

CLAY MINERALOGY AND OTHER PETROLOGIC ASPECTS  
OF THE GRENOLA LIMESTONE FORMATION  
IN THE MANHATTAN, KANSAS, AREA

by

GERALD DUANE HARGADINE

B. S., Kansas State University  
of Agriculture and Applied Science, 1958

---

A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Geology and Geography

KANSAS STATE UNIVERSITY  
OF AGRICULTURE AND APPLIED SCIENCE

1959

LD  
2608  
TH  
1959  
H37  
c.2  
Documents.

11

## TABLE OF CONTENTS

INTRODUCTION.....	1
Purpose of Investigation.....	1
Area of Investigation.....	1
REVIEW OF THE LITERATURE.....	4
Limestone.....	4
Shale.....	9
Clay Mineralogy.....	13
Insoluble Residues.....	15
FIELD PROCEDURE.....	16
LABORATORY PROCEDURE.....	17
Preparation of Samples for X-ray Analysis.....	17
Separation of Clay Size Fraction From Limestone and Shale Samples.....	17
Preparing Oriented Slides.....	18
X-ray Diffraction Analysis.....	19
Insoluble Residues.....	21
Heavy and Light Mineral Separation.....	22
X-RAY DETERMINATION OF CLAY MINERAL FRACTION, CARBONATES, AND NON-CARBONATES.....	24
Clay Minerals.....	24
Method of X-ray Determination of Clays.....	24
Lower Eskridge Shale.....	26
Neva Limestone.....	39
Salem Point Shale.....	40
Burr Limestone.....	41
Legion Shale.....	42

Sallyards Limestone.....	43
Upper Roca Shale.....	43
Carbonates.....	43
Method of X-ray Identification.....	43
Lower Eskridge Shale.....	44
Neva Limestone.....	44
Salem Point Shale.....	44
Burr Limestone.....	44
Legion Shale.....	44
Sallyards Limestone.....	44
Upper Roca Shale.....	45
NON-CLAY MINERALS.....	45
INSOLUBLE RESIDUE WEIGHT COMPARISON.....	45
Neva Limestone.....	45
Salem Point Shale.....	46
INSOLUBLE RESIDUE MINERAL DETERMINATION OTHER THAN CLAYS.....	46
Heavy Minerals.....	46
Celestite.....	52
Magnetite.....	52
Limonite and Limonite Coated Grains.....	52
Pyrite.....	58
Light Minerals.....	58
Quartz.....	58
Chalcedony.....	59
Volcanic Ash and Opal.....	59
Coarse Residue.....	59

DISCUSSION OF RESULTS.....	60
Possible Effects of Near Surface Weathering on Rock Containing Clay Minerals and Showing Little or No Visible Weathering.....	60
Effect of Alteration of Clay Minerals and Some Carbonates.....	61
Carbonate Minerals.....	64
Origin of the "Honeycomb" Zone of the Neva Limestone.....	66
Factors Pertaining to the Origin of the Neva Limestone and Salem Point Shale Which May Be Concluded From the Heavy and Light Mineral Analysis....	68
Heavy Minerals.....	68
Light Minerals.....	69
SUMMARY AND CONCLUSIONS.....	70
ACKNOWLEDGMENTS.....	74
REFERENCES.....	75

## INTRODUCTION

### Purpose of Investigation

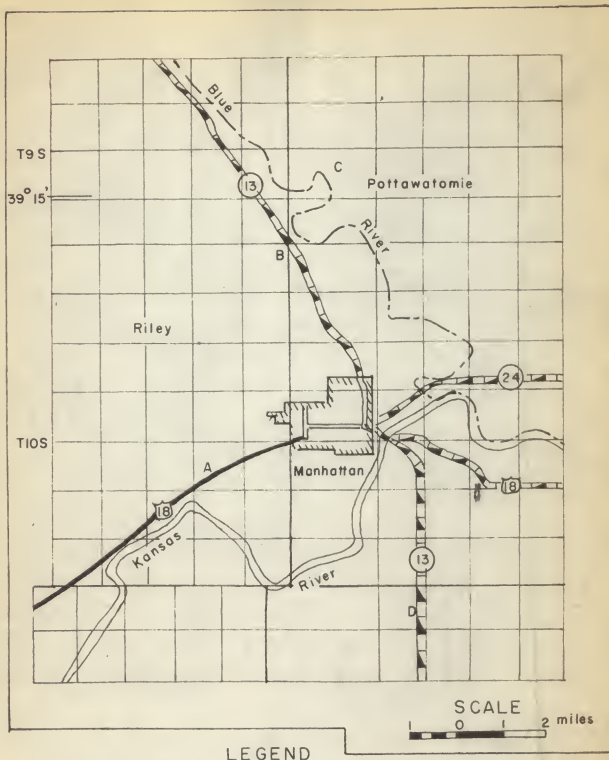
This investigation is concerned with the carbonate and non-carbonate mineralogy of the Grenola limestone formation in the Manhattan, Kansas, area. It also is hoped this investigation may give some indication of the effect of weathering on the clay mineralogy of limestones. Major emphasis was placed upon the Neva limestone member of the Grenola formation.

An investigation of this type has several aspects, two of which are of major importance. First, it is important from a geologic standpoint. A study of the minerals present may reveal information about origin and geologic history of the unit. Second, it is important from an economic point of view in engineering geology. The usability of a rock unit is determined by its mineralogy, texture, and structure. The clay mineralogy of the unit is essential when ascertaining the purpose for which the rock is to be used.

### Area of Investigation

Rock samples were taken from the units of the lower Permian Grenola limestone formation in the Manhattan, Kansas, area. Three of the sample locations were in Riley County, and the other in Pottawatomie County (Plate I). At locations A and B the complete Grenola formation was sampled, plus one sample from the basal portion of the overlying Eskridge shale, and one sample from

## PLATE I



## LEGEND

- BOUNDARIES
- COUNTY LINE
  - TOWNSHIP LINE
  - SECTION LINE
  - CORPORATION LINE

- ROADS AND ROADWAY FEATURES
- PAVED ROAD (concrete)
  - METAL SURFACE (stone, chat, etc.)
  - U.S. HIGHWAY SYSTEM
  - STATE HIGHWAY SYSTEM
  - SAMPLE LOCATION

the upper portion of the underlying Roca shale (Plate II). The samples from locations A and B were slightly weathered.

Samples collected at location C included the stratigraphic section from the lower Eskridge shale to the upper unit of the Burr limestone. The samples at location C were collected from the recently excavated spillway section at Tuttle Creek Dam. The overburden removed from above the Neva limestone was approximately 100 feet, thus those samples should be relatively unweathered. Samples from location D included one sample from the lower Eskridge shale, and the complete Neva limestone member. These samples were extremely weathered.

## REVIEW OF THE LITERATURE

### Limestone

The term limestone to the lime manufacturer is applied to that class of rocks which contains at least 80 per cent calcium or magnesium carbonate, and gives a product that slakes upon the addition of water (Pettijohn, 1957, pp. 381). The term limestone is generally applied to rocks in which the carbonate fraction exceeds the non-carbonate fraction. If shaly constituents exceed the carbonate constituents, then the rock is termed a calcareous shale. Likewise, if arenaceous constituents exceed calcareous constituents, then the rock is termed a calcareous sandstone.

Limestones have a chemical composition primarily of calcite,

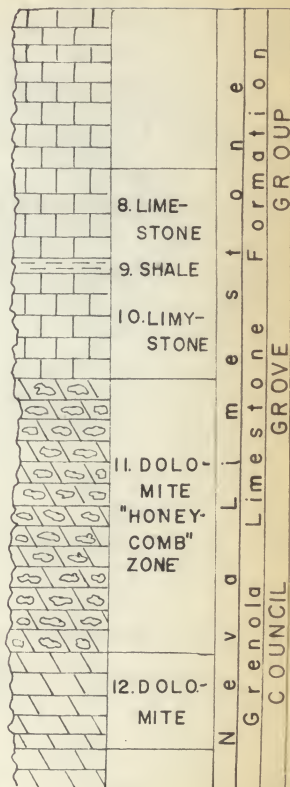
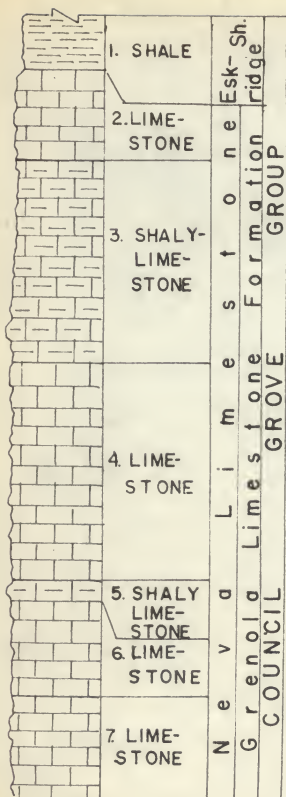


EXPLANATION OF PLATE II





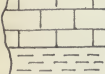
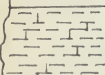
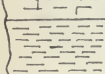



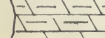
Generalized stratigraphic section showing location of samples.













