terminated crystals, or it may be derived from the chalcedony of cherts.
Chalcedony SiO_2		X	Dominant constituent of most cherts. It is commonly fibrous.

Table 1.(concl.)

	Detrital	Chemical Precipitate	Remarks
Noncarbonates			
Opal $SiO.nHO$		X	Occurs in some cherts. It is amorphous silica.
Feldspars	XX	X	Detrital feldspar is a very minor constituent in most limestones. The authigenic feldspars usually take the form of minute euhedra or secondary growths on detrital grains.
Glauconite $KMg(Fe,Al)(SiO_3)_6 \cdot 3H_2O$ (One of the illites.)	X	X	Notable occurrence in clastic limestones. May also occur as an envelope on heavy grains.
Pyrite and Marcasite FeS_2		X	Minor constituent in most limestones. May occur as nodules, as scattered crystals or spherulites, and as disseminated grains. Both will undergo oxidation.
Celestite $SrSO_4$		X	Present as authigenic mineral in some limestones. (Twiss, 1955.)
Collophane Tricalcium phosphate with variable composition	X	X	Occurs primarily as phosphatic skeletal debris and as oolites.
Volcanic Debris	X		Very minor constituent in limestones. Volcanic ash and various forms of silica discussed by Wilbur (1956).
Organic matter	---	---	Found as a minor constituent in limestones.

done by Ross and Kerr (1931); on the montmorillonite group by Ross and Heindricks (1945); the illite group by Grim, et. al., (1937); and the chlorites by Mac Ewan (1948).

Investigators of the clay minerals in recent years have been able to establish some relationship with respect to the clay minerals present in rocks and the environment of deposition, the age, and the lithology.

Millot (Grim, 1953, p. 351) has presented evidence that the calcium in an alkaline marine environment tends to block the formation of kaolinite. This environment tends to favor the formation of illite, montmorillonite, and chlorite. Millot found that illite was invariably present in sediments of marine origin.

Millot (Grim, 1953, p. 351) further showed that an environment of low cation content is more favorable for kaolinite, whereas a higher cation content favors montmorillonite.

Grim (1953), p. 356, stated that montmorillonite is generally absent in sediments older than Mesozoic. Volcanic ash falls which have altered to montmorillonite are responsible for the bentonites found in Mesozoic sediments. Grim explained the absence of montmorillonite in older sediments as the result of the collapse and dehydration of the montmorillonite structure with subsequent extraction of potassium and magnesium from the environment to become an illite-like clay.

Evidence has been presented, however, that montmorillonite is not restricted to Mesozoic and younger sediments. Hartig (1954), Swineford (1955), and McPherron (1956) have found

montmorillonite in Permian rocks in Kansas.

Studies of recent marine sediments by Grim, et. al. (1949) and Murray and Harrison (1956) revealed that montmorillonite has widespread occurrence. Murray and Harrison found montmorillonite to be the dominant clay mineral in the Sigsbee Deep in the Gulf of Mexico.

The literature concerning the clay mineralogy of limestones is not extensive. One reason for this may be the solubility of some clay minerals in acid. It is frequently necessary to dissolve away the carbonates in order to concentrate the clay minerals to get adequate analytical data. Acid treatment was not used in the research reported in this thesis.

Grim, et. al. (1937) found in an analysis of 35 Paleozoic limestones that illite was present in all of them. Kaolinite was present in about one-half of the samples in minor amounts. The glycol method was not developed at the time of investigation and, therefore, no montmorillonite was reported.

Weaver (1956), in an analysis of over 6,000 sedimentary rock samples, has shown that randomly interstratified clays are abundant. He estimates that over 70 percent of the samples contain some variety of mixed-layer clay. Illite-montmorillonite and illite-chlorite-montmorillonite are the most abundant and chlorite-montmorillonite and chlorite-vermiculite are common. Mixed-layer clays may form in all possible combinations of different layers (illite-montmorillonite, illite-chlorite, chlorite-montmorillonite, illite-chlorite-montmorillonite.)

AREA OF INVESTIGATION

The limestone screenings were collected by the Limestone Aggregate Association in cooperation with the Kansas Geological Survey. They were collected from eleven selected quarry sites which were located generally in the eastern third of Kansas. Limestones which are suitable for engineering and industrial uses are readily available in this portion of Kansas. The Permian and Pennsylvanian limestones are exposed at the surface in this section of Kansas making them accessible for quarrying operations.

The locations of each quarry site and the stratigraphic units are listed in Table 2. The sample number designations had the prefix "DR 160" which has been omitted in this thesis.

Table 2. Location of quarries and limestone units being quarried.

Sample Number	Member or Formation*	System	Land Description	County
21	Herington	Permian	Sec.12, T16S, R4E	Dickinson
101	Herington	Permian	Sec.17, T2S, R4E	Washington
57	Cresswell	Permian	Sec. 6, T20S, R4E	Marion
31	Towanda	Permian	Sec.24, T10S, R4E	Geary
8	Fort Riley	Permian	Sec.10, T29S, R4E	Butler
9	Neva	Permian	Sec.31, T19S, R8E	Chase
43	Topeka*	Pennsylvanian	Sec.27, T8S, R16E	Jackson
70	Oread*	Pennsylvanian	Sec. 3, T18S, R16E	Osage
23	Stoner	Pennsylvanian	Sec.20, T13S, R21E	Douglas
30	Capt.Creek	Pennsylvanian	Sec. 6, T17S, R19E	Franklin
105	Bethany Falls	Pennsylvanian	Sec.27, T11S, R24E	Wyandotte

LABORATORY PROCEDURE

Preparation of Samples for Microscopic Study

Since limestones are largely calcite or dolomite, the remaining constituents must be concentrated for study. The noncarbonate constituents may be concentrated by leaching the limestone sample with hydrochloric acid. That material which is not soluble in hydrochloric acid is referred to as "insoluble residue".

Leaching. The samples were quartered to obtain a representative fraction of each limestone sample. Crushing was unnecessary for the samples represented limestone screenings. Two hundred grams of the quartered sample were placed in a one-gallon glass jar for leaching. To reduce the initial reaction with the acid, enough distilled water was added to cover the sample in the bottom of the container. Chemically pure hydrochloric acid was used for leaching the sample. The result of this leaching action was the break-down of the carbonates into water soluble chlorides, carbon dioxide, and the solution of some of the clay fraction.

Hydrochloric acid was added gradually until all effervescence ceased. During the addition of acid, it was frequently necessary to add distilled water to prevent the solution from effervescing over the top of the container. After all effervescence ceased, the acid solution was diluted and the insoluble residue was allowed to settle to the bottom. The acid solution was then decanted and distilled water added to wash the unused acid and

water soluble material from the residue. The water was later decanted and distilled water added again until four washings had been completed.

Separation and Sizing Insoluble Residue. After final decantation, the residue was wet-screened through a U. S. #270 screen (53 microns). The residue which was collected on this screen was washed thoroughly to remove clay-sized particles which may hinder mineral identification. The clay size and fine to medium silt size particles which passed through the screen were dried and weighed.

The coarser material (greater than 53 microns) which was collected on the screen was washed into a 500 milliliter beaker and allowed to settle to the bottom. After settling, the excessive water was decanted. The residue was then transferred to a small electric oven to dry.

After drying, the insoluble residue was screened again using a U. S. #120 screen (125 microns). The material greater than 125 microns in size was weighed and then placed in labeled bottles and later used in the coarse residue analysis. The material less than 125 microns and greater than 53 microns in size was used in the heavy mineral separation.

Heavy Mineral Separation. Bromoform with a specific gravity of 2.7 was used as the separating medium. The apparatus for heavy mineral separation consisted of two conical funnels, one mounted above the other. The upper funnel was fitted with a hose and pinchcock to prevent the escape of bromoform. The lower

funnel was equipped with a filter paper to collect the mineral grains from the bromoform. Two such funnels were needed, one for the collection of heavy minerals and a second for the collection of light mineral grains. The upper funnel was filled with bromoform and a watch glass placed over the top to prevent evaporation.

The sample was heated prior to placing it in the bromoform. The purpose of heating was to remove absorbed moisture which may decrease the accuracy of the heavy mineral separation. The dried sample was placed in the bromoform and stirred every 15 minutes for two hours. It was then allowed to stand for one hour before filtration.

After filtration, the residue was washed three times; first with a bromoform-ethyl alcohol solution and twice with ethyl alcohol. The filter papers containing the heavy and light mineral grains were folded and set aside to air dry. After drying, the residue was weighed to determine the approximate weights of each fraction.

Preparation of Slides. Canada balsam with an index refraction of 1.53 was used as the mounting medium. A small electric heater was used to heat the glass slide, cover glass, and balsam. The balsam was placed on the glass slide and heated until it reached the proper consistency. The proper consistency was determined by withdrawing a drop of balsam on a dissecting needle, allowing it to cool, and then pressing the thumbnail against it. The balsam was the proper consistency if it was firm and did not stick to the thumbnail.

