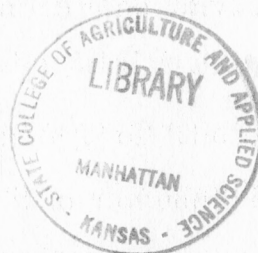


THE NON-CARBONATE MINERALOGY OF SOME PERMIAN
AND PENNSYLVANIAN LIMESTONES

by

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INTRODUCTION

Purpose of the Investigation

The purpose of this investigation is to determine the non-carbonate mineralogy of some Permian and Pennsylvanian limestones near Manhattan, Kansas. All limestones contain impurities such as sand, silt, and clay. Although these impurities compose a minor percentage of the limestones, they may offer important information about the origin and the history of the geologic formation. The mineralogy of the rock units will determine whether these units can be used for engineering purposes. These minor constituents may also be used as a means of correlating subsurface strata.

Scientific Importance. Geologists know very little about the mineralogy of sediments, especially limestones and shales. Most of the detailed study of sedimentary rocks has been concerned with sandstones. A study of the allogenic and authigenic minerals other than the carbonates in a limestone may reveal significant information about the origin and history of the rock unit. An attempt has been made in this study to describe the environmental conditions of each limestone.

Engineering Importance. The mineralogy, texture, and structure of a rock unit determines its usability in engineering. The minerals present as minor constituents in a limestone may prove to be major factors in ascertaining for what engineering purpose the rock may be used, and how it will behave when used. Limestones which contain flint or chert concretions should be avoided

in building stone. Mica when segregated from other minerals along bedding planes in some types of limestones may lead to splitting of the rock. Pyrite, when present in a rock in any greater quantity than a few fine grains uniformly spaced, is a potential source of trouble, as it weathers easily and may form sulphuric acid in the process. Fossils, if abundant and oriented along certain planes, may be a source of weakness in limestones. The presence of large amounts of iron oxides in a rock may make its use as a building or trim stone undesirable. All these factors may be determined by a study of the non-carbonate mineralogy of the limestones. (Legget, 1939, p. 518.)

Subsurface Correlation. The use of the insoluble residues of limestones as an aid in subsurface correlation in the petroleum industry has become very important in recent years (Ireland, 1950, p. 140). Limestones that lack diagnostic features in the hand specimen or in well cuttings may show microscopic characteristics that can be used for correlation purposes.

Procedure. In this study the insoluble residues of limestones were divided into coarse and fine fractions. The coarse fractions were further subdivided into heavy and light mineral fractions, and the mineral frequencies in each were determined by use of the petrographic microscope. The fine fractions were studied by use of the differential thermal analysis apparatus and from this analysis the dominant clay mineral was ascertained.

Review of Literature

Limestones. Some disagreement exists in geological literature about the definition of a limestone. The lime manufacturer uses the term "limestone" for a general class of rocks containing at least 80 per cent of the carbonates of calcium and magnesium and which, when calcined, give a product that slakes upon the addition of water (Pettijohn, 1949, p. 289). At the other extreme is Trask (1950), p. 33, who states that "a sediment should contain at least 30 per cent calcium carbonate to be called a limestone". Most geologists, however, accept the definition used by Pettijohn (1949), p. 290, and Twenhofel (1950), p. 350, which defines a limestone as a sediment that is composed of 50 per cent or more of the carbonates, calcite and dolomite. If the percentage is less than 50, the rocks should be given other names with the appropriate adjectives. According to Pettijohn (1949), p. 290, the non-carbonate part of a limestone is most commonly either elastic quartz or clay and may contain minor constituents, such as chert, feldspar, glauconite, collophanite, pyrite, and bituminous matter.

J. H. Johnson (1951) and Twenhofel (1950), p. 356, have classified limestones according to the mode of origin. The general classes are: (1) organic limestones, (2) inorganic limestones, and (3) mechanical limestones. The most complete classification is that used by Pettijohn (1949), p. 294, in which he further subdivided the classes and introduced metasomatism.

- A. Autochthonous (accretionary or biochemical) limestone
 - 1. Klintite or biohermal limestone (benthonic forms dominant)
 - 2. Biostromal or coquinaid limestone (mixed pelagic and benthonic forms)
 - 3. Pelagic limestone (pelagic forms dominant)
- B. Allochthonous (clastic) limestone
 - 1. Calcirudite
 - a. Coquina
 - b. Reef breccias
 - 2. Calcarenite
 - a. Microcoquina and encrinite
 - b. Spergenite
 - c. Oolite
 - 3. Arenaceous spergenite and oolite
 - 4. Calcilutite (lithographic stone and marlstone or marlite)
- C. Chemical limestone
 - 1. Travertine and tufa
 - 2. Caliche
- D. Metasomatic limestones and related rocks
 - 1. Dolomitic limestone, calcitic dolomite, and dolomite
 - 2. Siliceous limestone, porcellanite, and chert
 - 3. Sideritic limestone, sideritic porcellanite, siderites
 - 4. Phosphatic limestone, phosphorite

Twenhofel (1950), p. 355, states that limestones "may be deposited in seas, lakes, rivers, and on the lands. The most common area of deposition is on the bottom of the sea, mostly at depths of less than a few hundred meters, but deposits are made to at least 5,000 meters". He states further that "temperature, circulation, and the entrance of argillaceous, arenaceous, and ferruginous materials from the lands are factors that affect the deposition of calcitic sediments".