## PLATE II

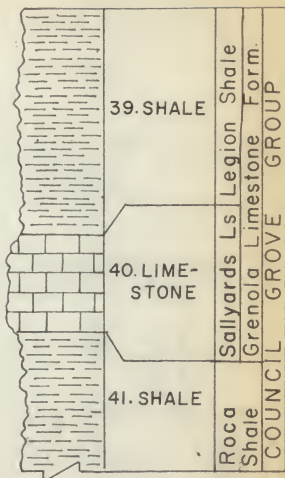
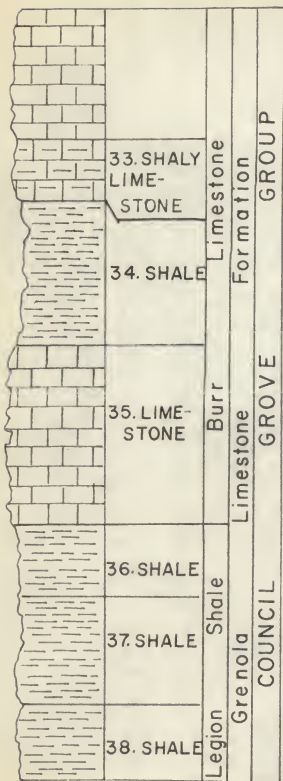


## PLATE II (cont)

	13. LIME- STONE	Neva Limestone Formation	Salem Point Shale Grenola Limestone COUNCIL GROVE	
	14. DOLO- MITE			
	15. SHALE			
	16. SHALE			
	17. SHALE			
	18. LIME- STONE	Neva Limestone Formation		
	19. SHALE			
	20. LIMY- SHALE			
	21. SHALE			
	22. SHALE			
	23. SHALY DOLO- MITE	Salem Point Shale		

	24. DOLO- MITE	Shale Point Formation	Salem Point Shale Grenola Limestone COUNCIL GROVE	
	25. SHALE			
	26. DOLO- MITIC SH.			
	27. SHALE			
	28. SHALE			
	29. DOLO- MITE	Salem Point Shale Grenola Limestone COUNCIL GROVE		
	30. SHALE			
	31. LIME - STONE			
	32. LIME - STONE			
		Grenola Limestone		

## PLATE II (cont.)



SCALE

ft.

LEGEND

- Limestone
- Shaly Limestone
- Shale
- Limy Shale
- Dolomitic Shale
- Dolomite
- Shaly Dolomite
- Honeycomb Zone

hence the content of  $\text{CaO}$  and  $\text{CO}_2$  is extremely high.  $\text{MgO}$  is commonly found in limestones. If it exceeds 1 or 2 per cent, dolomite may be present in the rock.

A classification of limestones according to mode of origin has been proposed by J. H. Johnson (1951) and Twenhofel (1950, pp. 356). The classes are (1) organic limestones, (2), inorganic limestones, and (3) mechanical limestones. Probably the best classification of limestones has been proposed by Pettijohn (1957, pp. 382), based on genetic relationships. Limestones are a polygenetic group of rocks, and as indicated in Plate II, Fig. 1, may be fragmental or detrital, and in other instances may be chemical or biochemical precipitates which have grown in place.

### Shale

Shale is essentially silt or clay that has been converted into rock. It is usually high in clay mineral constituents, and is termed an argillaceous rock. Fissility is a common characteristic of shale which causes the rock to split into flat, shell-like fragments which parallel the bedding. This parallel splitting is determined by the more or less parallel arrangement that the flaky minerals assumed during sedimentation, or developed subsequently.

Shales are the most abundant of all the common sediments, forming about one-half of the geologic column (Pettijohn, 1957, pp. 340). Although the shales are abundant they do not make

EXPLANATION OF PLATE III

- Fig. 1. Genetic classification of limestones (After Pettijohn, 1957, pp. 382).
- Fig. 2. Developed compositional tetrahedron showing nomenclature of mixtures of clay and nonelastic materials. (After Pettijohn, 1957, pp. 361).

# PLATE III

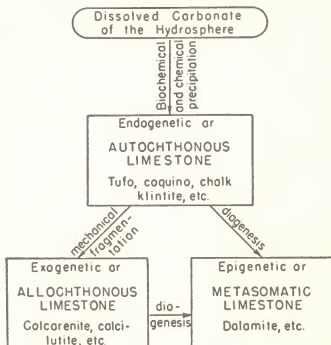


FIG. I

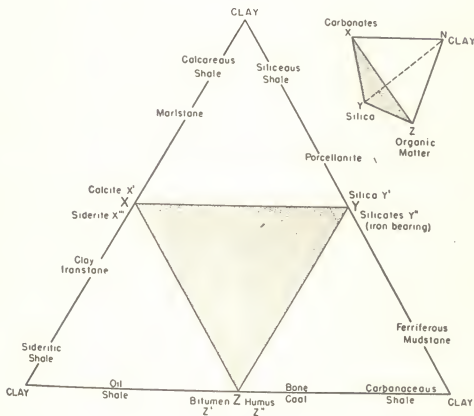


FIG. 2

prominent outcrops as do the more resistant limestones and sandstones.

The component particles of shale are too small to be determined by the eye, lens, or even the microscope in most cases. X-ray and chemical analysis indicate shale to be made up mostly of clay minerals, relict minerals, and authigenic constituents. Chemical analysis indicates that shales are high in aluminum content relative to lime and alkalies.

Shales are probably best classified according to their origin. Under such a heading they can be classified as residual or transported (Pettijohn, 1957, pp. 355). If the shale was formed as the product of weathering in position they are termed residual. The characteristic of residual deposits is dependent upon climate, drainage, and parent rock material. The constituents of transported shales are derived from three sources: (1) the product of abrasion, (2) the end product of weathering, and (3) chemical and biochemical additions (Pettijohn, 1957, pp. 357).

Pettijohn (1957, pp. 361) shows the nomenclature of mixtures of clay and nonclastic materials by a developed tetrahedron (Plate III, Fig. 2). These mixtures have been termed by Pettijohn as "hybrid rocks". If the shale is rich in quartz it is termed an arenaceous shale, and if rich in lime it is termed a calcareous shale or marl.



### Clay Mineralogy

The term clay may be used as a rock term, and also as a description of particle size. To the geologist clay size particles are less than 4 microns in diameter, and to the soil investigator the upper limit is 2 microns. According to Grim (1953, pp. 1) clay implies a natural, earthy, fine grained material which develops plasticity when mixed with a limited amount of water. The chemical components of clays are essentially silica, alumina, water, and generally some iron, alkalies and alkaline earth.

Prior to about 1920 there were two general schools of thought concerning clay composition. The first concept was that all clay minerals were derived from the mineral kaolinite. This idea was held because kaolinite was the only clay mineral which had particles large enough for identification under the microscope. According to this concept the difference in composition between kaolinite and other clay minerals was due to impurities.

The second early school of thought concerning clay minerals was that they were amorphous colloidal complexes. This concept was held because clays were similar to other truly amorphous materials with which the colloidal chemist was familiar.

Some investigators prior to 1920 believed that all clays were not amorphous colloidal complexes. The most notable of the believers in this concept was Defrenoy in 1856, Le Chatelier

in 1887, and Lowenstein in 1909. Views of this sort, for the most part, were not based on observation of the clay minerals, but on their properties which could be easily classified.

The crystallinity of clay minerals was not well established until about 1923 and 1924 when Hadding and Rinne respectively published the first X-ray diffraction analysis of clay minerals. Both investigators, working independently, found crystalline material in the finest fraction in a series of clays. They also found that all the samples studied seemed to be composed of particles of the same group of minerals.

Ross and his colleagues of the U. S. Geological Survey published a series of papers on the composition of clays about 1924. They first worked with bentonites, but later extended their studies to other clays used in industry. The study was based on careful optical work with the petrographic microscope, supplemented by excellent chemical data. The workers concluded that the components of clay materials were largely crystalline, and that there was a limited number of crystalline components. Later Ross and his colleagues added X-ray analysis to their investigation. X-ray analysis in general substantiated their earlier findings. By the early 1930's the clay mineral concept was well established. Since that date, workers have approached the study of clay mineralogy from many different fields-- mineralogy, geology, chemistry, physics, agronomy, etc. Work has also been done on applied clay mineralogy by ceramists,

engineers, etc., in universities, commercial and other laboratories.

### Insoluble Residues

Insoluble residue, as used in this study, is a term used to describe the material which remained after fragments of limestone and dolomite had been dissolved in chemically pure hydrochloric acid. The insoluble residue of a calcareous rock may be further classified as fine residue and coarse residue. The coarse residue consists of those particles of the total residue which are larger than clay size.

Most of the correlative work has been done with the coarse residue fraction (Drake, 1951, pp. 4). Relatively little work has been done with the fine residue fraction.

A classification of calcareous well cuttings was suggested by Claypool and Howard (1928, pp. 1147-1152), which was based on the calcite, dolomite, magnesium content. The sample was ground so as to pass through an 80 mesh sieve, and the light, medium, and heavy fractions were then separated by centrifuging in Thoulet's solutions of varied densities. The fractions were then treated with hydrochloric and nitric acids. Calcite was dissolved from the light fraction, dolomite from the medium, and magnesium from the heavy fraction.

McQueen (1931, pp. 102-131), of the Missouri Geological Survey, formulated a method of sample preparation, terminology, and application of insoluble residues to correlation of

calcareous rocks. He dissolved samples of well cuttings in dilute hydrochloric acid, decanted fine residues, and examined the coarse residues for diagnostic minerals.

Schoewe, et al., (1937, pp. 269-281) made a study of insoluble residues of some lower Pennsylvanian limestones in Kansas. They found that insoluble residues are diagnostic not only of formations, but also of members within the formation.

Drake (1951, pp. 97) made an insoluble residue analysis of some lower Permian and upper Pennsylvanian limestones in Riley, Pottawatomie, Geary, and Wabaunsee counties in Kansas. He concluded that no single diagnostic residue is present in either system of rocks which were examined. Drake (1951, pp. 97) stated:

The percentage volumes and weight volumes and weights of the total fine and coarse residue of each limestone vary from place to place. The colors of the fine residues of limestones in both systems were similar.

It is apparent that insoluble residues cannot replace lithologic analysis as the principal basis of stratigraphic correlation, according to Drake.

Insoluble residues were prepared in this investigation to attempt to establish a correlation between the weight of the insoluble residue, and the clay mineralogy of the limestones which were examined.

#### FIELD PROCEDURE

The first step in the field investigation was to measure

the stratigraphic section from which the samples were to be taken. This measurement was recorded in a field book, and a generalized stratigraphic section was drawn of each zone of the section. When the samples were collected, the point on the section from which the sample came was marked in the field book. A description of each sample was also recorded in the field book as they were collected.

The sample collecting method was of the spot type. The samples, in each case, were collected in three-pint cartons, and the stratigraphic location was recorded by a number on the box.