After the balsam had reached the proper consistency, the mineral grains were sprinkled uniformly over the balsam and covered with a cover glass. The slide was then removed from the heater and allowed to cool. The slides were labeled with the sample number and a notation "heavy" or "light" to denote the heavy and light minerals.

Petrographic Study. The heavy and light minerals were identified with a petrographic microscope. A mechanical stage was used to traverse the slide. Minerals requiring more exact identification were placed in immersion oils and the indices of refraction determined by the Becke Line method.

Two hundred grains or more were counted on each slide to determine the mineral frequency, which was expressed as a percentage of the total grains counted on each slide.

Binocular Microscope Study. The coarse residue greater than 125 microns in size was examined with a binocular microscope to determine the relative amount of each of the constituents.

Preparation of Clay-Size Material for X-ray Analysis

One of the problems in the laboratory preparation of limestone samples for clay mineral studies was the possible loss or modification of some of the clay minerals during the extraction of the carbonates with hydrochloric acid. Nontronite and hectorite of the montmorillonite group are soluble in hydrochloric acid. Chlorite may also be soluble if treated with warm

hydrochloric acid. Because of the solubility of these clay minerals in acid, no attempt was made to extract the carbonates by acid treatment. There are two possible disadvantages to this procedure; (1) the colloidal-size quartz and calcite may disrupt the preferred orientation of the clay minerals and (2) the clay-size material may have to be concentrated to get adequate analytical data.

Separation of Clay Fraction From Limestone Samples. The limestone sample was crushed and sieved through a U. S. #200 screen (74 microns). Two hundred grams of the sample less than 74 microns in size was used in this procedure.

The sample was disaggregated with a Waring Blender using 80 milliliters of sodium silicate and 400 milliliters of distilled water. The sample was agitated for 15 minutes in a Waring Blender. In one case, the Oread limestone sample, additional sodium silicate had to be added to get complete disaggregation.

The dispersed sample was then transferred to a sedimentation tube and distilled water added until the total volume reached 1,000 milliliters. The sedimentation tube was placed in a constant temperature bath, the temperature at approximately 20 degrees centigrade. The settling time allowed for the first separation was 12 hours for each 10 centimeters of settling distance. After 36 hours the upper 30 centimeters were siphoned from the tube and stored in a one-gallon glass jug. That portion of the sample in the bottom of the sedimentation tube was placed in the Waring Blender, agitated for one minute, and transferred back to

the sedimentation tube. The same procedure was followed for the second separation with the exception of the settling time which was reduced to 24 hours for the upper 30 centimeters. After 24 hours of settling time, the upper 30 centimeters were siphoned from the tube and placed in the one-gallon glass jar with the previously siphoned suspension. The material in the suspension siphoned from the upper 30 centimeters of the sedimentation tubes was taken as a representative fraction of the clay-size material.

Oriented Slides. Oriented aggregates of the clay-size material were made by placing a small amount of the suspended material on a glass microscope slide with an eye dropper. The suspension was allowed to air dry under room conditions. Upon drying, the basal surfaces of clay minerals were oriented with the surface of the slide. This orientation will give basal reflections in X-ray diffraction analysis.

Using the procedure outlined, it was found that colloidal sized quartz and calcite did not disrupt the preferred orientations of the slides. It was found, however, that in some cases the suspension had to be condensed to obtain more intense peaks on the X-ray diffraction pattern. The samples were condensed by placing a small amount of the suspension in an open beaker and evaporating the water with heat lamps. The condensed suspension was used in making oriented slides. The slides made of the condensed samples gave more intense peaks on the X-ray diffraction pattern.

X-ray Method. Identification of the clay minerals present

in the samples was done by X-ray diffraction using a North American Phillips diffraction unit. Nickel filtered copper radiation was used with a one degree slit system, rate meter scale factor of 400, time constant of four seconds at 20 milliamps and 40 kilovolts. The scanning speed was one-fourth degree two theta per minute. The oriented slides were examined from 30 degrees two theta to three degrees two theta.

After being examined through this angular distance, the oriented slide was treated with ethylene glycol which was applied with a small atomizer. Ethylene glycol will form an organic complex with montmorillonite causing the basal spacings to expand to 17.7 angstroms. After the glycol treatment, the diffraction pattern was recorded from 15 degrees two theta to four degrees two theta. This range included the (001) of illite, kaolinite, and montmorillonite in its expanded position, and the (001) and the (002) reflections of chlorite and vermiculite.

The diffraction patterns obtained from these two runs were recorded on a strip chart in degrees two theta. This unit of measurement was converted to d-spacings using "Tables for Conversion of X-ray Diffraction Angles to Interplanar Spacings". The d-spacings were then compared with known and theoretical spacings of minerals which may occur in the clay-size range.

DOLOMITE IN HIGH MAGNESIUM LIMESTONE SAMPLES

The chemical analysis of the limestone screenings was made by the State Geological Survey of Kansas in association with the

Limestone Aggregate Association. This analysis revealed that samples 101 (Herington), 43 (Topeka), 30 (Captain Creek) contained relatively high percentages of MgO (refer to Table 3). Two methods were used to determine if the magnesium was present in the form of dolomite: (1) staining tests and (2) X-ray analysis.

Stain Test

The staining test used was the method described by Otto (Krumbein and Pettijohn, 1938, p. 496) as most reliable. A 10 percent solution of silver nitrate and a neutral solution of potassium chromate (K_2CrO_4) were used. Distilled water was used for both solutions. A ground surface of a known calcite sample was treated with the silver nitrate for three minutes. The sample was then washed carefully with distilled water to remove the nitrate. The washed sample was immersed in the neutral solution of potassium chromate for about one minute and washed again. This staining test colored the calcite a red-brown color. Dolomite, or aragonite if present, will not be colored by this staining method.

A small fragment from sample 101, the Herington limestone from Washington County, was ground to have a flat surface and submitted to this staining procedure. The resulting color was a light reddish-tan, much lighter in color than the known calcite sample. This would indicate that there may be dolomite present.

The stained fragment was examined closely under the binocular

Table 3. Chemical analysis of limestone screenings[a]

Sample No.	Fm. or Mbr.	Calc. $CaCO_3$	Calc. $MgCO_3$	Calc. $CaCO_3$ equiv.	Chemical analysis, percent: CaO	MgO	L.O.I.[b]	SiO_2	Al_2O_3[c]	Fe_2O_3[d]	K_2O	Na_2O	SO_3	S[e]	P_2O_5	Total
21	Herington	77.33	3.39	81.30	43.47	1.85	0.67 0.43 35.77	13.86	2.06	0.94	0.34	0.17	0.10	Nil	0.03	100.23
101	Herington	43.85	33.55	83.61	24.66	16.26	0.71 0.48 36.79	14.49	3.06	1.90	0.62	0.24	0.07	0.06	0.03	99.31
57	Cresswells	84.56	1.19	85.91	47.48	0.44	0.46 0.55 37.80	9.72	1.96	0.66	0.29	0.10	0.10	0.01	0.02	99.58
31	Towanda	87.67	1.90	89.86	49.25	0.08	0.63 0.33 39.54	5.91	1.60	0.92	0.36	0.07	0.11	Nil	0.04	99.56
8	Ft. Riley	79.83	1.19	81.18	44.91	1.15	0.74 0.49 35.72	12.52	2.75	1.12	0.56	0.11	0.15	0.01	0.05	100.27
9	Neva	86.08	0.73	86.89	48.35	0.32	0.62 0.38 38.23	9.87	1.01	0.61	0.09	0.05	0.05	Nil	0.04	99.62
43	Topeka	71.23	7.34	79.89	40.04	3.50	0.75 0.52 35.15	12.36	3.25	3.13	0.64	0.19	0.07	0.07	0.06	99.56
70	Oread	75.69	4.02	80.41	42.66	1.96	0.70 0.60 35.38	11.89	3.07	2.07	0.49	0.16	0.24	0.19	0.06	99.28
23	Stoner	84.81	2.93	88.23	47.62	1.49	0.29 0.30 38.82	7.59	1.84	1.28	0.26	0.11	0.08	0.12	0.03	99.71
30	Captain Creek	73.44	6.61	81.18	41.34	3.49	0.39 0.50 35.74	11.73	3.34	2.31	0.55	0.19	0.15	0.25	0.06	99.79
105	Bethany Falls	87.74	2.20	90.30	49.20	1.45	0.26 0.39 39.73	6.48	1.52	0.83	0.23	0.11	Trace	0.10	0.03	100.23

a. Chemical analysis made by State Geological Survey of Kansas
b. Loss on ignition from 105°C to 1000°C
   Top figure 105°/550°C
   Middle figure 550°/600°C
   Bottom figure 600°/1000°C (represents CO_2)
c. Contains TiO_2, MnO_2 etc, if present
d. Total iron expressed as ferric oxide
e. Sulfide sulfur, reported in L.O.I.

microscope for unstained dolomite crystals. The small crystal size precluded the identification of dolomite crystals with the binocular microscope.