The following techniques have been used in the study of limestones according to LeRoy (1950), p. 77: "thin section analysis, polished surface, insoluble residue, chemical stain test, spectrochemical, porosity and permeability, relative solubility,

petrofabric and chemical analysis". Recently, Ives (1955) experimented with acid etching of limestones belonging to the Pennsylvanian System of Kansas.

Chert. Much confusion exists in recent literature concerning the exact meaning of the terms "chert" and "flint" and the differences between them. Tarr (1938) and Milner (1952), p. 401, appear to agree on the term "chert". They consider chert to be a compact cryptocrystalline rock comprised of chalcedony and microcrystalline quartz and having a splintery to conchoidal fracture with colors ranging from white to black.

The theories of the origin of chert are even more controversial. Bramlette (1946), pp. 41-42, has proposed the following "tentative genetic grouping of the various theories regarding the source of silica in siliceous formations":

- I. Inorganic source of silica
 - A. Deposition of sediment unusually high in clastic silica
 - B. Inorganic precipitation from siliceous waters
 1. Syngenetic
 - a. Siliceous emanations from volcanic rocks
 - b. Silica in solutions and as colloids introduced by streams
 2. Epigenetic
 - a. Secondary introduction of silica by ground or surface waters
 - C. Chemical alteration and redistribution of silica of tuffaceous sediments
 1. Syngenetic
 - a. Halmyrolysis or "submarine weathering"
 2. Epigenetic
 - a. During compaction and lithification or later
- II. Organic source of silica
 - A. Organic precipitation and accumulation of siliceous organisms

- B. Chemical alteration and redistribution of silica of organisms
 - 1. Syngenetic
 - a. Halmyrolysis or "submarine weathering"
 - 2. Epigenetic
 - a. Diagenetic alteration during compaction and lithification
 - b. Metamorphic alteration during deformation and igneous intrusion
 - c. Alteration by ground or surface waters

More recently Pettijohn (1949), p. 329, has outlined the following "stages of silica deposition and sources of silica in sedimentary deposits".

- I. Syngenetic silica
 - 1. Clastic quartz
 - 2. Chemical silica
 - a. Biochemical precipitate
 - b. Chemical precipitate
 - c. Magmatic precipitate
- II. Penecontemporaneous silica
- III. Epigenetic silica
 - 1. Precipitation in zone of cementation
 - 2. Precipitation in zone of weathering

Tarr (1917) was one of the first writers to develop the theory about the primary, or syngenetic, origin of silica. He believed that colloidal silica carried by streams was precipitated in sea water by electrolytes. He based his theory on experimental laboratory evidence in which a silica gel was formed when silica was added to a solution which had very nearly the same salinity as sea water. In his experiments silica was precipitated by the salts of sodium, potassium, calcium, and magnesium. He believed that calcium bicarbonate was capable of precipitating silica from sea water. The spherical silica gels grew by accretion of colloidal particles transported by water currents,

he believed, and were dehydrated by compaction, forming the nodular chert bodies found in many limestones.

Trefethen (1947) explained the unusual shapes encountered in the cherts of the Burlington limestone "as the result of deformation under load, beginning when the cherts were plastic masses of silica gel and continuing after the cherts had become rigid". In the chert lenses he found "V"-shaped cracks filled with limestone. This limestone filling was identical with the limestone which enclosed the chert lenses.

Folk (1949) in studying the lower Ordovician cherts in Pennsylvania found that the clastic limestone structures were preserved in the chert nodules, which indicated that the cherts originated by replacement. The color of the chert was identical with that of the enclosing limestone. All gross structural features of the limestone, such as conglomeritic, fossiliferous, and oolitic bands, were perfectly preserved by the chert. "Cracks in the chert nodules, filled by then unconsolidated limestone ooze from above, prove that replacement was early..."

Twenhofel (1919) believed that the chert of the Wreford and Foraker limestones along the state line of Kansas and Oklahoma resulted "from replacement of unconsolidated limestone, the silica being derived from silica in solution which was mingled with the sediments, from silica in solution in the sea water, and from solution of organic or other silica, or silicates deposited in some form with the sediments".

The replacement theory of chert nodules was strongly supported by Van Tuyl (1918), and he listed the following features as evidence:

1. Occurrence of chert along fissures in limestone
2. Very irregular shape of some chert nodules
3. Presence of irregular patches of limestone in some chert masses
4. Association of silicified fossils and chert in some limestones
5. Presence of replaced fossils in some cherts
6. Preservation of structures and textures in some cherts
7. Failure of some cherts to follow definite zones in limestone formations
8. Occurrence of silicified oolites formed by the replacement of calcareous ones.

Bastin (1933) further substantiated the replacement theory by the observation that some chert nodules have a stylolitic contact with adjacent limestones.

The opinion of contemporary writers seems to favor the replacement theory for explaining the origin of chert nodules, but the bedded cherts present a different problem.

In studying the origin of the Rex chert Keller (1941) specified that the silica is of primary origin with considerable diagenetic replacement of carbonates. He concluded that the tremendous thickness of the chert could not be explained by epigenesis. The silica was derived from the weathering of the lands and, possibly, from a magma.

Rubey (1929) interpreted the siliceous Mowry shale as being due to silica which re-enforced a normal marine shale. This silica was derived from unusually siliceous volcanic ash that was decomposed by long exposure to sea water; the silica which

dissolved from the ash was precipitated by decaying organic matter.