#### LABORATORY PROCEDURE

##### Preparation of Samples For X-ray Analysis

Separation of Clay Size Fraction From Limestone and Shale Samples. Each limestone was crushed in a jaw crusher and the size reduced to about 0.5 centimeter in diameter. The jaw crusher was rubbed clean with a dry cloth between each crushing to prevent contamination of other samples. The limestones were then further crushed with a mortar and pestle. Two hundred grams of the crushed limestone was sieved through a U. S. #200 mesh sieve (74 microns) to be used in further investigation. The remaining limestone was placed back in the three-pint container, some of which was used for insoluble residue analysis.

Each raw shale sample was placed in a 600 milliliter beaker with 400 milliliters of distilled water, and allowed to stand

24 hours for slaking. One hundred fifty grams of each untreated shale was used in this procedure.

Ten milliliters of sodium hexametaphosphate (37 grams Calgon, 7 grams sodium carbonate, 1 liter water) was added to prepared shales, and 20 milliliters was added to prepared limestones as a dispersing agent. The shale and limestone samples were then transferred to a Waring blender or malted milk type mixing cup. The mixer was filled to within one inch of the top with distilled water. The shales were mixed for 15 minutes, and the limestones were mixed for 30 minutes.

After agitation the sample was transferred to a sedimentation cylinder, and enough distilled water was added to make a total volume of 1000 milliliters. The tubes were placed in a constant temperature bath at 20 degrees centigrade, and were allowed to stand for 36 hours. Twelve hours was allowed for each 10 centimeters of settling distance. After 36 hours the upper 30 centimeters was decanted from each sedimentation cylinder into a glass jug.

The clay suspension which was drawn off into the jugs was mixed thoroughly. A 150 milliliter aliquot was taken from each jug for use in making oriented slides for X-ray diffraction analysis.

Preparing Oriented Slides. Oriented slides of clay size particles were made by placing a small amount of suspended material from the aliquot on a microscope slide with an eye



dropper. Upon drying, the basal surfaces of the clay minerals were oriented parallel to the surface of the slide. This orientation will give basal reflections in X-ray diffraction analysis.

X-ray Diffraction Analysis. The oriented slide of clay minerals and non-clay minerals in the clay size range was placed on the slide holder of the North American Phillips X-ray Diffractometer. The slide was then exposed to nickel filtered copper radiation, utilizing 20 milliamperes, 40 kilovolts; with a one degree slit opening; time constant of 4; and a rate scale factor which was generally kept at 8. On some of the limestone slides where the reflections were very weak a scale factor of 4 was used to intensify the size of the reflections. The oriented slides were X-rayed from 32 degrees to one degree two theta.

After the oriented slide had been examined through 32 degrees two theta, it was treated with ethylene glycol, and X-rayed through 15 degrees two theta. The use of organic complexes such as ethylene glycol expands the c-dimension of montmorillonite and provides a sharp (001) reflection from about 15.0 to 17.7 angstroms. Treatment with ethylene glycol permits the detection of montmorillonite and other minerals which may be masked by montmorillonite; e.g. chlorite and vermiculite.

All the oriented slides were heated to 450 degrees centigrade if peaks other than 10 angstrom illite peaks remained after glycolation. This was to detect the presence of poorly



crystalline chlorite and/or montmorillonite; the diffraction lines of poorly crystalline chlorite and montmorillonite disappear at this temperature. If any reflections remained except the 10 angstrom illite reflection on the slides heated to 450 degrees centigrade, the same slide was reheated to 600 degrees centigrade. This final heating will destroy the lattice of kaolinite. The peaks which remain after this final heating probably represent well crystalline chlorite and illite. It is possible, however, for chlorite, which is somewhat degraded, to show the presence of a 14 angstrom reflection after heating to 450 degrees centigrade, with the reflection disappearing after heating to 600 degrees centigrade.

The angular spacings, which were recorded directly on the strip chart of the X-ray diffractometer in degrees two theta, were converted to d-spacings. This conversion was made by using the "Table for Conversion of X-ray Diffraction Angles to Interplanar Spacing" (Swanson, 1950). The d-spacings were compared with the theoretical and measured d-spacings of minerals that might be found in the clay size range.

Random oriented slides of the limestone zones were X-rayed to obtain calcite-dolomite ratio, and the relative amount of quartz present. These slides were prepared by crushing about 5 grams of sample, and passing it through a U. S. #270 sieve (53 microns). The material obtained was then placed on a slide especially constructed to hold the powder. The "powder slide" was placed in the slide holder of the North American Phillips

X-ray Diffractometer, and were X-rayed from 33 degrees to 26 degrees two theta, and from 21 degrees to 20 degrees two theta.

### Insoluble Residues

Insoluble residues were analyzed on the Neva limestone member in all four sample locations (Table I), and the Salem point shale member was included at location D. Only the limestone and dolomite zones were considered in this insoluble residue analysis.

Some of the rock material which was not used in the X-ray work was used for the insoluble residues. Two hundred grams of oven dried sample was weighed out carefully. The sample was placed in a one-gallon jar, and a small amount of distilled water was added so that the sample would not effervesce over the top of the jar when the acid was added. The jar containing the sample was then placed under a hood, and chemically pure hydrochloric acid was added gradually until all the carbonates were digested. 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 the effervescence ceased the samples were vacuum-filtered in Buechner funnels, and washed several times to insure the removal of all acid.

Following the washing procedure in the Buechner funnels, the samples were transferred back to the oven where they were dried for 24 hours. At the end of this time, the samples were removed from the oven and weighed. The per cent of carbonate

was computed by taking the total weight of the sample, minus the weight of the insoluble residue, over the weight of sample before treatment.

After the per cent of carbonate had been determined, the insoluble residues were placed back in distilled water and allowed to stand for 12 hours. At the end of the 12 hours, the samples were mixed by use of a magnetic mixer for 15 minutes each. After mixing, insoluble residues were sieved through a U. S. #140 sieve (105 microns), and a U. S. #270 sieve (53 microns). The material on each screen was washed thoroughly several times to insure removal of all the clay.

The residue from both #140 and #270 sieves were placed in separate pyrex dishes and oven-dried. After drying the material from the #140 sieve was taken from the oven and placed in small paper bags for later binocular microscope analysis. The oven dried material from the #270 sieve was left in the oven for later use in heavy and light mineral separation.

#### Heavy and Light Mineral Separation

Bromoform, with a specific gravity of 2.7 was used as a separation medium for the heavy and light minerals. The apparatus consisted of three conical funnels, pinchcocks, funnel stand, rubber tube, and Whatman #42 filter paper. The funnels were mounted on the funnel stand, one above the other, with the upper funnel having a rubber tube and pinchcock to prevent the loss of bromoform. The funnel on the lower bracket of the stand

contained the filter paper to collect the mineral grains from the bromoform. Two funnels containing filter paper were needed; one for collecting the heavy minerals, and the other for collecting the light minerals. Bromoform was placed in the upper funnel, and a watch glass was placed over the top to prevent evaporation.

The samples were placed in the bromoform shortly after they were taken from the oven. The purpose of heating was to remove absorbed moisture which might decrease the accuracy of the heavy mineral separation. The bromoform and sample were stirred every 15 minutes for two hours. The mixture was then allowed to stand for two hours before filtration.

Following filtration the samples were washed once with bromoform--ethyl alcohol, and twice with ethyl alcohol. The filter paper containing the heavy and light minerals was then clamped shut with a paper clip, and allowed to air dry.

Heavy and light mineral slides were prepared using stick-type Lakeside 70 cementing material, with a refractive index of about 1.54. Slides were heated by the use of a small electric heater. When the slide became hot, one end of the stick was placed on the glass slide. This melted some of the Lakeside 70 cement, and when a sufficient amount was present on the slide the sample was sprinkled on it. A cover glass was then placed over the hot cement and sample, with care being taken to prevent any air bubbles from remaining in the cement. After the slides cooled, they were carefully cleaned of all excess cement with xylol.

The slides were studied by use of a petrographic microscope. A binocular study was made on the residue which did not pass through the U. S. #140 mesh sieve.

X-RAY DETERMINATION OF CLAY MINERAL  
FRACTION, CARBONATES, AND NON-CARBONATES

Clay Minerals

Method of X-ray Determination of Clays. Illite was by far the most important clay mineral in all the samples examined. It was identified on the basis of the characteristic 10-A reflection, and other reflections of a 10-A periodicity which remained unchanged after glycolation.

Chlorite was present in most of the samples, and was identified by a 14-A reflection, with successive (001) reflections. Most of the chlorite encountered in this investigation was of the iron rich variety, with a weak first and third order reflection, and strong second and fourth order reflection. The reflections of the second and fourth order were at 7-A and 3.5-A respectively. The second and fourth order reflections of chlorite correspond to the first and second order reflections of kaolinite. Heat treatment was used to distinguish between the two minerals. Heating to 450 degrees centigrade for one-half hour results in the disappearance of the 14-A and the 7-A reflections of chlorite if the mineral was poorly crystalline. Kaolinite was unaffected by this temperature. If any reflections remained at 14-A and/or 7-A the slide was again heated, this time to 600



degrees centigrade for 30 minutes. Kaolinite is destroyed at this temperature, and well crystalline chlorite remains relatively unchanged.

Montmorillonite was distinguished from chlorite by glycol treatment. The 14-A reflection of montmorillonite expands out to approximately 17.5-A upon glycolation, whereas the 14-A chlorite reflection is generally unaffected by glycol treatment. In recent studies by Brindley (1951) and Lippman (1956) swelling chlorite has been reported. This type of chlorite is relatively uncommon, and was not found in any of the samples studied in this investigation.

Some mixed-layer clays were found in nearly all the samples examined. The mixed-layer clays gave reflections which were averages of the component clay minerals. Mixed-layer clays are of two types; the regular mixed layer, and the random mixed layer. Regular mixed-layer clays were distinguished from random mixed-layer clays by determining if the reflections from the basal planes formed on an integral or non-integrated series. Regular mixed-layer clays fall in the first class, while random mixed-layer clays fall in the latter class. Both types were encountered in this investigation.

Illite-montmorillonite was recognized as a random interlayer which could be distinguished easily before glycolation by the change in symmetry on the low angle side of the 10-A illite reflection. This interlayer clay could also be distinguished by the unsymmetrical shape of the high angle side of

the 3.5-A illite reflection. After glycolation the montmorillonite expanded and the symmetry of the illite peaks was restored.