A test was made to determine the depth of staining. A stained fragment was polished using a dampened ground glass surface. One stroke across the glass was sufficient to remove most of the stain from the ground surface of the sample.

X-ray Analysis

An X-ray analysis was made of samples 101, 43, and 30 to determine if dolomite was present. To prepare the sample for X-ray analysis, the sample was crushed and screened through a U. S. #325 screen (44 microns). The material less than 44 microns in size was used in preparing an unoriented slide for X-ray analysis.

The unoriented sample was examined from 35 degrees two theta to 26 degrees two theta and the reflections were recorded on a strip chart in degrees two theta. This unit of measurement was converted to d-spacings and compared with known and theoretical d-spacings of common carbonate minerals. Sample 101, the Herington limestone from Washington County, contained an abundance of dolomite with little or no calcite. Sample 43, the Topeka limestone, and sample 30, the Captain Creek limestone, contained both calcite and dolomite with calcite being more abundant. The dolomite-calcite ratio was not determined in this investigation, but may be determined by applying the method outlined by Tennant and Berger (1957).

NON-CARBONATE MINERALOGY OTHER THAN CLAYS

Heavy Minerals

Pyrite, celestite, and limonite were the most abundant minerals in the heavy mineral fraction of the limestone samples studied. No attempt was made to remove the limonite during the laboratory procedure. Magnetite, muscovite, biotite, chlorite, tourmaline, rutile, hornblende, epidote, zircon, zoisite, garnet, and corundum were present in minor amounts. Chalcedony and quartz were present in the heavy mineral fraction as coated grains.

Pyrite. Pyrite is an iron-disulfide (FeS_2) which is opaque and has a uniform, pale brass-yellow, metallic luster under reflected light. Marcasite is another iron-disulfide quite similar to pyrite, but differing in crystal habit. No attempt was made to distinguish between pyrite and marcasite in this investigation.

Pyrite, in the samples studied, occurred in several forms; as euhedral crystals, as a composite of small equidimensional crystals, as pyritized fossil fragments, as coatings on chalcedony and quartz grains, and in nodular form coating unidentified grains. The quartz grains which were coated with pyrite commonly exhibited wavy extinction in polarized light.

Celestite. Celestite is strontium sulfate ($SrSO_4$) with the following optical properties: biaxial positive, birefringence of .009, interference color white to straw yellow, and indices of

refraction greater than Canada balsam. The celestite occurred as cleavage fragments and as clay-coated grains. It was very commonly coated with a cryptocrystalline material which was tan in color. The author interpreted this material to be clay-size material which had been colored by limonite stain.

Limonite. Limonite is a hydrous iron-oxide ($Fe_2O_3.nH_2O$) and is an alteration product of iron-bearing minerals. It is commonly referred to as an amorphous mineral, but Winchell and Winchell (1951), p. 80, points out that much of it is actually cryptocrystalline goethite ($aFe_2O_3.H_2O$).

Limonite was found in the limestone samples as hard, concretionary masses, soft, porous particles, and as a coating on other mineral grains. All stages of alteration were noted between pyrite and limonite and, in some cases, the limonite was pseudomorphous after pyrite. Pyrite seemed to be the principle source of the iron for limonite. The limonite coated grains listed in Table 4 represent grains which were coated to the extent that mineral identification of the coated grain could not be made.

Chlorite. Samples 21, the Herington limestone from Dickinson County, and 31, the Towanda limestone, contained mineral grains which were subrounded, platy, isotropic-appearing, and green to slight brownish-green. The indices of refraction were determined using immersion oils and the Becke Line method. The index of refraction of the grains which were green and more isotropic-appearing was approximately 1.62. The brownish-green

grains had a higher index of refraction, but never exceeded 1.65. In one case a brownish-green grain which was partially isotropic was observed to have a biaxial negative interference figure with a low 2V. Reference was made to the classification of the varieties of chlorite on the basis of optical properties by Winchell and Winchell, (1951), p. 382. It was found that several varieties of chlorite may have birefringence of .000 which would make them isotropic-appearing.

The chlorite present in other limestone samples did not exhibit this low birefringence.

Hornblende. The Neva and Towanda limestone samples contained mineral grains which possessed all of the optical properties of hornblende except for the extinction angle, which was less than 12 degrees. These grains were brown to green-brown and were deeply pleochroic. They were listed in Table 4 as hornblende.

Light Minerals

The light mineral fraction of the samples studied was predominantly chalcedony with quartz, plagioclase, orthoclase, and microcline in minor amounts. The chalcedony was colorless to yellow and was observed to have the characteristic aggregate polarization in polarized light.

The quartz was subdivided on the basis of extinction characteristics in polarized light. The subdivisions were quartz with wavy extinction and quartz with snappy extinction. The quartz grains observed in the petrographic analysis did not have

secondary overgrowths.

In samples in which the type of plagioclase could be determined, it was found to be the soda-rich variety. Only one example was found of a feldspar grain showing secondary overgrowth; that was in the sample from the Cresswell limestone.

Coarse Residue

The most common constituent of the coarse residue was chalcedony which occurred as irregular fragments and as replaced skeletal structures. The Echnoid and Crinoid skeletal structures were common as chalcedonic fossil fragments.

Numerous particles with lace-like structure were noted in the coarse residue. These particles were interpreted as networks of siliceous and calcareous material. The calcareous material had been removed by acid leaching leaving a lace-like structure of siliceous material.

Organic residue was present in the coarse residue in all samples except the Fort Riley limestone. It was generally the case that samples containing greater quantities of organic residue also contained pyrite. All stages of alteration from pyrite to limonite were noted and pseudomorphs of limonite after pyrite were common.

The Stoner limestone contained an abundance of detrital quartz. The quartz grains were well-sorted, subrounded, with a frosted surface. The frosted surface indicated that the grains had either been etched by wind erosion or etched by solution be-

fore or after deposition. The quartz grains present in the other samples were subrounded and well-sorted, but generally did not have frosted surfaces.

Table 4. Summary of heavy mineral analysis of insoluble residue in the size range from 53-125 microns.[a]

Sample Number	Magnetite	Limonite Coated	Pyrite	Pyrite Coated	Muscovite	Biotite	Chlorite	Celestite	Tourmaline	Rutile	Hornblende	Epidote	Zircon	Garnet	Corundum	Clay Coated	Total
21	1.5	48.2	.4		17.3	16.5	.8	1.5	3.0	.4	.8			.8		8.7	99.9
101		7.7	12.2	1.8	4.8		.4	63.0		.4	.8	.4			.4	7.8	99.7
57	1.8	7.3			10.4			64.5				.8				15.0	99.8
31	2.6	71.5			1.3	2.2	.9	.4			11.5		.4	.9		7.9	99.6
8	.5	3.5			19.5			75.0								1.0	99.5
9		85.4		2.6	1.6			2.6			2.9		.9	.9		2.1	100.0
43		75.5	6.6		.4	.4		14.1			.4					2.4	99.8
70	.4	10.8	73.0	2.8	.4			7.7			.4		.4			3.2	99.1
23	.5		81.6	.4	5.6				1.0	1.0						9.6	99.7
30		1.0	86.2	6.6				1.5		.5	1.0			.5		3.0	100.3
105			81.6	14.4				3.0								1.0	100.0

[a]The heavy mineral fraction was less than five-tenths of one percent of the total weight.

Table 5. Summary of light mineral analysis of insoluble residue in the size range from 53-125 microns.

Sample Number	Formation or Member	Percent of Total Weight	Chalcedony	Quartz with Snappy Extinction	Quartz with Wavy Extinction	Plagioclase	Orthoclase	Microcline	Clay Coated	Total Percent
21	Herington	2.5	57.4	7.0	26.4	8.8	.5			100.1
101	Herington	1.2	96.8		1.8	.5	1.0			100.1
57	Cresswell	.8	84.5	1.9	12.5	.5		.5		99.9
31	Towanda	.3	84.4		10.7	5.0				100.1
8	Fort Riley	1.2	94.0	.5	5.5					100.0
9	Neva	2.4	98.5		1.0			.5		100.0
43	Topeka	1.2	98.0		2.0					100.0
70	Oread	1.8	96.5		1.5	2.0		.5		100.5
23	Stoner	1.5	64.3	3.0	31.3				.9	99.5
30	Captain Creek	2.2	88.6		10.0	1.5				100.1
105	Bethany Falls	.9	98.4		1.0			.5		99.9

Table 6. Summary of coarse residue analysis of insoluble residue greater than 125 microns in size.

Sample Number	Formation or Member	Percent of Total Weight	Chalcedonic Fragments	Calcedonic Fossil Frag.	Detrital Quartz	Pyrite	Limonite Coated	Organic Residue	Muscovite Flakes	Green Shaly Material	Gray Shaly Material
21	Herington	1.1	Major		XX			X			
101	Herington	.8	XXX		Major	X	X	XX			
57	Cresswell	1.4	Major	XXX	X	Trace		Trace			
31	Towanda	1.2		X	Major		XX	X			
8	Fort Riley	2.5	Major	XXX							
9	Neva	3.6	Major	X			XX	XXX			
43	Topeka	1.8	XX		Trace	X	XX	X		Major	
70	Oread	1.5	Major			Trace	XX	XXX	Trace		Major
23	Stoner	2.2	X	Trace	Major	X		X	Trace		Major
30	Captain Creek	1.8	XX			XXX	X	XXX			
105	Bethany Falls	1.2	XX		X	XX		XXX			

Scale of abundance: Major, XXX, XX, X, Trace.