Bramlette (1946) has given evidence that the Monterey cherts of California have resulted from the alteration of diatomite deposits. Volcanic ash supplied to the sea water an abundance of silica, which was extracted by diatoms and radiolarians.

The diagenetic origin of chert lenses in the limestone at Soyatal, Mexico, was proposed by White (1947). Light colored chert lenses contained dark streaks and bands that correlated with the bedding of the adjacent limestones.

Newell, et al. (1953), p. 163, after studying the Permian Reef Complex declared:

It is clear that both the chert and the calcareous spiculites are of diagenetic and more specifically, of replacement origin.... There are various potential sources of silica, all of which were given serious consideration. Discovery that the siliceous spicules are extensively replaced by calcite shows that vast quantities of silica passed into connate waters from this source alone. Possibly subordinate amounts of silica were derived from other sources: (1) from silica dissolved in sea water, (2) from devitrification of volcanic ash, and (3) from quartz sand, which forms a large proportion of the basin rocks.

Finally, Markley (1953) and Hartig (1954) concluded that the cherts of the Three-mile, Schroyer, and Florence limestones near Manhattan, Kansas, resulted largely from contemporaneous deposition of volcanic ash and lime and the alteration of part of the ash. Hartig also believed that volcanic ash falling in a muddy environment would produce montmorillonite, and that ash falling on a limey bottom would produce chert.

In conclusion, Pettijohn (1949), p. 332, says "it may be

said that the chert problem is unsolved as yet. Neither the question of primary versus secondary origin nor the source of the silica is certainly known". Probably cherts are formed under a variety of conditions.

Insoluble Residues. The term "insoluble residue" as used in this study may be defined as the material remaining after fragments of limestone have been dissolved in chemically pure hydrochloric acid. The residue was composed of quartz, chalcedony, opal, volcanic ash, feldspars, micas, clay, tourmaline, garnet, zircon, celestite, pyrite, ilmenite, and staurolite.

The necessity of making more exact mineralogical studies of calcareous well-cuttings for use as an aid in subsurface correlation resulted in the development of insoluble residue techniques.

Claypool and Howard (1928), pp. 1147-1152, classified calcareous well-cuttings according to the calcite, dolomite, and magnesite content. The sample was ground so as to pass through an 80-mesh sieve and was separated into light, medium, and heavy fractions by centrifuging in heavy solutions. The fractions were treated with hydrochloric and nitric acid, and calcite was dissolved from the light fraction, dolomite from the medium, and magnesite from the heavy fraction. The volume of shale and sand was measured after removal of calcite from the light fraction.

Mc Queen (1931), pp. 102-131, published methods of preparation, terminology, and application of insoluble residues to

correlation of calcareous rocks. He treated calcareous well-cuttings with dilute hydrochloric acid, which removed the carbonates, and he decanted the fine residue, and examined the coarse residue with a binocular microscope to determine any diagnostic characteristics. A technique basically the same has been used with excellent results by the United States Geological Survey and several state surveys.

Schoewe, et al. (1937), pp. 269-281, made a preliminary study of insoluble residues of some of the lower Pennsylvanian limestones in Kansas and found that the insoluble residues are diagnostic not only of formations, but also of members within the formations. They stated that this technique had more than a local application.

Hiestand (1938), pp. 1588-1599, compared the insoluble residues of the "Mississippi lime" of central Kansas with the Boone limestone of Missouri and found that members within the two formations correlated excellently.

Because of a diversity in nomenclature used by workers in Texas and by Mc Queen, Ireland (1947), pp. 1479-1490, arranged a conference in Midland, Texas, for the purpose of standardizing the terminology used in the study of insoluble residues. The terminology adopted by this conference closely follows that used by the Missouri Geological Survey which was proposed by Mc Queen in his earlier reports.

Most of the correlation work in insoluble residues has been done with the aid of a binocular microscope. The petrographic