Chlorite-montmorillonite was the only regular interlayer which was found. Two different forms of chlorite-montmorillonite interlayer was distinguished. The first type gave reflections with the same periodicity as the chlorite reflections in the unglycolated sample. Upon glycolation the 14-A reflection shifted to approximately 16-A, and the 7-A reflection was shifted to approximately 7.7-A. The second type of regular interlayer chlorite-montmorillonite contained the so-called super-lattice structure. The glycolated sample gave reflections in the following integrated series: 31.5-A, 15.7-A, 10.1-A, 7.7-A, 6.3-A, and 5.15-A.

Lower Eskridge Shale. X-ray analysis indicated illite to be the major clay constituent of the lower Eskridge shale. Some chlorite and chlorite-montmorillonite interlayer was found in all the samples which were examined. All the chlorite was iron rich, poorly crystalline except the sample from location D which contained iron free, well crystalline chlorite. Illite-montmorillonite interlayer clay was found in the samples from locations A and B. However, the mineral was not found at the other locations. Free montmorillonite was found in the shale collected at Tuttle Creek Dam (location C), but was not found in samples from the other locations. A summary of the clay minerals found in this formation is shown in Table 1.



Table 1. Summary of the clay mineral fraction and the carbonate content of the Grenola limestone formation.

Geologic Section	Classification	Illite	Iron Rich, Poorly Crystalline	Iron Free, Well Crystallized	Iron Free, Moderate Crystalline	Iron Free, Poorly Crystalline	Trace	Montmorillonite	Chlorite			Minerals			Non-Clay Minerals	
									Chlorite	Clay	Interlayer Clays	Minerals	Minerals			
ESKRIDGE SHALE	1-A Sh	xxx	x				x									
	1-B Sh	xxx														
	1-C Sh	xxx	x													
	1-D Sh	xxx		xx												
NEVA LIMESTONE	2-A Ls	xx					x									
	2-B Ls	xx														
	2-C Ls	xx														
	2-D Ls	xxx	x													

Scale of abundance of minerals: xxx (major), xx (moderate), x (minor)

Symbols: Ls (limestone), Sh (shale), Dol (dolomite), Ls-Sh (limy shale), Sh-Ls (shaly limestone), Dol-Sh (dolomitic shale), Sh-Dol (shaly dolomite)





Table 1. (cont.)

Geologic Section	Classification	Illite	Iron Rich, Poorly Crystalline	Iron Free, Well Crystallized	Iron Free, Moderate Crystalline	Iron Free, Poorly Crystalline	Trace	Montmorillonite	Illite-Montmorillonite (Random)	Chlorite-Montmorillonite (Regular)	Chlorite-Montmorillonite (Super-Lattice Regular)	Minerals	
												Clay	Non-Clay Minerals
9-C Sh	xxx											xx	xx
9-D Sh	xxx											x	x
10-A Ls	xxx											x	x
10-B Ls	xx											xxx	xxx
10-C Ls	xx											xxx	xxx
10-D Ls	xx											xxx	xxx
11-A Dol	xx											x	xx
*11-A Cl-C	xxx											x	xxx
11-B Dol	xxx											x	xxx
*11-B Cl-C	xxx											x	xxx
11-C Dol	xxx											x	xxx
*11-C Cl-S	xxx											x	xxx

\*Clay coating separated from 11-A and 11-B

\*\*Clay Seam separated from 11-C

Table 1. (cont.)

Geologic Section	Classification	Illite	Iron Rich, Poorly Crystalline	Iron Free, Well Crystallized	Iron Free, Moderate Crystalline	Iron Free, Poorly Crystalline	Trace	Montmorillonite	Illite-Montmorillonite (Random)	Chlorite-Montmorillonite (Regular)	Chlorite-Montmorillonite (Regular)	Chlorite-Montmorillonite Super-lattice (Regular)	Minerals		Non-Clay Minerals	
													Clay	Interlayer Clays	Minerals	Non-Clay Minerals
11-D Dol	xx						x	xxx	xx	x	x		x		x	xxx
11-D Cl-C							x	xxx								
12-A Dol	xxx		xx					x	xx	x	x		x		x	xx
12-B Dol	xxx		xx					xx		xx			x		x	xxx
12-C Dol	xxx							xx					x		x	xx
12-D Ls	xxx						x	xx	xx	x	x		x		x	xxx
13-A Dol	xxx								xx	x	x		x		x	xxx
13-B Dol	xxx		x						xx	x	x		x		x	xxx
13-C Ls	xxx								xx				x		x	xxx
13-D Ls	xx							xxx	xx	x	x		x		x	xxx
14-A Dol	xxx		xx				x		x	x	x		x		x	xx

\*Clay coating separated from 11-D

Table 1. (cont.)

		Clay		Minerals		Non-Clay Minerals	
		Illite	Chlorite	Illite-Montmorillonite	Chlorite-Montmorillonite (Regular)	Chlorite-Montmorillonite (Random)	Montmorillonite
Geologic Section	Glassification						
	Crystalline						
	Iron Rich, Poorly						
	Crystallized						
	Iron Free, Well						
	Crystalline						
	Iron Free, Moderate						
	Crystalline						
	Iron Free, Poorly						
	Crystalline						
	Trace						
	Montmorillonite						
	Illite-Montmorillonite						
	Chlorite-Montmorillonite (Regular)						
	Chlorite-Montmorillonite						
	Super-Lattice						
	Regular						
	Quartz						
	Calcite						
	Dolomite						
14-B	Dol xxx						
14-C	Dol xxx						
14-D	Dol xxx						
15-A	Sh xxx						
15-B	Sh xxx						
15-C	Sh xxx						
15-D	Sh xxx						
16-A	Sh xxx						
16-B	Sh xxx						
16-C	Sh xxx						
16-D	Sh xxx						
17-A	Sh xxx						
17-B	Sh xxx						





Table 1. (cont.)

	Geologic Section					
	Illite	Iron Rich, Poorly Crystalline	Iron Free, Well Crystallized	Iron Free, Moderate Crystalline	Iron Free, Poorly Crystalline	Trace
Classifcation						
21-A Dol-Sh xxx	x					
21-B Dol-Sh xxx	x					
21-C Dol-Sh xxx	x					
22-A Ls-Sh xxx						
22-B Dol-Sh xxx						
22-C Dol-Sh xxx						
23-A Sh-Dol xxx						
23-B Sh-Dol xxx						
23-C Sh-Dol xxx						
24-A Dol						
24-B Dol						
24-C Dol						

Table 1. (cont.)

Geologic Section	Classification	Illite	Iron Rich, Poorly Crystalline	Iron Free, Well Crystallized	Iron Free, Moderate Crystalline	Iron Free, Poorly Crystalline	Trace	Montmorillonite	Minerals			Non-Clay Minerals		
									Clay	Chlorite	Interlayer Clays	Quartz	Galinite	Dolomite
25-A Sh	xxx	xxx	x									x	x	x
25-B Sh	xxx	xxx	xx									x	x	xxx
25-C Sh	xxx	xxx		xx								x	x	xxx
26-A Dol-Shxxx	xxx	xxx	x									x	xx	x
26-B Dol-Shxxx	xxx	xxx	xx									x	xx	xxx
26-C Ls-Sh xxx	xxx	xxx		xx								x	xx	x
27-A Sh	xxx	xxx	x									x	x	x
27-B Sh	xxx	xxx		x								x	x	xx
27-C Sh	xxx	xxx										x	x	xx
28-A Sh	xxx	xxx	x									x	x	x
28-B Sh	xxx	xxx		x								x	x	xx
28-C Sh	xxx	xxx		x								x	x	xx

Table 1. (cont.)

Geologic Section	Classification	Illite	Iron Rich, Poorly Crystalline	Iron Free, Well Crystallized	Iron Free, Moderate Crystalline	Iron Free, Poorly Crystalline	Trace	Montmorillonite	Illite-Montmorillonite (Random)	Chlorite-Montmorillonite (Regular)	Chlorite-Montmorillonite (Super-Lattice (Regular))	Quartz	Galeite	Dolomite
29-A	Ls	xxx	x	x						xx		x	x	x
29-B	Ls	xxx								xx		xx	xx	
29-C	Dol	xxx									xx	x	xx	
30-A	Sh	xxx								xx		x	x	
30-B	Sh	xxx								xx		x	x	
30-C	Sh	xxx										x	x	
BUFR LIMESTONE														
31-A	Ls	xxx										x	xxx	x
31-B	Ls	xxx								xx		x	xxx	
32-A	Ls	xxx								x		x	xxx	
32-B	Ls	xxx	x							xx		x	xxx	
33-A	Ls	xxx	xx							xx		x	xxx	
33-B	Ls	xxx	x							xx		x	xxx	x



Table 1. (cont.)

Geologic Section	Classification	Illite	Iron Rich, Poorly Crystalline	Iron Free, Well Crystallized	Iron Free, Moderate Crystalline	Iron Free, Poorly Crystalline	Trace	Minerals			Non-Clay Minerals			
								Clay	Chlorite	Interlayer Clays	Minerals	Minerals		
								Montmorillonite	Illite-Montmorillonite (Random)	Chlorite-Montmorillonite (Regular)	Chlorite-Montmorillonite Super-Lattice (Regular)	Quartz	Calcite	Dolomite
SALLYARDS LIMESTONE														
40-A Ls	xxx	x								x	x	x	xxx	x
40-B Ls	xxx								x	xx			xx	
ROCA SHALE														
41-A Sh	xxx	x												x
41-B Sh	xxx								x	xx	xx		xx	x
NEVA LIMESTONE (Test on Ion Exchange)														
*11-D Cl-C	xx						xxx							
*10-A Ls	xxx												x	xxx
* After treatment with KOH      ** After treatment with HgCl2														

The samples from locations A and B were moderately weathered while the shale from C and D locations were fresh samples. The major difference between the weathered and unweathered samples was that the two moderately weathered samples contained illite-montmorillonite interlayer, while in the unweathered samples the interlayer clay was absent. Also of significance is the fact that free montmorillonite was found in the unweathered sample only. This fact may indicate that montmorillonite alters to chlorite or illite on weathering. This sequence of alteration would be in reverse to that suggested by most authors.