CLAY MINERALOGY OF LIMESTONE SAMPLES

X-Ray Analysis of the Clay-Size Fraction

The bulk of the clay minerals in the samples studied were three-layer silicates (montmorillonite, illite, and chlorite). X-ray identification of these clay minerals is based largely upon the variation in spacings of the reflections. Different interlayer components will occupy different volumes producing differences in the c-axis periodicities (basal reflections). The X-ray diffraction patterns of the oriented slides were recorded as basal reflections.

Illite was the most abundant clay mineral present in the limestone samples. It was abundant in all samples except sample 9, the Neva limestone, in which clay size calcite was the dominant component. Illite was identified on the basis of the characteristic 10-A peak and other reflections of a 10-A periodicity which remained unchanged after glycolation.

Chlorite was present in many of the samples and was identified by an integral series of basal reflections from 14-A. Chlorite, when identified by X-ray analysis, may be confused with kaolinite, montmorillonite, and vermiculite. The chlorite found in this investigation was commonly the iron-rich variety with weak first and third order reflections and strong second and fourth order reflections. The second and fourth order reflections at 7-A and 3.5-A respectively, correspond to the first and second order reflections of kaolinite. Heat treatment was used to

distinguish between the two. Heating to 450 degrees centigrade for one hour resulted in the disappearance of the reflections of a 14-A periodicity. This indicated that kaolinite was not present in the limestone samples studied. Kaolinite, if present, will withstand heat treatment up to 600 degrees centigrade.

Chlorite was distinguished from montmorillonite by glycolation treatment. Montmorillonite basal reflections expand when glycolated, whereas chlorite spacings are unaffected. Recently a swelling chlorite has been reported which has made the distinction between chlorite and montmorillonite more difficult (Brindley, 1951; Lippman, 1956). Brindley (1951), p. 116, however, has pointed out that the common types of chlorite do not show this swelling behavior.

Chlorite may be distinguished from vermiculite by the differences in the intensities of the basal reflections. The 14-A reflections of vermiculite is strong and subsequent reflections weaker. The basal reflections of chlorite may be of equal intensity except for iron-rich varieties.

Weaver (1956) pointed out the widespread occurrence of mixed-layer clays. Relatively stable mixed-layer structures may form because of the structural similarity of many of the clay minerals. There are several ways in which the mixed-layer structures may occur (Brindley, 1951, p. 66): (1) the existence of two different degrees of hydration, i.e., a mixture of mica-type layers with montmorillonoid--or vermiculite--type layers, (2) having

brucite-like layers mixed with mica-type layers, or layers of water molecules, i.e., in mixed vermiculite-chlorite structures, or (3) having two successive montmorillonoid "hydrates". There are three ways in which the layers may be distributed in mixed-layer clays: (1) regularly, (2) randomly, and (3) segregated into zones in the crystallites. The mixed-layer structures in the limestone samples studied in this investigation were identified as regularly interlayered chlorite and vermiculite-chlorite and randomly interlayered illite-montmorillonite, illite-chlorite, and chlorite-vermiculite.

The mixed-layer clays gave reflections which were averages of the component clay minerals which were present. The regular mixed-layer was distinguished from the random mixed-layer by determining if the reflections from the (001) planes formed an integral or non-integral series. The regular mixed-layer will give a high spacing reflection and a series of sharp, higher order reflections which form an integral series. The random mixed-layer clays will give spacings which do not form an integral series.

Chlorite was identified as a regular mixed-layer clay mineral with an integral series of reflections from 14-A (Grim, 1953, p. 27). The mixed-layer structure of chlorite consists of alternating mica-like and brucite-like layers.

A random interlayering of illite-montmorillonite was recognized by the change in symmetry of the 10-A peak before and after glycolation. The X-ray spectrometer tracings in Plate II show this change in symmetry. The 10-A peak before glycolation was

quite asymmetrical and became more symmetrical after glycolation. This was interpreted as a result of expansion of the montmorillonite layers in the interlayered structure. There are, however, other irregularities which may also cause some asymmetry of the 10-A peak, i.e., degraded illite or water layers interpolated between the illite sheets. There was also the possibility that a small amount of chlorite may be interlayered with illite causing some modification which would persist after glycolation.

Mixed-layer illite-chlorite was recognized by shoulders on the 10-A peak which failed to expand after glycolation. In some cases distinct peaks were not present, but an asymmetrical 10-A peak persisted after glycolation. As previously mentioned, this may indicate a small amount of chlorite interlayered with illite. Plate III shows the 10-A peak of a sample containing interlayered illite-chlorite.

Mixed-layer clays with a 14-A spacing which expanded to 15.5-A after glycolation were identified as vermiculite-chlorite. X-ray spectrometer tracings of samples containing mixed-layer vermiculite-chlorite are shown in Plates IV and V. A quantitative evaluation may be made by comparing the intensities of the 14.2-A and 7.1-A peaks, but this method is subject to error because the intensity of the 14.2-A and 7.1-A peaks of chlorite may vary with composition. For example, if iron-rich chlorite were present in the mixed-layer structure, a comparison of the 14.2-A and 7.1-A peaks would indicate a greater abundance of chlorite than was actually present.

In the X-ray spectrometer tracings shown in Plates IV and V, the 14.2-A peaks are much more intense than the 7.1-A peaks and indicated that vermiculite was the dominant component of the mixed-layer structure. There was evidence from the shift of the 7.1-A peak after glycolation that these structures were regularly interstratified.

The Fort Riley limestone contained on interlayered structures with a doublet at 13.18-A and 13.80-A. The X-ray spectrometer tracings are shown in Plate VI. After glycolation, there was a broad peak at 16.35-A which was identified as montmorillonite-illite. A quantitative determination based on the amount of expansion indicated that this mixed clay was approximately 70 percent montmorillonite and 30 percent illite. The 14.48-A shoulder was identified as chlorite-vermiculite.

Two common non-clay minerals present in the clay-size range were quartz and calcite. Quartz was identified by the 4.2-A reflections. The 3.35-A reflection of quartz occurred as a modification of the (003) reflection of illite. Calcite was identified by a 3.03-A reflection.