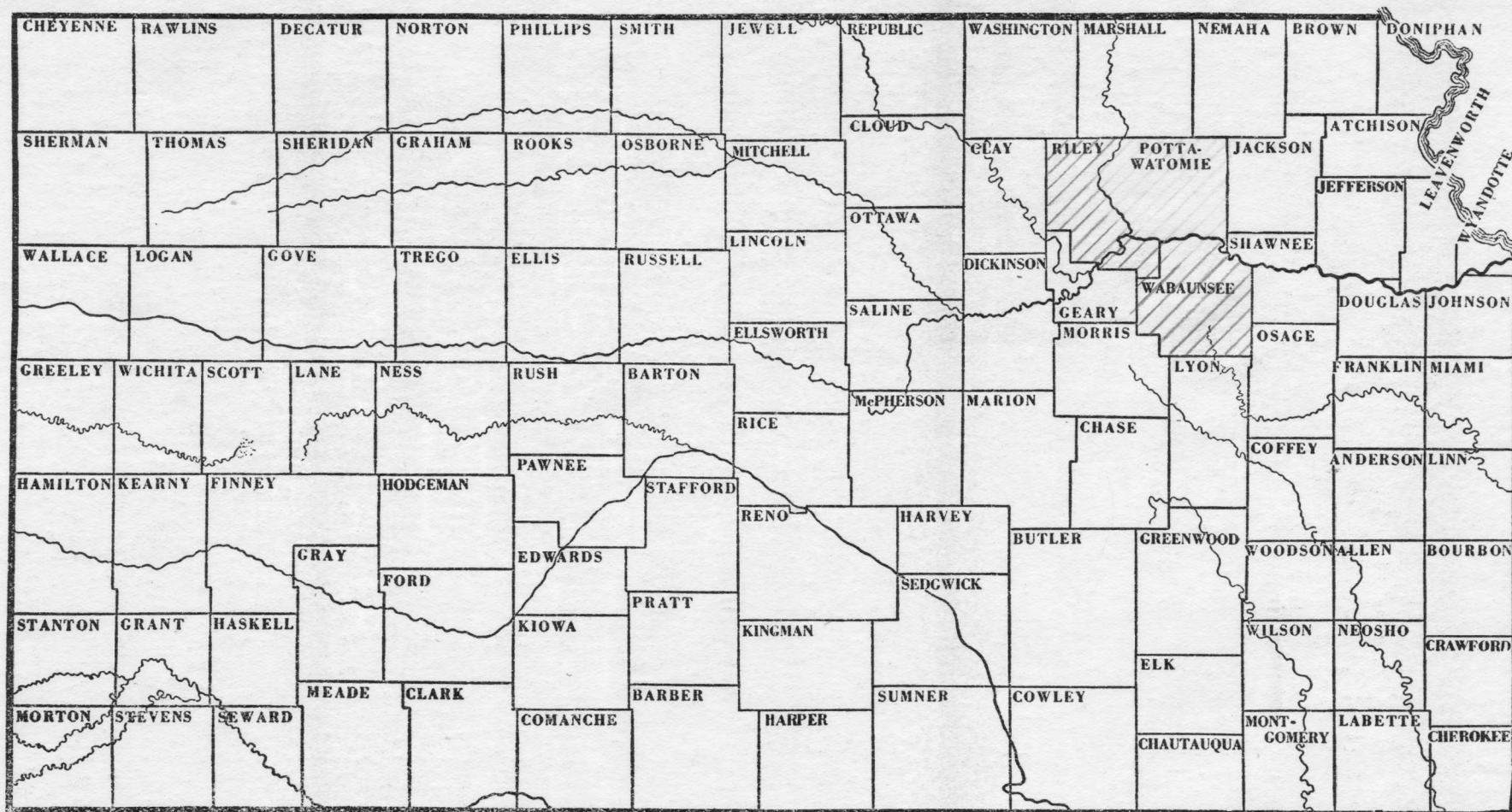
microscope has been used in this study and the author believes that the additional time required for this procedure is in many cases worthwhile. Not only can the optical properties be used for an exact identification of the minerals, but a more accurate mineral frequency can be obtained and valuable information about the environments and origin of the formations can be gained.

Area of Investigation and Stratigraphic Units Sampled

Limestones which compose the lower Permian and upper Pennsylvanian Systems in Riley, Pottawatomie, and Wabaunsee counties in Kansas were sampled, and the non-carbonate mineralogy determined. (Fig. 1). These limestones were located stratigraphically between the Hamlin shale of the Admire group (Wolfcampian Series of the Permian System) and the Pierson Point shale of the Richardson subgroup (Wabaunsee group, Virgilian Series of the Pennsylvanian System). The Permian limestones examined from youngest to oldest are: the Five Point, Falls City, and Aspinwall. The Pennsylvanian limestones examined are, from youngest to oldest: the Brownville, Caneyville (Grayhorse and Nebraska City members), Jim Creek, Grandhaven, Dover, and Maple Hill (Fig. 2). From three to five samples were taken from each stratigraphic unit.

Investigation Procedure

Field Procedure. Because the average characteristics of the formations were to be determined in this investigation,




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Fig. 1. Index map of Kansas showing area of investigation.