Neva Limestone. The Neva limestone was analyzed by X-ray diffraction in four localities with 18 samples collected at each location. The samples at locations A and B were moderately weathered, location C samples were generally unweathered, and location D samples were severely weathered.

Illite was found to be the most abundant clay mineral in all the shales and limestones of the Neva. A summary of the minerals found is given in Table 1.

Some chlorite was found in nearly all the samples. Most of the chlorite was of the iron rich, poorly crystalline variety. There was, however, iron free and well crystalline chlorite present. For the most part the unweathered sample showed better chlorite crystal structure than did the weathered samples. The chlorite at location C and at some areas of locations A and B was well crystalline enough to withstand heating to 450 degrees centigrade, but not crystalline enough to withstand the 600 degree



centigrade temperature. Most of the chlorite in the severely weathered samples from location D was destroyed upon heating to 450 degrees centigrade.

Free montmorillonite was found in scattered samples from the top of the Neva to the base. The most abundant montmorillonite was found in zones 11 and 12 (Plate II). This zone has been termed by Jewett (1941, pp. 54) and others as having a "honeycomb" appearance. It was found that the carbonate minerals of the "honeycomb" zone were predominately dolomite. Within this zone at locations A, B, and D was a "clay coating" material which was predominately montmorillonite. A similar zone in the "honeycomb" zone at location C has been termed by the author as a "clay seam" zone. This "clay seam" was largely illite.

The interlayer clays were found in most of the samples examined. Two types of interlayers were found; illite-montmorillonite and chlorite-montmorillonite. Chlorite-montmorillonite was the most abundant of the two types.

The X-ray diffraction patterns indicated that there was less free montmorillonite, and less montmorillonite in the mixed-layer clays in the weathered samples at location D, as compared to the unweathered samples at location C.

Salem Point Shale. Twelve samples of the Salem Point shale were collected from three locations; A, B, and C. The samples collected at locations A and B were moderately weathered, and the sample from location C was relatively unweathered.

Like the Neva, the Salem Point was found to have illite as

its major clay constituent. Chlorite was found in all the samples except 29-C (dolomite). There was about an equal amount of iron rich and iron free chlorite. Most of the iron free chlorite in this formation was well crystalline, while the iron rich chlorite was mostly poorly crystalline.

Free montmorillonite was not found in the Salem Point shale in any samples examined.

The interlayer clays were similar to those found in the Neva, except for super-lattice clays which were found in four samples. The illite-montmorillonite was the only random interlayer found. It seems to be somewhat less abundant in the Salem Point as compared to the Neva.

There was more chlorite-montmorillonite regular interlayer clay in the Salem Point than in the Neva. Super-lattice structures of chlorite-montmorillonite were found in samples 21-B (dolomite), 28-C (shale), 29-C (dolomite), and 30-C (shale). The super-lattice clays which were found did not correlate from one location to another. These were found in three unweathered samples, and in one sample which was only slightly weathered. This may indicate that the super-lattice tends to be altered to regular chlorite-montmorillonite when subjected to weathering. A summary of the clay minerals present in the Salem Point shale is shown in Table 1.

Burr Limestone. Five samples of the Burr limestone were collected at both the A and B locations. The samples from both localities were moderately weathered.

The major clay mineral of the Burr limestone, like the Neva and the Salem Point, was illite.

Chlorite was the second most abundant clay mineral found. Of the ten samples which were analyzed, six contained iron rich, poorly crystalline chlorite. Some of the samples from location B contained iron free, well crystalline chlorite, and some of the iron rich, well crystalline variety.

Illite-montmorillonite random interlayer clay was found to be present in all the samples. In samples 32-A (limestone) and 34-A (shale) the interlayer was a major constituent. The X-ray reflections in these samples were very intense from 10 to 14-A on the unglycolated samples.

Chlorite-montmorillonite regular interlayer was found in all samples of the Burr except 33-A (limestone). There was less chlorite-montmorillonite interlayer in the Burr than in either the Neva or the Salem Point.

Legion Shale. Illite was found to be the most abundant clay mineral in the Legion shale, and probably made up a dominate part of the mineralogical composition of the unit.

Chlorite was found in all the samples, and was composed mostly of the iron free, well crystalline variety. The lowermost sample from both locations A and B contained iron free, poorly crystalline chlorite (Table 1).

Montmorillonite was sparse in the Legion shale. A small amount was found in samples 32-B (limestone), 33-B (limestone), and 35-A (limestone).

The two mixed layer clays (illite-montmorillonite and chlorite-montmorillonite) were found in nearly equal abundance from top to bottom of the Legion.

Sallyards Limestone. One sample of the Sallyards was collected at location A and one sample at location B. The major clay mineral of the unit was illite. A minor amount of chlorite was present in both samples. The chlorite from location A was iron rich, poorly crystalline, and the chlorite from location B contained some iron and was moderately crystalline. None of the samples contained montmorillonite. Both regular and random interlayer clay was found in the samples examined. These included illite-montmorillonite and chlorite-montmorillonite. Chlorite-montmorillonite was more abundant than the illite montmorillonite.

Upper Roca Shale. Two samples were taken from the Roca shale; one sample was collected at location A and one at location B. The Roca, like the members of the Grenola limestone formation, contained illite as its major clay constituent. Chlorite was found to be present in both samples. The chlorite in the sample from location A was iron rich, poorly crystalline, and that from location B was iron free with a moderate amount of crystallinity. Both regular and random interlayer clay was present in the Roca. There was more chlorite-montmorillonite regular interlayer than illite-montmorillonite random interlayer.

#### Carbonates

Method of X-ray Identification. Random powder slides were

X-rayed on all the limestones to obtain the relative calcite-dolomite ratio. Calcite was identified on the basis of its 3.03-A reflection, and dolomite by its 2.90-A reflection. Calcite and dolomite were the only carbonate minerals identified by X-ray diffraction analysis.

Lower Eskridge Shale. The lower Eskridge shale contained a small amount of dolomite in the carbonate fraction. No calcite was identified in the shale. A summary of the carbonate mineralogy identified by X-ray analysis is shown in Table 1.

Neva Limestone. Calcite was the major carbonate mineral in the upper half of the Neva (Table 1). The lower half of the limestone contained nearly as much dolomite as calcite. In zones 11, 12, and 14 dolomite was more abundant than calcite.

Salem Point Shale. Dolomite was the major carbonate constituent in the Salem Point shale (Table 1). However, calcite was found in nearly all the samples, and was a major carbonate constituent in some zones within the unit.

Burr Limestone. The limestone units of the Burr were largely calcite with a small amount of dolomite. The shale units in the Burr showed a slight predominance of dolomite over calcite.

Legion Shale. Dolomite was slightly predominate over calcite in the Legion shale. Both of the minerals were present in all the samples examined.

Sallyards Limestone. The Sallyards limestone was composed largely of calcite. There was a minor amount of dolomite in the sample taken from location B. No dolomite was found in the sample



from location A.

Upper Roca Shale. Both calcite and dolomite were present in the samples of Roca shale taken from location A. Calcite, in this sample, was predominate over dolomite. The sample from location B had neither calcite or dolomite.

#### NON-CLAY MINERALS

The only non-clay mineral which was distinguished by X-ray diffraction analysis was quartz. The mineral was identified by its 4.27-A reflection. Quartz was found as a minor constituent in nearly all the samples which were examined in this investigation. A list of the zones which contained quartz is shown in Table 1.

#### INSOLUBLE RESIDUE WEIGHT COMPARISON

##### Neva Limestone

The insoluble residues found in the Neva limestone member displayed a color range from green to gray and brown. The color of the untreated sample ranged from buff to tan and brown. There seemed to be little correlation between the color of the untreated sample, and the color of the insoluble residue.

The per cent of insoluble residue ranged from 1.8 to 37.5. The "honeycomb" zone (zone 11) contained the smallest amount of insoluble residue. This zone, composed essentially of dolomite, was highly solutioned and nearly unconsolidated in some places.

A comparison of the amount of insoluble residue from similar zones in the Neva at different localities is shown in Table 2.



There seems to be a good correlation of the per cent of insoluble residue from one location to another. There was a better correlation of the per cent of insolubles in the upper part of the Neva than in the lower part (Table 2).

In general the softer limestones contained more insoluble residue than the hard limestones in the samples examined.

#### Salem Point Shale

Insoluble residues were prepared on four dolomites and limestones from the Salem Point shale (Table 2). All of the untreated samples were gray to light gray in color, and the insoluble residue was gray to dark gray in color. There was some correlation between the color of the untreated samples and the color of the insoluble residue.

The amount of insoluble residue ranged from 12 to 31 per cent. The dolomite in the upper portion of the Salem Point contained more insoluble residue than the lower portion.

#### INSOLUBLE RESIDUE MINERAL DETERMINATION OTHER THAN CLAYS

##### Heavy Minerals

Celestite, magnetite, limonite, limonite coated grains, and pyrite were the most abundant constituents found in the heavy mineral fraction of the limestones from the Neva and Salem Point. Ilmenite, apatite, biotite, tourmaline, zircon, and hornblende were present in minor amounts. A summary of the minerals found

Table 2. Percent insoluble residue and color of sample before and after HCL treatment in the limestone zones of the Neva limestone and Salem Point shale.

Geologic Section	Classification	Percent Insoluble Residue	Color of sample	Color of sample after HCL treatment
NEVA LIMESTONE				
2-A	Limestone	5	Cream	Light brown
2-B	Limestone	5	Light tan	Gray to Green
2-C	Limestone	2	Buff	Gray
2-D	Limestone	5	Buff	Gray
3-A	Shaly Ls.	15	Light tan	Gray
3-B	Shaly Ls.	15	Light tan	Gray
3-C	Shaly Ls.	15	Tan	Gray
3-D	Shaly Ls.	15	Light tan	Gray
4-A	Limestone	10	Light tan	Gray
4-B	Limestone	2	Light tan	Gray
4-C	Limestone	8	Buff to tan	Gray
4-D	Limestone	8	Light tan	Gray
5-D	Shaly Ls.	10	Light tan	Gray

Table 2. (cont.)