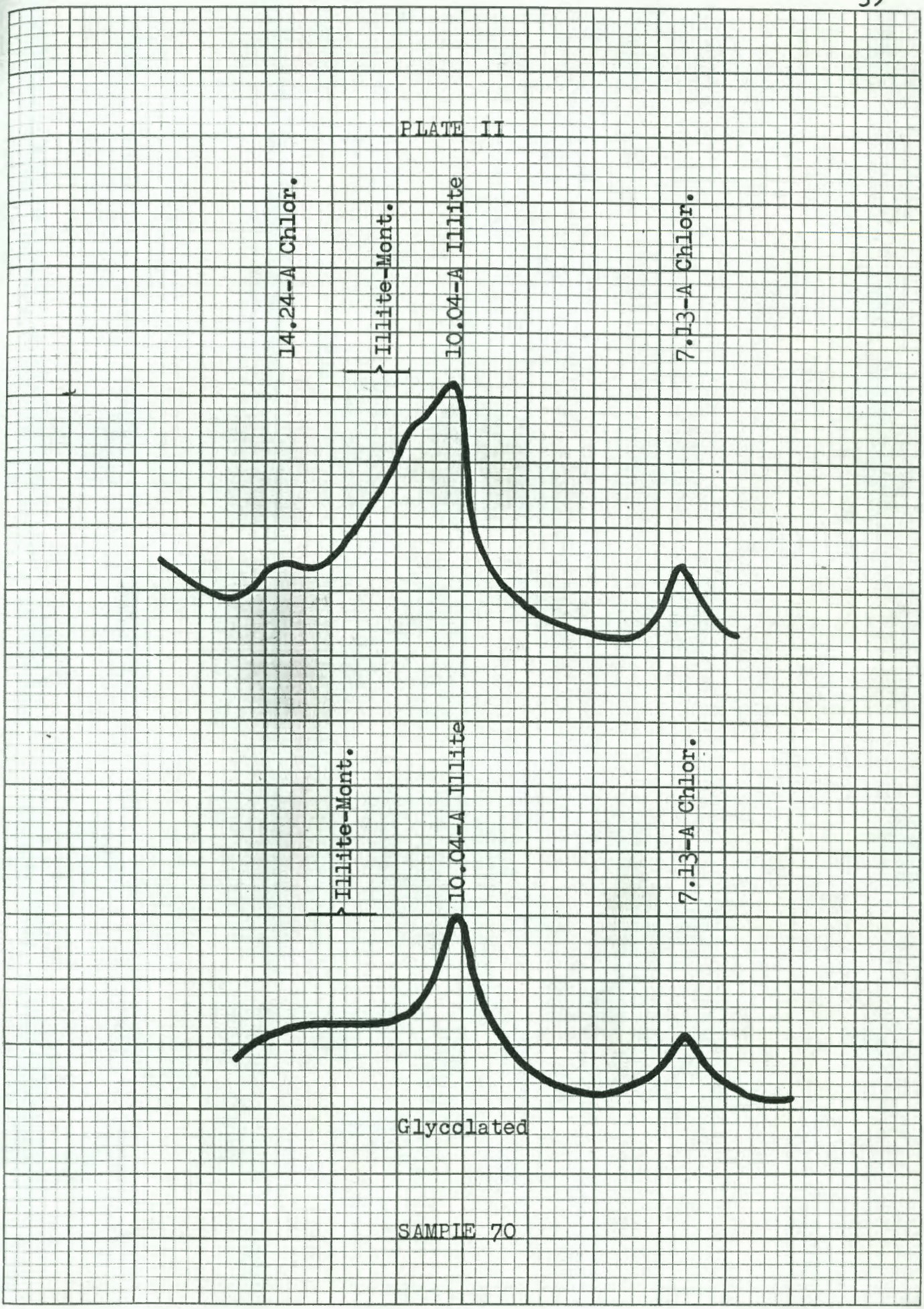
EXPLANATION OF PLATE I

X-ray spectrometer tracings of sample 9, the Neva limestone from Chase County, showing the weak 10-A peak and randomly interlayered illite-montmorillonite.

EXPLANATION OF PLATE II

X-ray spectrometer tracings of sample 70, the Oread limestone, showing the change in symmetry of the 10-A peak produced by glycolation. This plate also shows the relative intensities of the 14.24-A and 7.13-A peaks of iron-rich chlorite.

PLATE II



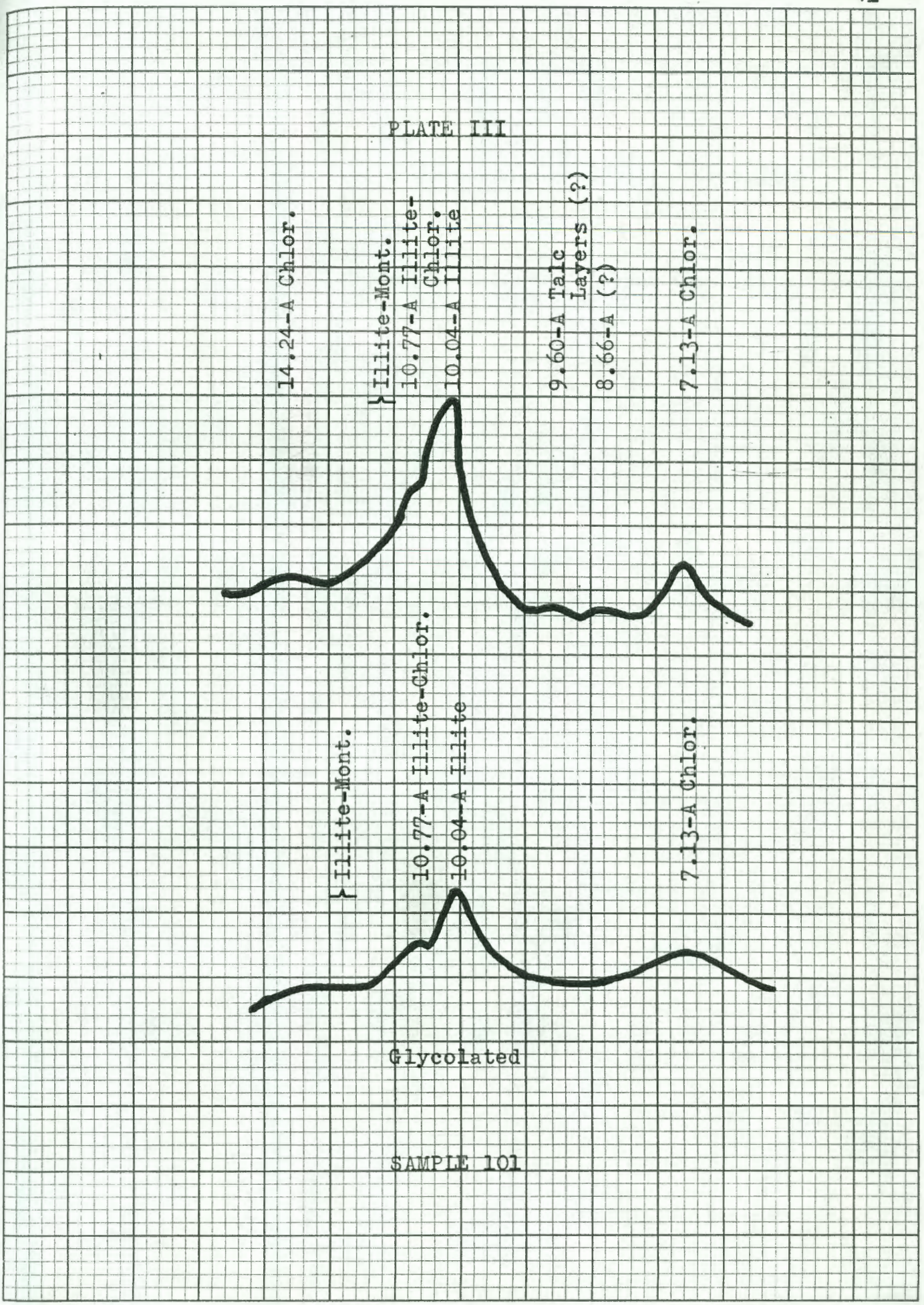
Glycolated

SAMPLE 70

EXPLANATION OF PLATE III

X-ray spectrometer tracings of sample 101, the Herington limestone from Washington County, showing interlayered illite-chlorite. The expansion of illite-montmorillonite after glycolation has obscured the 14.24-A peak.

PLATE III



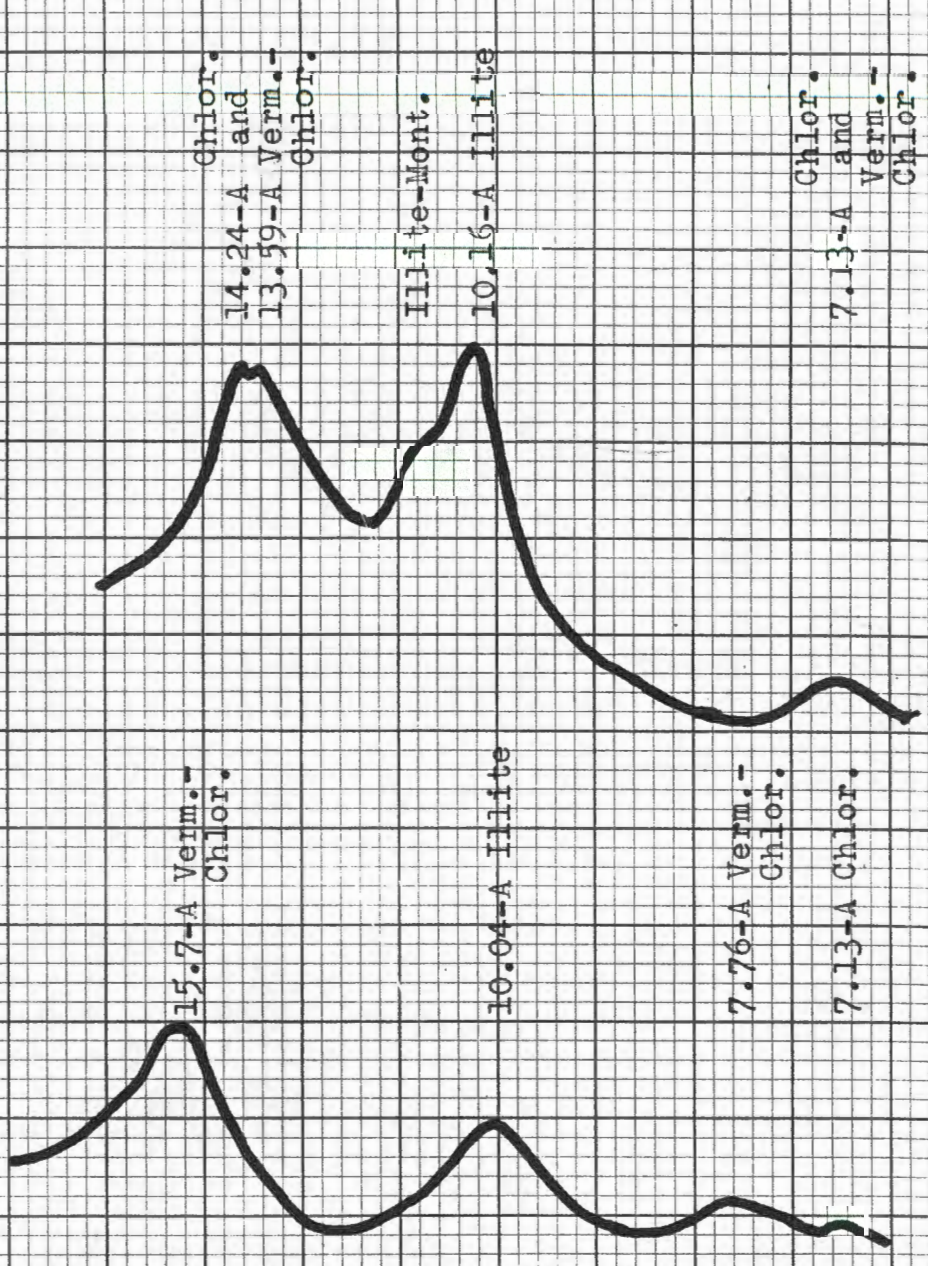
Glycolated

SAMPLE 101

EXPLANATION OF PLATE IV

X-ray spectrometer tracings of sample 21, the Herington limestone from Dickinson County, showing the shift of the 14.24-A and 13.59-A peaks after glycolation.