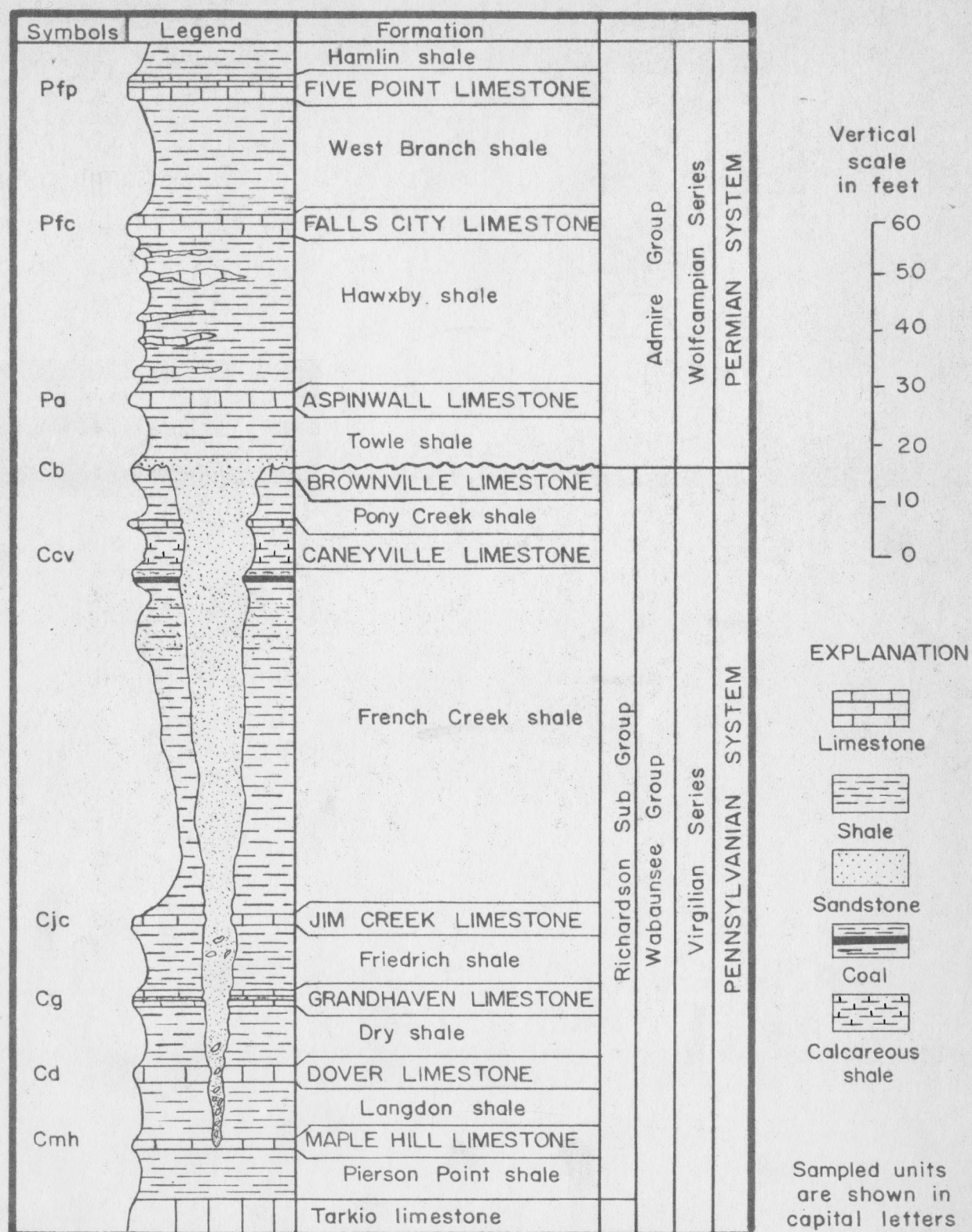
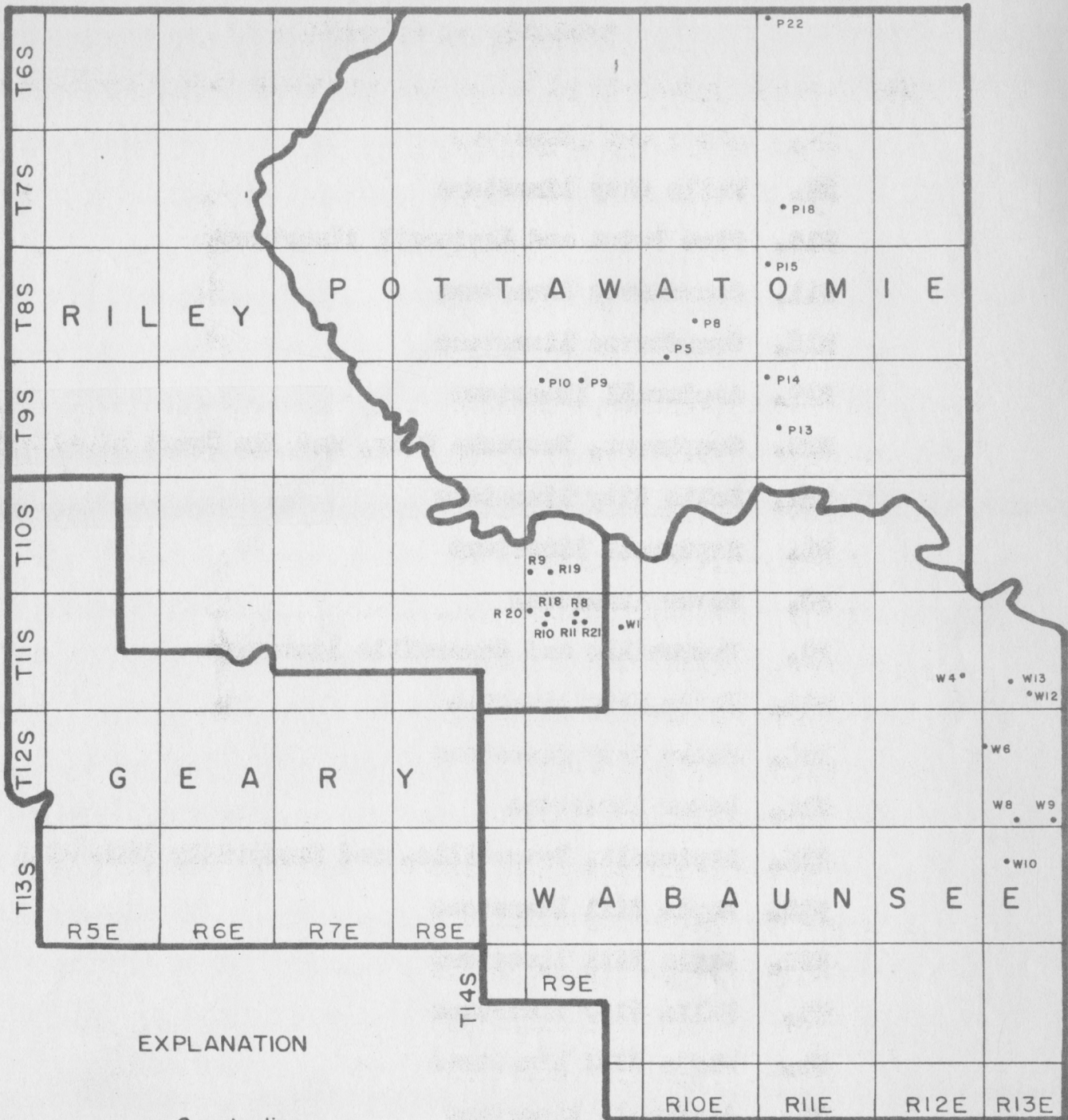