Geologic Section	Classification:	Percent Insoluble Residue	Color of raw sample :sample	Color of raw sample after HCL treatment :HCL treatment
6-A	Limestone	10	Light tan	Gray
6-B	Limestone	10	Tan	Gray
6-C	Limestone	10	Light tan	Brown to gray
6-D	Limestone	15	Light tan	Brown to gray
7-A	Limestone	5	Light tan	Gray
7-B	Limestone	10	Light tan	Gray
7-C	Limestone	5	Light tan	Gray
7-D	Limestone	10	Tan to white	Brownish gray
8-A	Limestone	10	Tan	Brown
8-B	Limestone	10	Tan	Brown
8-C	Limestone	25	Buff to tan	Gray
8-D	Limestone	5	Rusty tan	Brown
9-B	Shale	25	Buff to tan	Gray

Table 2. (cont.)

Geologic Section	Classification	Percent Insoluble Residue	Color of raw: Color of	
			: sample	: sample after : HCL treatment
10-A	Limestone	■	Tan	Gray
10-B	Limestone	■	Tan	Gray
10-C	Limestone	■	Tanish brown	Gray
10-D	Limestone	■	Tanish brown	Gray
11-A	Limestone	■	Brown to tan	Gray
11-B	Dolomite	■	Brown to tan	Gray
11-C	Dolomite	■	Buff to tan	Gray
11-D	Dolomite	■	Brown to tan	Gray
12-A	Dolomite	■	Buff to tan	Gray
12-B	Dolomite	■	Tan to brown	Gray
12-C	Dolomite	■	Tan to brown	Gray
12-D	Limestone	■	Brown	Brown to gray
13-A	Dolomite	■	Brown to tan	Gray

0 10 20 30 40 50

Table 2. (cont.)

Geologic:		Section:		Classification:		Percent Insoluble Residue		Color of raw:		Color of sample after HCL treatment	
								sample		sample after HCL treatment	
13-B	Dolomite							Tan		Gray	
13-C	Limestone							Tan to brown		Gray to brown	
13-D	Limestone							Reddish brown		Gray	
14-A	Dolomite							Tan		Gray	
14-B	Dolomite							Tan		Gray	
14-C	Dolomite							Light gray		Gray	
14-D	Dolomite							Reddish brown		Brown to gray	
16-D	Shale							Light tan		Gray	
18-A	Limestone							Buff to tan		Gray	
18-B	Limestone							Light tan		Gray	
18-C	Limestone							Rusty buff		Gray	
18-D	Limestone							Light tan		Gray	
SALEM POINT SHALE											
20-C	Shaly Dol.							Gray		Dark gray	

Table 2. (cont.)

Geologic:		Percent Insoluble Residue		Color of raw:Color of			
Section :	Classification:	:	:	sample	sample after		
:	:	:	:	:	:HCL treatment		
23-C	Shaly Dol.			Gray	Dark gray		
24-C	Dolomite			Light gray	Dark gray		
29-C	Limestone			Light gray	Gray		
		0	10	20	30	40	50



in the two units is shown in Table 3.

Celestite. Celestite ( $\text{SrSO}_4$ ) was identified on the following optical properties; biaxial positive,  $2V=50$  degrees, birefringence of .009, white to straw yellow interference color, and an indices of refraction greater than Lakeside 70 (1.54). Celestite was commonly found stained with limonite and coated with cryptocrystalline quartz.

The largest amount of celestite was found in the "honeycomb" zone. This zone showed evidence of some kind of solutioning which undoubtedly favored the formation of the mineral. There seemed to be no correlation between the degree of subaerial weathering which the limestone was subjected to and the amount of celestite present in the sample.

Magnetite. Magnetite ( $\text{Fe}_3\text{O}_4$ ) was identified on the following optical properties; black, opaque to transmitted light and steel gray in reflected light. Most of the magnetite was probably detrital in origin. The amount of magnetite present was very small compared to the amount of celestite. The zones where magnetite was found is shown in Table 3.

Limonite and Limonite Coated Grains. Limonite ( $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ ) is a hydrous iron-oxide, and is an alteration product of iron bearing minerals. According to Wahlstrom (1955, pp. 220) goethite in cryptocrystalline form is the chief constituent of limonite. Limonite was easily identified under the petrographic microscope by its rusty red appearance under plain light.

Limonite was found in the limestone samples both as individual







Table 3. (cont.)

Geologic Section		Heavy Minerals		Light Minerals		Organic Material																		
		Magnetite	Hematite	Ilmenite	Pyrite	Apatite	Biotite	Celestite	Tourmaline	Zircon	Hornblende	Garnet	Limonite and Limonite coated grains	Quartz	Chalcedony	Volcanic Ash	Opal	Muscovite	Orthoclase	Microcline	Gypsum	Limonite coated grains	Clay coated grains	
13-B	Dol	x			x			xxx	x	x	x	x	x	xxx	xxx	x	x	x				x		x
13-C	Ls							xxx	x				x	xxx	xx	x	x						x	
13-D	Ls		x					xxx		x	x		x	xx	xxx		x		x				x	
14-A	Dol	x								x		x			xxx							x		x
14-B	Dol								x	x		x		xx	xxx	x			x			x		x
14-C	Dol	x			x						x		x	xx	xxx				x			x		x
14-D	Dol							.xx					x	xx	xxx	x								
16-D	Sh	x								x				xxx										
18-A	Ls	x								x				xx	x									
18-B	Ls													xx	xxx									
18-C	Ls													xxx	xx									
18-D	Ls		x										x	xx	xxx									
			x										x	xx	xxx									





grains, and as a coating over other minerals. Most of the limonite coated grains were probably quartz and chalcedony, some perhaps were pyrite.

Pyrite. Pyrite ( $\text{FeS}_2$ ) was identified most easily by the use of the binocular microscope. Most of the pyrite grains were euhedral or subhedral in crystal outline. Under the petrographic microscope pyrite is opaque in plain light, and in reflected light a pale brass-yellow metallic luster is noted.

Pyrite was not as essential heavy mineral in the Neva limestone. It was, however, a major constituent in the heavy minerals of the Salem Point shale. Pyrite was found coating other minerals in some of the samples.

#### Light Minerals

Quartz, chalcedony, volcanic ash, and opal were the major constituents of the light mineral fraction. Other light minerals which were found included muscovite, orthoclase, microcline, gypsum, limonite coated grains, and clay coated grains. Organic material was found in many of the samples. Grinoid stems, brachiopod spines, fragments of brachiopods, and fragments of bryozoans were very common. Most of the fossils had been replaced by cryptocrystalline quartz. A summary of the light minerals found in the Neva limestone and Salem Point shale is shown in Table 3.

Quartz. Quartz ( $\text{SiO}_2$ ) was identified mainly on the basis of its uniaxial positive sign, and its indices of refraction which was very near that of Lakeside 70 (1.54). Most of the quartz

was probably detrital in origin. Quartz was a very important mineral in the light mineral fraction in both the Neva limestone and the Salem Point shale. The mineral was not found in all the samples examined.

Chalcedony. Chalcedony ( $\text{SiO}_2$ ) was identified on the basis of its characteristic feathery extinction under cross nicols. Chalcedony was slightly more abundant than quartz in the samples which were examined. Most of the chalcedony was probably secondary in origin. Evidence of this is shown by fossils which were replaced with the mineral. The fossils were probably originally calcite.

Volcanic Ash and Opal. The isotropic constituents in the light mineral fraction included mainly opal and volcanic ash. Some distinction between the two constituents could be assumed by the inclusions which were found in the grains and the shape of the grains. It is probable that the grains which contained inclusions were volcanic ash. The fact that the grains did not contain inclusions is, however, no evidence that the silica was not of volcanic origin. Some of the grains were shard shaped. It is probable that these were volcanic ash.

#### Coarse Residue

The most common mineral found in the coarse residue was chalcedony. Crinoid stems, brachiopod spines, brachiopod shell fragments, and fragments of bryozoans were common as chalcedonic fossil fragments.

Quartz was also common in the coarse residue. The grains were found both as angular fragments and as rounded grains. Rounded grains were more common than angular fragments. Many of the quartz grains were frosted and pitted, giving evidence that they were transported for some distance, or pitted by solution.

Celestite was easily distinguishable under the binocular microscope by its limonite stained outer surface, giving the mineral an orange colored cast around the margins of some of the grains. It was found to be very abundant in the coarse residue from the "honeycomb" zone in the Neva limestone.

Other constituents which were easily distinguishable in the coarse residue included magnetite, hematite, ilmenite, limonite, limonite coated grains, clay coated grains, and organic material. Pyrite was highly abundant in the coarse residue from the Salem Point shale.

#### DISCUSSION OF RESULTS

##### Possible Effects of Near Surface Weathering on Rock Containing Clay Minerals and Showing Little or No Visible Weathering

In such a study of the weathering effects on clay minerals several factors must be considered: (1) Leaching of the potash from clay minerals and its possible redeposition in lower zones. (2) Leaching of magnesium from chlorite clays and its possible redeposition in zones directly below. (3) The leaching and redeposition of iron. (4) Leaching of potassium, magnesium, and

iron from the clay minerals without their redeposition. (5) Combinations of all the previously mentioned factors.

Some evidence of leaching and redeposition of potassium, magnesium, and iron may be shown by the variability of the clay mineralogy from the same zone at different localities; e.g., the various zones of 2 (limestone), 11 (dolomite), 12 (dolomite and limestone), 13 (dolomite and limestone), 14 (dolomite), 15 (shale), 16 (shale), and 17 (shale), in the Neva limestone. In the clay mineralogy there seemed to be a greater variability in the amount of iron and the type of crystallinity of the chlorite as compared to other clay minerals; e.g., sample 16-A (shale), 16-B (shale), 16-C (shale), 16-D (shale). The leaching effect probably tended to have a more marked effect upon the magnesium and iron in the brucite sheet of chlorite than on the potassium in the illite lattice. It is also probable that some of the elements which were leached out of the clay minerals were carried away by circulating waters.