PLATE IV



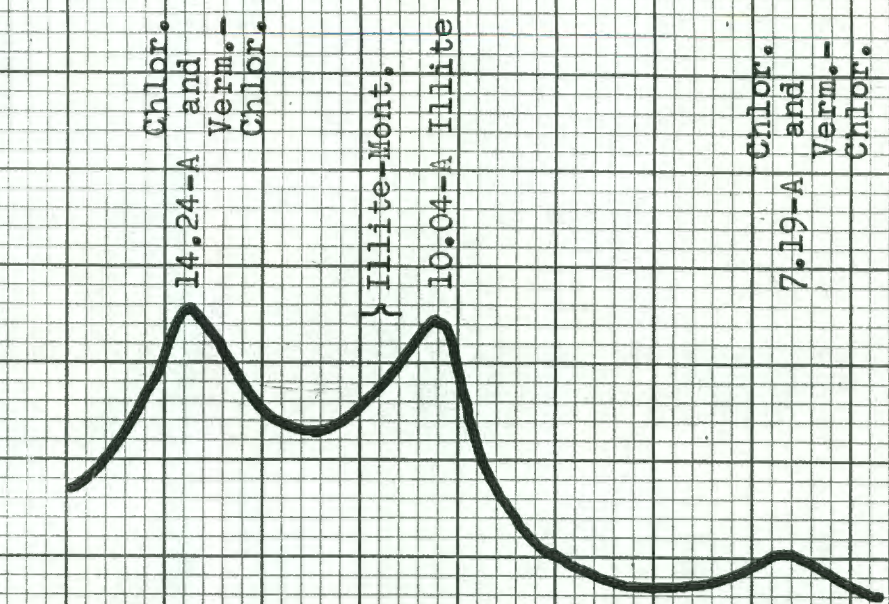
Glycolated

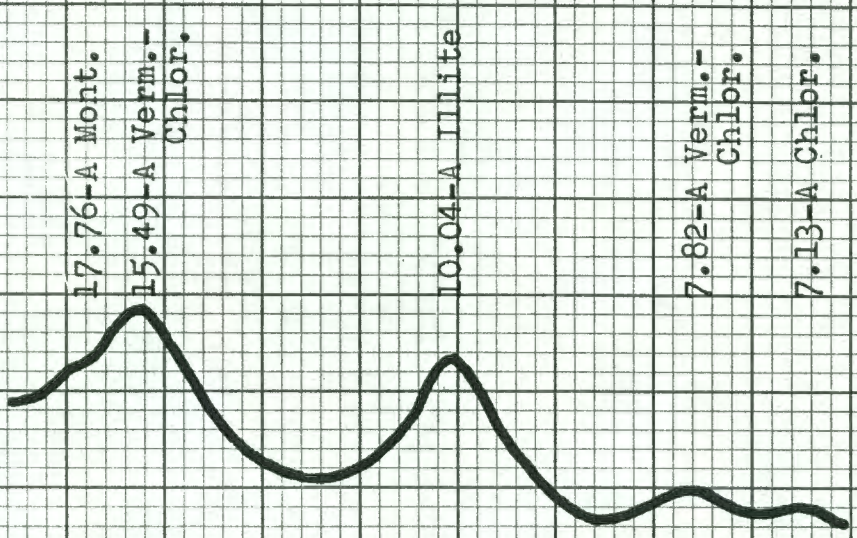
SAMPLE 21

EXPLANATION OF PLATE V

X-ray spectrometer tracings of sample 57, the Cresswell limestone, showing the shift of the 14.24-A peak after glycolation. This plate also shows an indistinct peak at 17.76-A after glycolation.

PLATE V





Glycolated

SAMPLE 57

EXPLANATION OF PLATE VI

X-ray spectrometer tracings of sample 8, the Fort Riley limestone, showing the shift of 13.80-A and 13.18-A peaks after glycolation.

PLATE VI

Glycolated

SAMPLE 8

Table 7. Summary of the components of the clay-size fraction from limestone samples.

Sample Number	Formation or Member	Percent of Total Weight[a]	Percent of MgO	Illite	Chlorite	Illite-Montmorillonite		Illite-Chlorite	Chlorite-Vermiculite		Montmorillonite	Calcite	Quartz
21	Herington	13.1	1.85	Major	X	X				XX		XXX	Trace
101	Herington	18.0	16.26	Major	XX	XX		Trace					
57	Cresswell	11.1	.44	Major	Trace	Trace				XX	Trace	XXX	Trace
31	Towanda	7.9	.08	Major		X	Trace	Trace			Trace	XXX	
8	Fort Riley	13.9	1.15	Major	Trace	Trace	XX		Trace			XXX	Trace
9	Neva	5.4	.32	X		X	X					Major	Trace
43	Topeka	16.3	3.50	Major	XX	XX						XX	
70	Oread	15.5	1.96	Major	XX	XX						XXX	Trace
23	Stoner	7.9	1.49	Major	X	X						XXX	
30	Capt.Creek	14.0	3.49	Major	XX	XX			Trace			XX	X
105	Bethany Falls	7.6	1.45	Major	X	X		X				XXX	X

Scale of Abundance: Major, XXX, XX, X, Trace.
[a]Includes insoluble residue less than 5 microns in size.

Genesis of Clay Minerals

The clay minerals found in the limestone samples were three-layer clay minerals which are characteristic of sediments that accumulated in an alkaline marine environment. Since the alkaline marine environment favored the preservation of three-layer clay minerals, there was the possibility of some three-layer clay minerals existing as allogenic or detrital minerals. Powers, (1954), p. 73, reported illite being transported as a well crystallized mineral and Grim and Johns (1954), p. 101, reported well-crystallized chloritic clay minerals as detrital.

The authigenic clay minerals are believed to have formed as a result of two processes (Murray, 1954, p. 63). The first is the formation of clay minerals from detrital skeletal aluminum silicate sheet structures. These structures are comparable to what Grim (1953), p. 351, referred to as "degraded illite and degraded chloritic mica". These degraded structures, which may be introduced into the marine environment as land-derived sediments, are partially leached of their constituent alkalies and alkaline earths during weathering and transportation. The leaching, however, is not sufficient to transform these structures into new minerals. These degraded structures have a strong negative charge and may utilize available potassium and magnesium ions in the salt water environment to build clay minerals.

The second process involves the concentration and flocculation of colloids of silica and aluminum hydroxide. This flocculant

may form a loose colloidal sediment which may adsorb many cations, but only those cations which fit into the clay structure are retained. Studies of recent marine sediments has revealed that montmorillonite is a common constituent and Murray (1954), p. 65, has pointed out that the poorly crystalline montmorillonite may represent the first stage in the formation of clay minerals from silica and aluminum colloids.

Authigenic illite may have formed from the degraded clay structures and from montmorillonite. The adsorption and fixation of potassium ions between the unit layers of degraded structures, particularly degraded illite, would have perfected the mica-like structure. The formation of illite from montmorillonite may have been a slow process involving the dehydration and collapse of the montmorillonite structure after burial and subsequent adsorption of potassium and magnesium ions. Studies of recent marine sediments have revealed that the initial adsorption of potassium and magnesium may occur shortly after introduction into the marine environment. The process may have, therefore, involved the initial adsorption of potassium ions with subsequent collapse of the structure during compaction. Intermediate stages in the dehydration and fixation of potassium ions in the interlayer position may have resulted in the illite-montmorillonite mixed-layers which were common in this investigation.

Authigenic chlorite may form from montmorillonite (Murray, 1954, p. 65), degraded illite (Powers, 1954, p. 73), degraded chlorite, and kaolinite (Grim, 1953, p. 352). The authigenic

chlorite may have formed from montmorillonite and the degraded clay structures by the interlayer adsorption of magnesium and hydroxyl ions as brucite sheets. The precipitation of brucite sheets in the interlayer space of montmorillonite has been accomplished under laboratory conditions (Grim and Johns, 1954, p. 101).