Fig. 2. Generalized stratigraphic section

EXPLANATION OF PLATE I

Map showing locations of limestone outcrops used in this thesis.

- R8. Jim Creek limestone
- R9. Falls City limestone
- R10. Five Point and Aspinwall limestones
- R11. Grandhaven limestone
- R18. Grandhaven limestone
- R19. Aspinwall limestone
- R20. Grayhorse, Nebraska City, and Jim Creek limestone
- R21. Falls City limestone
- P5. Aspinwall limestone
- P8. Dover limestone
- P9. Brownville and Caneyville limestone
- P10. Falls City limestone
- P13. Falls City limestone
- P14. Dover limestone
- P15. Aspinwall, Brownville, and Caneyville limestone
- P18. Maple Hill limestone
- P22. Maple Hill limestone
- W1. Falls City limestone
- W4. Maple Hill limestone
- W6. Aspinwall limestone
- W8. Brownville and Jim Creek limestone
- W9. Grandhaven limestone
- W10. Brownville and Caneyville limestone
- W12. Dover limestone
- W13. Brownville, Grayhorse, and Nebraska City limestones



"channel" samples were collected from limestones cropping out in roadcuts, streamcuts, and ditches. Krumbein and Pettijohn (1938) define a "channel" sample as an elongated sample taken from a relatively narrow zone of an outcrop. This sample is taken normal to the bedding plane of the formation. Since the rock units encountered appeared homogeneous throughout, this type of sample should be representative of the formation.

The vertical face of the outcrop normal to the bedding plane was cleared of all weathered and extraneous material for a width of about one foot, extending from top to bottom of the formation. A shallow indentation was made at the base of the formation and a large cloth placed under the sampling area. By use of a geologic pick and a chisel rock chips were broken from the cleared face of the outcrop and collected on the cloth below.

The sample was placed in a paper bag which contained a slip of paper indicating the sample number and the geographic location. This information was also noted on the outside of the paper bag in pencil and the sample number, geographic location, and lithology of the stratigraphic unit were recorded in a field notebook.

If the formation was composed entirely of limestone, a "channel" sample of entire rock unit was obtained. If the limestone had a shale "break", "channel" samples were taken from each unit with the exception of the intervening shale. The samples were either combined to form a composite sample of the limestone, or each was treated as an individual sample in order to

study the differences between the upper and lower members of the limestone. The amount of each sample varied in direct proportion to the thickness of the formation. In all cases the sample was large enough to permit repetition of laboratory processing in the event of accident or in case the results needed further verification.

The major field problems included the inability to collect samples according to a statistical grid because of the absence of outcrops; and the difficulty in finding complete exposures of the various formations. For this reason many more samples were collected than were actually used in the course of this investigation.

Sample-number Symbols. The symbols listed below are used to indicate the system, geologic formation, county, and outcrop number within a county for all samples collected during this investigation.

<u>Symbol</u>	<u>Definition</u>
P	Permian System
C	Pennsylvanian System
fp	Five Point limestone
fc	Falls City limestone
a	Aspinwall limestone
b	Brownville limestone
cv	Caneyville limestone
cvg	Grayhorse limestone member
cvn	Nebraska City limestone member
g	Grandhaven limestone

<u>Symbol</u>	<u>Definition</u>
d	Dover limestone
mh	Maple Hill Limestone
R	Riley County, Kansas
P	Pottawatomie County, Kansas
W	Wabaunsee County, Kansas

Arabic numerals from 1 to 25 were assigned in a chronological sequence to outcrops as they were sampled within a county.

Laboratory Procedure. In the laboratory the samples were oven dried and then passed through a rock crusher. The size of the individual fragments was reduced to increase the surface area of the sample, thereby increasing the rate of chemical reaction. The samples were then quartered and treated with chemically pure hydrochloric acid to remove all carbonates.

It was found that from 200 to 400 grams of limestone sample produced an adequate quantity of heavy minerals after digestion with hydrochloric acid. The sample was placed in a one-quart mason jar and de-ionized water was added so that the sample was barely covered. The jar containing sample was placed on a metal tray under a hood, and chemically pure hydrochloric acid was added gradually until all the carbonates had been digested. The acid was added gradually to prevent the sample from spewing over the sides of the container and losing some of the residue. De-ionized water was used throughout the procedure so that the structure and composition of the clay minerals would not be changed except as altered by the acid.