#### Effect of Alteration of Clay Minerals and Some Carbonates

Clay Minerals. Alteration effects upon the clay minerals are many. The weathering of illite may cause the potassium to be leached out of the lattice, with it being replaced by water, such as in zone 11-A (dolomite), 11-B (dolomite), and 11-C (dolomite). The mineral may then become montmorillonite. The reverse of this process is probably more common, since illite was much more common

in the rocks examined than montmorillonite. It is probable that the marine environment contained abundant potassium ions in the sea water, and any montmorillonite or degraded illite which was present was converted to illite by addition of the potassium to the lattice. This phenomena may partially account for an abundance of illite in marine sediments as a whole.

Alteration processes which acted upon the chlorite caused a leaching out of some of the magnesium in the brucite layer of the chlorite. Although some of the unweathered samples contained poorly crystalline chlorite, the crystallinity of the mineral was generally better in sediments which were not subjected to sub-aerial weathering. A good example of this phenomena is shown in 24-A (dolomite), 24-B (dolomite), 24-C (dolomite), 25-A (shale), 25-B (shale), 25-C (shale), 26-A (shaly limestone), 26-B (shaly dolomite), and 26-C (limy dolomite). In all of the above cited examples, the chlorite from locations A and B was iron rich, poorly crystalline, and the samples from location C contained iron free, well crystalline chlorite. The A and B samples were slightly weathered, while the samples from C were relatively unweathered.

Some evidence which substantiates the phenomena of alteration of clays by leaching may be shown by the ion exchange experiments which were performed in the laboratory. In the experiments the montmorillonite from zone 11-D (clay coating) and the limestone from 10-A (limestone) was saturated with potassium hydroxide and magnesium chloride respectively. The montmorillonite from zone



11-D (clay coating) showed some reversion back to illite and the poorly crystalline chlorite in zone 11-A (limestone) showed reversion to well crystalline chlorite (Table 1). The potassium evidently replaced some of the water in the montmorillonite lattice and formed illite. The magnesium in the magnesium chlorite probably filled some of the openings in the mica sheet and brucite sheet of chlorite where magnesium had been prior to leachings. The saturation with magnesium increased the crystallinity of the chlorite structure.

Rocks containing dolomite generally contained a sizable amount of chlorite; e.g., zones 9-D (shale), 11-C (dolomite), 12-B (dolomite), 13-A (dolomite), 13-B (dolomite), 14-A (dolomite), 14-B (dolomite), 14-C (dolomite), 14-D (dolomite) in the Neva limestone. The chlorite was present in the free state, as chlorite-montmorillonite regular interlayer, and as chlorite-montmorillonite super-lattice regular interlayer. It is evident from the examples cited that an environment which was favorable for the formation of dolomite was also favorable for the formation of chlorite. There is a great probability that such an environment was marine. The dolomite was probably not primary in origin, but developed by alteration of other carbonates (mainly calcite and/or aragonite).

Three interlayer clays were found in this investigation. These included illite-montmorillonite random interlayer, chlorite-montmorillonite regular interlayer, and super-lattice chlorite-montmorillonite regular interlayer. The author believes that the



interlayer clays are an intermediate step toward the more stable end-product clay, e.g., chlorite and illite. The montmorillonite part of an interlayer clay is somewhat unstable and tends to be transformed toward the more stable end-products, illite and chlorite. It is possible that the transformation of montmorillonite to chlorite and illite is somewhat reversible, and under certain environmental conditions the process could be reversed. Such a reversal might be caused by leaching processes. A possible illustration of the reversal of the process of transformation of montmorillonite to a more stable clay may be shown in zones 11-A (dolomite), 11-B (dolomite), and 11-D (dolomite).

Super-lattice chlorite-montmorillonite regular interlayer was found in four samples, three of which were fresh; e.g., 28-C (shale), 24-C (limestone), and 30-C (shale). Sample 21-B (dolomite) from a slightly weathered zone contained super-lattice clay. The fact that a major amount of the super-lattice clay which was found was in unweathered zones may give evidence that the clay was altered upon weathering to chlorite-montmorillonite regular interlayer and/or chlorite.

Carbonate Minerals. The alteration of dolomite has already been considered in the discussion of the clay minerals. A more thorough discussion is necessary, however, for a good understanding of the effects of alteration upon the carbonate mineralogy.

It is probable that most of the carbonate minerals of the Grenola limestone formation were deposited as calcite and aragonite. Much of the rock in the Grenola has probably remained

unchanged through the periods following the Permian. In other cases the calcite was altered to dolomite, and the aragonite was altered to calcite and/or dolomite.

Alteration of calcite to dolomite, and the aragonite to calcite and/or dolomite probably took place early in the depositional history of the rock. The environmental conditions for such a process to take place was probably a marine condition in which the water was highly saline, and rich in magnesium.

One may then ask: why does a similiar zone vary in calcite and dolomite content from place to place within a short horizontal distance? The author believes that the salinity of the water in the marine environment varies from place to place due to the irregular shape of the sea bottom, and as the water retreated from the land, small low areas became isolated basins, and the water became more saline. The higher areas of the irregular sea bottom were not affected by the concentrated saline waters. The higher areas were not high enough to be affected by subaerial weathering in most cases. The dolomite probably tended to form in the more saline environment. The spotted character of the dolomitization is well shown by variation in zones 9-A (shale), 9-B (shale), 9-C (shale), and 9-D (shale); 12-A (dolomite), 12-B (dolomite), 12-C (dolomite), and 12-D (limestone); 13-A (dolomite), 13-B (dolomite), 13-C (limestone), and 13-D (limestone); 20-A (limy shale), 20-B (limy shale), and 20-C (dolomitic shale); 25-A (shale), 25-B (shale), and 25-C (shale); 26-A (limy shale), 26-B (dolomitic shale),

and 26-C (limy shale); 30-A (shale), 30-B (shale), and 30-C (shale); 37-A (shale), and 37-B (shale); 38-A (shale), and 38-B (shale); 39-A (shale), and 39-B (shale); 41-A (shale), and 41-B (shale).

#### Origin of the "Honeycomb" Zone of the Neva Limestone

There are several different ways in which the "honeycomb" zone may have formed. Some of the possible origins are as follows:

- (1) Groundwater solution; (2) Intrastratital solution; (3) Metasomatic replacement; (4) The effect of subaerial weathering; (5) Some combination of the above mentioned factors.

It is the author's belief that the dolomite which makes up the "honeycomb" zone was originally deposited as aragonite. Some evidence that the zone was originally aragonite is shown by the abundance of celestite in the insoluble residue fraction from the zone; e.g., sample 11-A (dolomite), 11-B (dolomite), 11-C (dolomite), and 11-D (dolomite). It is a known fact that strontium is present in most aragonite (Noll, 1934, pp. 507). Other evidence that the zone was originally aragonite is shown by the porosity of the zone. The zone is very porous and possibly shows loss of volume. There would be a volume loss in the transformation of aragonite to dolomite. An environment favorable for the change of aragonite to dolomite would be similar to an environmental condition favorable for the change of calcite to dolomite. None of the other dolomite or dolomitic limestone show any evident

porosity. Therefore the dolomitization of the "honeycomb" zone must have occurred in a different way or at a different time.

The sequence of events for the "honeycomb" zone must have been as follows: (1) Deposition; (2) Exposure to subaerial weathering; (3) Submergence and dolomitization. The evidence that short periods of exposure to subaerial weathering was not uncommon is shown by the occurrence of marine red shales in the Permian rocks of the area, both above and below the Grenola formation.

Some curiosity may be aroused when the origin of the "clay coating" and "clay seam" zones within the "honeycomb" zone is considered. The "clay coating" was nearly pure montmorillonite, and was found in abundance in samples 11-A (dolomite), 11-B (dolomite), and 11-D (dolomite). The "clay seam" zone at location 11-C (dolomite), which probably corresponded to the "clay coating" zone at the other three locations, was nearly pure illite. The difference in the clay mineral types in samples 11-A, 11-B, 11-D, as compared to 11-C, may possibly be explained by variability in the depth of burial.

The "clay coating" and "clay seam" zones were probably deposited originally as illite. At the present time the zone has been subjected to near surface weathering at locations 11-A, 11-B, and 11-D. Zone 11-C, until late in 1958, was under nearly 100 feet of overburden, and was not affected by the surface weathering process to any extent. Subjection to near surface weathering effects probably caused leaching of the potash from the illite

clay present at locations 11-A (dolomite), 11-B (dolomite), and 11-D (dolomite). The leaching in these zones of the potassium from the illite probably resulted in the formation of the montmorillonite, with coatings being formed around dolomite grains. The illite at location 11-C (dolomite) has not been subjected to leaching, and has remained nearly unchanged from the form which it had at the time of deposition.

Factors Pertaining to the Origin of the  
Neva Limestone and Salem Point Shale Which May Be  
Concluded From the Heavy and Light Mineral Analysis

Heavy Minerals. Emphasis has already been placed upon the importance of celestite in regard to the origin of the rock units containing the mineral. The strontium which is present in the celestite probably originated in aragonite which has been altered after deposition to calcite and/or dolomite. This alteration of aragonite sets strontium free to unite chemically with any sulfate present to form celestite.

A reciprocal relationship seems to exist between the amount of celestite and the amount of chlorite and dolomite. The "honeycomb" zone and 12-C (dolomite) were exceptions. It is known that strontium, calcium, and magnesium are in the same chemical group. However, the strontium is more closely related to calcium than magnesium in chemical properties. It is assumed that calcite would thus be found more commonly with strontium than dolomite.

There are two possible reasons why there was more pyrite in the Salem Point shale than in the Neva limestone. It is



possible that the pyrite was leached out of the Neva by penetrating water from the surface early in the geologic history of the rock, and concentrated in the Salem Point shale. Such a process probably occurred while the unit was under marine waters. It is also possible that the pyrite formed by reaction between the sulphur of decaying organic material and iron which was enclosed in the sediments.