Kaolinite was absent in the limestone samples investigated and its absence may have been the result of diagenetic processes which transformed it to chlorite. Grim (1953), p. 351, has stated that the presence of calcium ions may block the formation of kaolinite. The rate of accumulation may have been an important factor explaining the absence of kaolinite. If the rate of accumulation of the sediments were rapid, kaolinite might have persisted in an environment which was unfavorable. The slower rate of accumulation of the limestones probably resulted in the formation of chlorite from kaolinite. Grim and Johns (1954), p. 101, have stated that the process involves the shifting of every other silicon sheet and the replacement of some aluminum by magnesium ions within the structure.

The presence of iron-rich chlorite in the limestone samples investigated indicated that the chlorite was exposed to solutions containing iron. The presence of authigenic pyrite in some cases also indicates the presence of iron. Substitutions of ferrous iron for magnesium and ferric iron for aluminum in the octahedral sheets may have transformed the chlorite to the iron-rich variety.

The amount of chlorite formed and its degree of crystallinity

may have been, in part, a function of the magnesium in solution and the ratio of well-crystallized clay structures to degraded clay structures and montmorillonite. There was a notable relationship between the low MgO content in the chemical analysis and the absence of chlorite in the clay-size fraction. The poorly crystalline nature of the chlorite was probably caused by poorly developed brucite sheets.

The presence of organic residue may also have been an important factor determining the degree of crystallinity of chlorite. Grim and Johns (1954), p. 101, have written that "in the presence of organic material, it would be expected that some organic molecules would be absorbed between the montmorillonite layers blocking the adsorption of the inorganic cations". This may be a possible explanation for the poor crystallinity of the chlorite in the limestone samples.

The limestone samples studied in this investigation which contained relatively larger amounts of chlorite also contained pyrite, more organic material, and a greater amount of insoluble residue less than 53 microns in size. The chemical analysis showed that these samples contained 1.96 percent MgO or more.

Grim and Johns (1954) found in a study of recent marine sediments in the Rockport, Texas area that the greatest abundance of chlorite occurred in an environment in which the magnesium content of the interstitial waters was relatively high and the pH relatively low. The lower pH was correlated with high organic content. Rowland (1952), p. 225, has reported that the

precipitation of brucite layers between the layers of fragmentary montmorillonite-like material may indicate a silica-poor, reducing environment. The association of chlorite with pyrite and organic residue, may therefore be a notable relationship.

The precipitation of magnesium hydroxide between layers of fragmentary montmorillonite-like structures, such as vermiculite, may have formed the vermiculite-chlorite mixed-layer structures. These structures may also have formed in a silica-poor, reducing environment (Rowland, 1952, p. 225). The association of chlorite with pyrite and organic residue may indicate that it was formed in an reducing environment, but the abundance of chalcedony would indicate that the environment may not have been silica-poor.

The illite-chlorite mixed-layers may have formed by the interlayer adsorption of magnesium and hydroxyl ions in degraded illite structures or by the interlayer adsorption of potassium ions in degraded chlorite structures. The mixed layer structure of illite-chlorite may have also formed by the partial interlayer adsorption of $Mg(OH)_2$ in montmorillonite with subsequent collapse of the structure.

SUMMARY

The non-carbonate mineralogy of samples of limestone screenings was determined by petrographic analysis, binocular microscope study, and X-ray diffraction. A mineral frequency determination was made of the insoluble residue in the size range from 53 to 125 microns. The most abundant minerals in this size range

were pyrite, celestite, limonite, and chalcedony. Minerals present in minor amounts were magnetite, muscovite, biotite, chlorite, tourmaline, rutile, hornblende, epidote, zircon, garnet, corundum, quartz, plagioclase, orthoclase, and microcline. The quantity of insoluble residue examined in the petrographic analysis represented less than two percent of the total weight of sample used.

Signigicant constituents of the coarse residue greater than 125 microns in size included pyritized and silicified fossil fragments and organic residue.

There was considerable variation in the amount of MgO in the samples. Larger percentages of MgO was accompanied by larger percentages of SiO_2.

The carbonate mineralogy of the Herington (Washington County), Topeka, and Captain Creek limestones was determined. These samples contained the highest percentages of MgO. The Herington limestone from Washington County was nearly all dolomite. The chemical analysis revealed that Herington limestone sample from Dickinson County was nearly all calcite. The Topeka and Captain Creek limestones contained both calcite and dolomite with calcite far more abundant.

The clay-size material was not concentrated by acid leaching of the carbonates because of loss or possible modification of some of the montmorillonites and chlorite. The clay-size fraction, including clay-size calcite, was extracted by gravity sedimentation. The presence of clay-size calcite did not disrupt the

preferred orientation of the clay minerals.

Illite was the most abundant clay mineral and was present in every sample. The Neva limestone from Chase County contained the least amount of illite. Quantitatively, this sample contained the least amount of insoluble residue less than 53 microns in size and chemically, it contained the least amount of K_2O and Al_2O_3.

The presence or absence of chlorite in the clay fraction was related to the amount of MgO in the chemical analysis. The samples containing the least amount of MgO and iron commonly contained little or no chlorite. The chlorite was iron-rich and poorly crystalline in all cases.

The most common mixed-layer structure was illite-montmorillonite which was present in all samples. Other mixed-layer structures consisting of illite-chlorite and chlorite-vermiculite were present, but were not common. Whether the chlorite in the mixed-layer clays was iron-rich or not could not be determined.

Calcite was a common non-clay constituent in the clay-size fraction because the samples were not subjected to acid treatment. It was present in all samples except the Herington limestone from Washington County which was a dolomite. Quartz was present in the clay-size fraction in a few of the samples, but occurred in minor amounts.

The clay mineralogy of the Herington limestone from Washington County, which was actually a dolomite, was not appreciably different from clays found in limestone samples investigated.

The three-layer clay minerals probably formed in an alkaline marine environment by interlayer adsorption of potassium and

magnesium ions in degraded illite, degraded chlorite, and montmorillonite. There was the possibility that some of the three-layer clay minerals represented allogenic or detrital minerals. An alkaline marine environment would have preserved these minerals.

A summary of the genesis of the clay minerals in an alkaline marine environment appears in Table 8. This table was not meant to be a complete table, but represents information found in the review of literature during the course of this investigation.

Table 8. Summary of genesis of clay minerals in an alkaline marine environment.

Parental Material	Early or incomplete stages	Late or more complete stages
Degraded illite	Illite-montmorillonite Illite-chlorite Chlorite	Illite Illite-chlorite Chlorite
Degraded chlorite	Chlorite-vermiculite Illite-chlorite Illite	Chlorite Illite-chlorite Illite
Montmorillonite	Illite-montmorillonite Chlorite-vermiculite	Illite Chlorite
Kaolinite	Chlorite (Dioctahedral)	Chlorite

Samples containing relatively larger amounts of chlorite also contained pyrite, larger amounts of organic residue, and larger amounts of the insoluble residue less than 53 microns in size. Although the amount of chlorite could be explained in part by the amount of insoluble residue, the presence of organic

residue and pyrite may have been indicative of important environmental conditions which favored the formation of chlorite.

The presence of organic material may have been an important factor affecting the crystallinity of the chlorite. The absorption of organic molecules may have partially blocked the interlayer adsorption of magnesium ions.

There was some correlation between the clay minerals present (particularly chlorite) and the chemical composition, but the clay mineralogy could not be predicted from the latter. The presence of celestite and other minerals found in the insoluble residue was not apparent in the chemical analysis.

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BIBLIOGRAPHY

Allen, E. T., J. L. Crenshaw, and J. Johnson
The mineral sulfides of iron. Am. Jour. of Sci. 33:169-236. 1912.

Bradley, W. F., and C. E. Weaver
A regularly interstratified chlorite-vermiculite clay mineral. Amer. Miner. 41:497-504. May, 1956.

Bradley, W. F.
X-ray diffraction critera for the characterization of chloritic material in sediments. Clays and Clay Minerals. A symposium. Second Nat. Conf. on Clays and Clay Minerals, Proc. Washington, D. C.: Nat. Acad. Sci. - Nat. Res. Council Pub. 327:209-217. 1954.

Brindley, G. W.
X-ray identification and crystal structure of the clay minerals. The Miner. Soc. (Clay Minerals Group) London: Taylor and Francis, 1951.

Brindley, G. W., and F. H. Gillery
X-ray identification of the chlorite species. Amer. Miner. 41:169-186. March, 1956.

Brown, G.
The effects of isomorphous substitution on the intensities of (001) reflections of mica and chlorite. Miner. Mag. 30:657-665. 1955.

Chilingar, G. V.
Relationship between Ca/Mg ratio and geologic age. Am. Assoc. Petrol. Geol. Bull. 40:2256-2266. September, 1956.

_____.
Use of Ca/Mg ratio in porosity studies. Am. Assoc. Petrol. Geol. Bull. 40:2489-2493. October, 1956.

Clark, F. W., and W. C. Wheeler
The inorganic constituents of marine invertebrates. U. S. Geol. Survey, Prof. Paper 124. 1922.