After effervescence ceased the jar was filled with de-ionized water, and the sample was allowed to stand until all the residue had settled to the bottom. The upper three-fourths of the liquid was siphoned off and more de-ionized water added to the jar. This washing was repeated (at least five times) until the unused acid and the calcium chloride formed had been removed from the residue. It was found that 10 samples could be processed simultaneously.

The residue was then washed into a U. S. #230 sieve and the sample was divided into a coarse and a fine residue. The coarse fraction was retained on the sieve, the particle size being greater than 62 microns. All material less than 62 microns that passed through the screen was called the fine residue and was caught in a large pyrex bowl. The coarse and fine fractions were oven-dried and the approximate weight of both was determined and recorded.

Coarse Residue. The coarse residue was placed in a 250 milliliter pyrex beaker and boiled in a 50 per cent solution of hydrochloric acid for 30 minutes to remove all iron stains and coatings. If any organic carbon was likely to be present, the sample was treated with a 15 per cent solution of hydrogen peroxide.

There has been some criticism in literature about the use of hydrochloric acid in removing carbonates. Not only does it dissolve the carbonates but Twenhoffel and Tyler (1941), p. 121, state that hot concentrated hydrochloric acid also dissolves apatite, anhydrite, hematite, limonite, magnetite, pyrrhotite,

and orthosilicates. Reed (1924), however, says:

In spite of published assertions to the effect that this treatment destroys apatite, hypersthene, and other minerals of a similar degree of stability, in several experiments these minerals were not visibly affected by boiling for as much as an hour in 50 per cent acid.

At any rate, it is a good practice to check the reaction of the insoluble residue periodically, when treating it with strong acids. It is also important to realize that if a large percentage of the mineral grains are coated, the only means of identifying them is to remove these coatings. If a mineral is to be used for correlation purposes, it must be able to withstand laboratory treatment.

After all coatings had been removed, the coarse residue was washed onto a filter paper and then washed further to remove all impurities. The sample was then ready for the separation into heavy and light mineral fractions.

The author followed the technique of separation of minerals by bromoform advocated by Twenhofel and Tyler (1941), p. 78. Bromoform is an organic compound consisting of tribrom-methane and has a specific gravity of 2.72. The apparatus consisted of two conical open-type funnels with steep sides to minimize adherence of particles. Watch glasses covered the funnels to prevent evaporation of bromoform. The bottom of one funnel was fitted with a rubber tube and pinchcock.

The separatory funnel was partially filled with bromoform and the stem of the funnel placed directly over a second funnel which was equipped with filter paper for the collection of the

heavy fraction and another filter paper was then used to collect the light fraction. A bottle was provided for each sequence of funnels in order to collect the washings, which were emptied into a common receptacle.

The coarse residue was heated in an oven to remove all atmospheric moisture, which reduced the tendency of mineral grains to adhere to the side of the funnels. The residue was slowly poured into the bromoform which was stirred at first and later permitted to stand over night.

After the settling of minerals was completed, the pinch-cock on the separatory funnel was released gradually, and the heavy liquid containing the heavy minerals was allowed to enter the second funnel equipped with filter paper. The heavy minerals were retained on the filter paper, and the bromoform was caught in a receptacle below.

The filter paper was washed three or more times with ethyl alcohol (and later water) to remove all bromoform from the grains and filter paper. The filter paper was then removed and dried at 110 degrees Centigrade.

Another filter paper was placed in the lower funnel, and the light minerals floating in the bromoform collected on the paper. Then the light fraction also was washed with ethyl alcohol several times and later with water. The light mineral fraction was composed of quartz, chalcedony, opal, volcanic glass, orthoclase, microcline, plagioclase, and carbon. The heavies were minerals having a specific gravity above 2.72 and included

the micas, iron oxides, celestite, pyrite, tourmaline, garnet, zircon, staurolite, and corundum.

The heavy and light mineral fractions were mounted permanently on glass slides in Canada balsam (refractive index of 1.537). The grains to be mounted were uniformly distributed in a drop of de-ionized water on a thoroughly clean glass slide.

The glass slide was placed upon a hot plate, and the water evaporated, causing the grains to adhere to the slide. The balsam then was added to the slide and heated slowly over the hot plate until it reached the proper consistency. (Rapid heating produces numerous air bubbles, and overheating discolors the balsam and makes it brittle.) The balsam was tested by withdrawing a small drop with a dissecting needle, immersing it in water to cool, then pressing the thumbnail against it. The balsam was considered done when it was firm and showed only a slight tendency to stick to the thumbnail.

When the balsam was properly cooked the slide was placed on a cold piece of iron to promote rapid cooling. The slide was examined under a microscope to be sure that the grains were uniformly dispersed in the balsam. With a cover glass in a nearly vertical position at one of the margins of the balsam the slide was placed again on the hot plate. As the balsam became soft the cover glass sank to a horizontal position, forcing all air bubbles away from the cover glass. Excess balsam was removed with a knife. The slides were then labeled appropriately and stored for future petrographic analysis.

The mineral mounts of heavy and light fractions were examined under the petrographic microscope to determine what minerals were present, their relative abundance, and their physical properties (degree of rounding and sorting, weathering and alteration, inclusions, etc.). A mechanical stage was employed and a traverse was made in which 300 mineral grains were counted on each slide. Krumbein and Pettijohn (1938), p. 471, "recommend that for research work the entire residue or a carefully quartered portion be mounted, which will contain about 300 grains, and the mineral frequencies be determined by count". The mineral frequencies were expressed directly as percentage of the total number of grains counted. In several cases the oil immersion method was used to determine the refractive indexes of mineral grains which demanded more positive identification.