The latter explanation for the origin of pyrite is probably the most reasonable. The basis of the assumption that the environmental conditions were favorable for the formation of pyrite may be shown by the presence of darker colored shales near the base of the Neva limestone, and into the Salem Point shale.

Light Minerals. Much of the silica in the limestone was chalcedony. The mineral was probably secondary in origin and possibly resulted partially from water percolating through the rock which contained colloidal silica. This process was probably much more active in the early geological history of the rock than at the present time. There is also a possibility that some of the silica which was necessary for the formation of chalcedony may have originated from ash falls simultaneous with deposition. Another possible origin of the silica necessary for the formation of chalcedony could be from silica bearing marine organisms which were present in the environment at the time of deposition; e.g., sponge spicules and radiolarians.

Volcanic ash shards were found in some of the samples of the Neva limestone and Salem Point shale, but not all the samples



contained the ash. Most of the samples which contained abundant volcanic ash also contained abundant chalcedony; e.g., samples 2-C (limestone), 2-D (limestone), 6-B (limestone), 6-C (limestone), 6-D (limestone), 7-D (limestone), 8-B (limestone), 8-C (limestone), 13-C (limestone), 14-B (dolomite), and 14-D (dolomite). However, the samples which contained abundant chalcedony did not necessarily show an abundance of ash. It is possible that some of the ash may have been absorbed in aqueous solutions as a silica gel and redeposited as chalcedony, or used by marine organisms. The larger volcanic ash shards were probably not transformed to chalcedony as readily as the smaller ones.

The volcanic ash, if present, may have also been altered to montmorillonite. The amount of montmorillonite was so small, however, that it was not recognized on X-ray in the samples containing ash. The montmorillonite, on the other hand, which developed from the volcanic ash may have again been altered to the interlayer clays. No change in the clay minerals was observed in samples which contained ash as compared to those which did not contain ash.

#### SUMMARY AND CONCLUSIONS

The following observations and conclusions were made from the analytical data obtained.

There seemed to be a correlation between the iron content, the crystallinity of the clay, and the degree of weathering to which the rock was subjected. There was more iron rich, poorly

crystalline chlorite in weathered rock than in unweathered rock. A good example of this phenomena is shown in 24-A (dolomite), 24-B (dolomite), and 24-C (dolomite); 25-A (shale), 25-B (shale), and 25-C (shale); 26-A (limy shale), 26-B (dolomitic shale), and 26-C (limy dolomite). In all the examples cited the chlorite at location A and location B was iron rich, poorly crystalline, and the samples from location C contained iron free, well crystalline chlorite. The A and B locations were slightly weathered while the C location was relatively unweathered.

Super-lattice chlorite-montmorillonite regular interlayer clay was found predominately in fresh samples; e.g., 28-C (shale), 29-C (limestone), and 30-C (shale). Sample 21-B (dolomite) from a slightly weathered zone contained super-lattice clay. This data gives some indication that the super-lattice chlorite-montmorillonite was altered upon weathering to chlorite-montmorillonite regular interlayer and/or chlorite.

Some correlation was found between the abundance of chlorite and dolomite. Where there was an abundance of dolomite, there was also an abundance of chlorite and/or chlorite-montmorillonite interlayer; e.g., 2-B (shale), 9-D (shale), 11-C (dolomite), 12-A (dolomite), 12-B (dolomite), 12-C (dolomite), 13-A (dolomite), and 20-C (shaly dolomite) in the Neva limestone. This factor may indicate that the environment favorable for the origin of the two minerals was one rich in magnesium.

There was some correlation between the amount of insoluble

residue and the amount of chlorite. The rocks which contained the higher insoluble residue also contained a larger amount of chlorite. A good example of this is shown in samples 14-A (dolomite), 14-B (dolomite), 14-C (dolomite), and 14-D (dolomite).

A reciprocal relationship seemed to exist between the amount of celestite and the amount of chlorite and dolomite. The "honeycomb" zone and sample 12-C (dolomite) were exceptions. These two zones contained abundant celestite, and also contained abundant dolomite. It is known that strontium, calcium, and magnesium are in the same chemical group. However, strontium is much more closely related to calcium in chemical properties. It may thus be assumed that celestite would be found more commonly with calcite than with dolomite.

It is probable that the origin of the "honeycomb" zone, which is largely dolomite, is different from the origin of other dolomites. The suggested history of this zone is: (1) Probable deposition of aragonite. (2) Exposure to subaerial weathering. (3) Submergence and then dolomitization.

The final significant factor which was concluded from the investigation was the origin of the "clay coatings" and "clay seam" zones within the "honeycomb" zone. The author believes that the clay found at the four locations was deposited originally as illite. Due to recent near surface weathering the potassium ion was leached out of the illite in zones 11-A (dolomite), 11-B (dolomite) and 11-D (dolomite), and montmorillonite which coated dolomite grains was formed. The illite in zone 11-C (dolomite)

was under nearly 100 feet of overburden until late in 1958, and therefore the zone has not been subjected to near surface leaching effects, and the illite remains unaltered.

## ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Arthur B. Sperry, Professor of geology, Emeritus, for his assistance and guidance during the course of the investigation.

Thanks are also due Mr. Carl Crumpton and Mr. William Badgley of the Kansas State Highway Commission for assistance and advice on laboratory procedure and analysis.

To others who have extended advice and criticism, the author wishes to express thanks.

## REFERENCES

- Brindley, G. W.  
X-ray Identification and Crystal Structure of the Clay Minerals, The Miner. Soc. (Clay Minerals Group). London: Taylor and Francis, 1951.
- Claypool, C. B., and H. V. Howard.  
Methods of Examining Calcareous Well Cuttings. Am. Assoc. Petrol. Geol. Bull. 12:1149-1152. 1928.
- Drake, L. Y.  
Insoluble Residues of Some Permian and Pennsylvanian Limestones. Unpublished M. S. thesis, Kansas State College, Manhattan, Kansas. 1951.
- Grim, R. E.  
Clay Mineralogy. New York: McGraw-Hill. 1953.
- Jewett, John M.  
The Geology of Riley and Ceary Counties, Kansas. University of Kansas Publications, State Geological Survey of Kansas. Bulletin 39: Dec., 1941.
- Johnson, J. H.  
An Introduction To The Study of Organic Limestone. Rev. Ed. Quart. of the Colo. Sch. of Mines. 46, 1951.
- Lippman, F.  
Clay Minerals From the Rot Member of the Triassic near Göttingen, Germany. Jour. Sediment. Petrol. 26:125-139. June, 1956.
- McQueen, H. S.  
Insoluble Residues as a Guide in Stratigraphic Studies. Missouri Bureau of Geology and Mines, 56. Biannual Report to State Geologist, 1929-30. 1:102-30, 1:102-139, 1931.
- Noll, W.  
Geochemie des Strontium. Mit Bemerkungen Zur Geochemie des Bariums. Translated by K. Rankama and T. G. Schama. Chem Erde, 1934. pp. 507.
- Pettijohn, R. S.  
Sedimentary Rocks. New York: Harper and Bros. 1957.
- Pirsson, L. V., and A. Knopf.  
Rock and Rock Minerals. New York: John Wiley and Sons. 1947.



- Schoewe, W. H., G. C. Kercher, and R. P. Kercher.  
Preliminary Study of Residues of Kansas Pennsylvanian Rocks.  
Kans. Acad. Sci. Trans. 40:269-281. 1937.
- Swanson, H. E.  
Tables for Conversion of X-ray Diffraction Angles to Interplanar Spacing. Nat. Bur. of Stand. App. Math. Series 10.  
U. S. Govt. Printing Office.
- Twenhofel, W. H.  
Principles of Sedimentation, 2nd. ed. New York: McGraw-Hill.  
1950.
- Wahlstrom, E. E.  
Petrographic Mineralogy. New York: John Wiley and Son, Inc.  
1955.

CLAY MINERALOGY AND OTHER PETROLOGIC ASPECTS  
OF THE GRENOLA LIMESTONE FORMATION  
IN THE MANHATTAN, KANSAS, AREA

by

GERALD DUANE HARGADINE

B. S., Kansas State University  
of Agriculture and Applied Science, 1958

---

AN ABSTRACT OF THE THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Geology and Geography

KANSAS STATE UNIVERSITY  
OF AGRICULTURE AND APPLIED SCIENCE

1959

The purpose of this investigation was to determine the carbonate and non-carbonate mineralogy of the Grenola limestone formation in the Manhattan, Kansas, area. An investigation was made of the effect of weathering on the clay mineralogy of the Grenola.

The methods employed in this study included X-ray diffraction, petrographic analysis, binocular microscope study, and insoluble residue analysis. Identification of clay minerals and carbonates was accomplished mainly by X-ray diffraction. The minerals other than carbonates and clays were studied by petrographic means.

From this investigation the following observations were made:

1. Illite was by far the most abundant clay mineral in the rocks of the Grenola limestone formation.
2. The chlorite in unweathered zones generally had better crystallinity and less iron than chlorite in the same zones now near the surface.
3. The largest amount of montmorillonite was found in the "honeycomb" zone of the Neva limestone, and was present as "clay coatings" around dolomite grains. The "clay coatings" were found in three sample locations. The fourth location, which was unweathered, contained a "clay seam" of illite in the "honeycomb" zone instead of montmorillonite like that found at other locations.
4. Super-lattice chlorite-montmorillonite regular interlayer clay was more abundant in unweathered samples than in weathered samples.
5. Celestite was the most abundant heavy mineral in the Neva

limestone.

6. Pyrite was the most abundant heavy mineral in the Salem Point shale.
7. Quartz and chalcedony were the most abundant of the light minerals found in both the Neva limestone and the Salem Point shale.
8. Where there was a large amount of dolomite in a sample there was generally a large amount of chlorite.
9. There seemed to be a reciprocal relationship between the amount of celestite and the amount of dolomite and chlorite in the Crenola limestone formation. An exception to this was the "honeycomb" zone and the zone directly below the "honeycomb" zone in the Neva limestone.
10. The "honeycomb" zone of the Neva limestone was nearly pure dolomite, and was very porous in all the sample locations.