Earley, J. W., G. W. Brindley, W. J. Mc Veagh, and R. C. Vanden
A regularly interstratified montmorillonite-chlorite. Amer. Miner. 41:258-267. March, 1956.

Fairbanks, R. W.
The dolomite question. A symposium. Regional Aspects of Carbonate Deposition. Special Pub. No. 5, Soc. Econ. Paleon. and Miner. 1957.

Galliher, E. W.
Glauconite genesis. Bull. of Geol. Soc. of Am. 46:1351-1366. 1935.

Ginsburg, R. N.
Diagenesis and lithification of carbonate sediments in South Florida. A symposium. Recent Marine Sediments. Special Pub. No. 4, Soc. Econ. Paleon. and Miner. 1954.

Glass, H.
A start toward environmental geology, problems of clay and laterite genesis. A symposium. New York: Am. Inst. of Miner. and Metal. Eng. pp. 230-232. 1952.

Grim, R. E.
The depositional environment of red and green shales. Jour. Sediment. Petrol. 21:226-232. December, 1951.

_____.
Clay Mineralogy. New York: McGray-Hill, 1953.

Grim, R. E., R. M. Bray, and W. F. Bradley
The mica in argillaceous sediments. Amer. Iner. 22:813-829. 1937.

Grim, R. E., J. E. Lamar, and W. F. Bradley
The clay minerals in Illinois limestones and dolomites. Jour. Geol. 45:829-843. 1937.

Grim, R. E., R. S. Dietz, and W. F. Bradley
Clay mineral composition of some sediments from the Pacific Ocean off the California coast and the Gulf of California. Geol. Soc. Am. Bull. 60:1785-1808. 1949.

Grim, R. E., and W. D. Johns
Clay mineral investigation of sediments in the northern Gulf of Mexico. Clays and Clay Minerals. A symposium. Second Nat. Conf. on Clays and Clay Minerals, Proc. Washington, D. C.: Nat. Acad. Sci.-Nat. Res. Council Pub. 327:81-103. 1954.

Hartig, R. L.
Minor petrographic constituents of some Permian rocks. Unpublished M. S. thesis, Kansas State College, Manhattan, Kansas, 1954.

Hauser, E. A.
Genesis of clay minerals, problems of clay and laterite genesis. A symposium. New York: Am. Inst. of Min. and Metal. Eng. pp. 100-106. 1952.

Heinrich, E. M.
Microscopic petrography. New York: McGraw-Hill, 1956.

Johnson, J. H.
An introduction to the study of organic limestones. Rev. ed. Quart. of the Colo. Sch. of Mines. 46. 1951.

Krumbein, W. C., and F. J. Pettijohn
Manual of Sedimentary Petrology. New York: Appleton-Century-Crofts. 1938.

Krynine, P. D.
Petrology, stratigraphy, and origin of the Triassic sedimentary rocks of Connecticut. State Geol. and Nat. Hist. Sur. of Conn., Bull. 73, Hartford. 1950.

_____.
The megascopic study and field classification of sedimentary rocks. Jour. Geol. 56:130-165. 1948.

Levinson, A. A.
Studies in the mica group: polymorphism among illites and hydrous micas. Amer. Miner. 40:41-49. January, 1955.

Lippman, F.
Clay minerals from the Rot Member of the Triassic near Gottingen, Germany. Jour. Sediment. Petrol. 26:125-139. June, 1956.

Lowenstam, H. A.
Factors affecting the aragonite: calcite ratios in carbonate-secreting marine organisms. Jour. Geol. 62:284-322. 1954.

MacEwan, D. M. C.
Chlorites and vermiculites in soil clays. Verre et. silicates ind. 13:41-46. 1948. (Cited by Grim, 1953.)

McAtee, J. L., Jr.
Determination of random interstratification in montmorillonite. Amer. Miner. 41:627-631. July, 1956.

McPherron, D. S.
Clay mineralogy of some of the Permian shales. Unpublished M. S. thesis, Kansas State College, Manhattan, Kansas. 1956.

Millot, George
Prospecting for useful clays in relation with their conditions of genesis, problems of clays and laterite genesis. A symposium. New York: Am. Inst. of Min. and Metal. Eng. pp. 107-114. 1952.

Milner, H. B.
Sedimentary petrography. 3rd. ed. London: Thomas Murby, 1952.

Moore, R. C., and others
The Kansas rock column. State Geol. Sur. of Kansas, Bull. 89, 1951.

Murray, H. H.
Genesis of clay minerals in some Pennsylvanian shales of Indiana and Illinois. A symposium. Second Nat. Conf. on Clays and Clay Minerals, Proc. Washington, D. C.: Nat. Acad. Sci. - Nat. Res. Council Pub. 327:47-66. 1954.

Murray, H. H., and J. L. Harrison
Clay mineral composition of recent sediments from Sigsbee Deep. Journ. Sediment. Petrol. 26:363-368. December, 1956.

Pelto, C. R.
A study of chalcedony. Am. Jour. Sci. 254:32-50. January, 1956.

Pettijohn, F. J.
Sedimentary rocks. New York: Harper and Bros. 1949.

_____.
Sedimentary rocks. New York: Harper and Bros. 1957.

Powers, M. C.
Clay diagenesis in the Chesapeake Bay area. Clays and Clay Minerals. A symposium. Second Nat. Conf. on Clays and Clay Minerals, Proc. Washington, D. C.: Nat. Acad. Sci. - Nat. Res. Council Pub. 327:68-80. 1954.

Ramberg, H.
The origin of metamorphic and metasomatic rocks. Chicago: University of Chicago Press. 1952.

Rankama, K. and T. G. Sahama
Geochemistry. Chicago: Univ. of Chicago Press. 1950.

Rodgers, J.
Terminology of limestone and related rocks. An interim report. Jour. Sediment. Petrol. 24:225-234. Dec., 1954.

Ross, C. S., and P. F. Kerr
The kaolin minerals. U. S. Geol. Sur. Prof. Paper 165E. 1931.

Ross, C. B., and S. B. Heindricks
Minerals of the montmorillonite group. U. S. Geol. Survey Prof. Paper 205B. 1945.

Rowland, R. A.
Chlorites in argillaceous sediments. Problems in clay and laterite genesis. A symposium. New York: Am. Inst. of Min. and Metal. Eng. pp. 225. 1952.

Runnels, R. T., and J. A. Schleicher
Chemical composition of Eastern Kansas limestones. State Geol. Sur. of Kansas, Bull. 119, Part 3. 1956.

Ryan, J. D.
The sediments of Chesapeake Bay. Dept. of Geol., Mines and Water Res. State of Maryland, Bull. 12, 1953.

Simmons, L. H., and M. S. Taggart, Jr.
Clay mineral content of Gulf Coast cutcrop samples. Clays and Clay Minerals. A symposium. Second Nat. Conf. on Clays and Clay Minerals, Proc. Washington, D. C.: Nat. Acad. Sci.-Nat. Res. Council Pub. 327:104-110. 1954.

Sloss, L. L.
Environments of limestone deposition. Jour. Sediment. Petrol. 17:109-114. December, 1947.

_____.
The significance of evaporites. Jour. Sediment. Petrol. 23:143-161. 1953.

Steidtmann, E.
Origin of dolomite as disclosed by stains and other methods. Geol. Soc. Am., Bull. 28:431-450. 1917.

Swineford, Ada
Petrography of upper Permian rocks in South-Central Kansas. State Geol. Sur. of Kansas, Bull. 111. 1955.

Tamura, T.
Identification of the 14-A clay mineral component. Am. Miner. 41:107-110. January, 1957.

Tennant, C. B., and R. W. Berger
X-ray determination of dolomite-calcite ratio of carbonate rock. Amer. Miner. 42:23-29. January, 1957.

Twenhofel, W. H.
Principles of sedimentation. 2nd ed. New York: McGraw-Hill, 1950.

_____.
Environments of deposition of calcareous sediments. Am. Assoc. Petrol. Geol. Bull. 37:2607-2608. November, 1953.

Twiss, P. C.
The non-carbonate mineralogy of some Permian and Pennsylvanian limestones. Unpublished M. S. thesis, Kansas State College, Manhattan, Kansas. 1955.

Van Tuyl, F. M.
The origin of dolomite. Iowa Geol. Sur. Bull. 25:241-422. 1916.

Weaver, C. E.
The distribution and identification of mixed layer clay minerals in sedimentary rocks. Amer. Miner. 41:212-221. March, 1956.

Weiss, E. J., and R. A. Rowland
Effect of heat on vermiculite and mixed layered vermiculite-chlorite. Amer. Miner. 41:889-914. November, 1956.

Wilbur, R. O.
Petrographic analysis of the insoluble residue of the Permian Chase and Council Grove limestones with regard to the origin of chert. Unpublished M. S. thesis, Kansas State College, Manhattan, Kansas. 1956.

Winchell, A. N., and H. Winchell
Elements of optical mineralogy. Part 2, Description of minerals. 4th ed. New York: John Wiley and Sons, 1951.