Fine Residue. The fine residue which passed through the U. S. #230 sieve was washed several times with de-ionized water to remove any trace of unused acid and soluble salts. The fine residue was then oven-dried and weighed. After the weighing 500 milliliters of de-ionized water were added, and the sample was placed in a "Waring Blender". To this sample 5 milliliters of sodium silicate were added to disperse the clay particles. The sample was agitated for five minutes or until the entire residue was completely dispersed.

The entire contents of the "Waring Blender" was washed into a sedimentation cylinder, and enough de-ionized water added to reach a 1000 milliliter level. The sample number was marked on

the sedimentation cylinder with grease pencil and the cylinder placed in a temperature bath where it remained for about six hours. When the sample had attained the temperature of the temperature bath (70 degrees Fahrenheit), it was shaken by hand for one minute to disperse the sample again. The sample was covered with a watch glass and allowed to stand for 36 hours. Then the upper 30 centimeters of suspension were siphoned into a one gallon glass container. The sedimentation cylinder was refilled to the 1000 milliliter level, was shaken by hand, replaced in the temperature bath, and allowed to settle an additional 24 hours. Again the upper 30 centimeters of suspension were siphoned into the one gallon container, and the remaining residue was discarded.

The pH of the sample was lowered to 3.5 by adding a one normal solution of hydrochloric acid in order to flocculate the colloidal suspension. The excess water was siphoned from the clay, and the remaining sample was passed through a vacuum filtration unit to remove all water. After thorough washing the sample was dried and crushed and the clay mineral determined by differential thermal analysis.

The differential thermal analysis apparatus records the temperature of exothermic and endothermic reactions that take place as the clay sample is heated at a constant rate of increase up to 1000 degrees centigrade. In all cases the clay mineral present in the samples studied was illite.

THE NON-CARBONATE MINERALOGY OF SOME PERMIAN AND PENNSYLVANIAN LIMESTONES

Order of Discussion

The limestones investigated are geologic formations of the Admire group of the Permian System and of the Richardson subgroup, Wabaunsee group of the Pennsylvanian System. The Permian limestones examined are, from youngest to oldest: the Five Point, Falls City, and Aspinwall. The Pennsylvanian limestones examined, from youngest to oldest, are: the Brownville, Caneyville (Grayhorse and Nebraska City members), Jim Creek, Grandhaven, Dover and Maple Hill.

Each limestone formation has been discussed separately in this thesis and the stratigraphic and geographical locations, lithology, and mineralogy have been included. The frequency of the mineral species (other than carbonates) for each formation has been represented by a series of frequency numbers proposed by Evans, et al. (1933), p. 254. These frequency numbers are similar to logarithms of the frequency determined by counting mineral grains. This system brings out the fact that a change in frequency from 6 to 11 per cent is more significant than is a change from 76 to 81 per cent. This system is given below:

<u>Frequency</u>	<u>Approximate Percentage</u>
8+	90-100%
8	75-89%
8-	60-74%
7+	45-59%
7	35-44%
7-	28-34%

Frequency Approximate Percentage

6+	23-27%
6	18-22%
6-	13-16%
5	7-14%
4	4-6%
3	2-3%
2	1-2%
1	$\frac{1}{2}$ -1%
1*	1 grain only

This system has been applied to the light and heavy mineral fractions of each sample. A discussion of the physical and optical properties of the minerals has been given, if these were significant.

Finally, the environmental conditions in which illite, silica, pyrite, celestite, and carbon were formed are discussed under "Authigenic and Biogenic Substances Found in These Limestones".

Permian System

Five Point Limestone. The Five Point limestone is the youngest limestone in the Admire group. It underlies the Hamlin shale and overlies the West Branch shale.

Sample Location

Sample number	Type of outcrop	Geographic Location
PfpR10	Road ditch	NW $\frac{1}{4}$ NE $\frac{1}{4}$ sec. 9, T. 11 S., R. 9 E., Riley County
PfpP13	Road ditch	SE $\frac{1}{4}$ SW $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 20, T. 9 S., R. 11 E., Pottawatomie County
PfpW1	Road cut	SW $\frac{1}{4}$ SW $\frac{1}{4}$ SW $\frac{1}{4}$ sec. 12, T. 11 S., R. 9 E., Wabaunsee County

Lithologic Description. The upper part of the Five Point limestone is platy and argillaceous, and the lower part is hard, massive, and fossiliferous. The limestone is gray and usually weathers tan-gray. The lower massive part forms a prominent hillside bench. The average thickness of the Five Point is about three feet. (This and other lithologic descriptions of the limestones used in this investigation have been adapted from Moore (1949), Moore et al. (1951), Mudge (1949), and Drake (1951)).

Mineralogy

Mineral	PfpR10	PfpP13	PfpW1
Light Fraction			
Quartz	6+	8+	5+
Chalcedony	7	3	8-
Opal	7-		6
Volcanic ash	1		1
Orthoclase	1	4	1
Microcline		1*	
Oligoclase	1*		
Heavy Fraction			
Muscovite	8	7+	8
Biotite		1	
Chlorite		4	
Ilmenite	1	1	1
Leucoxene	5	6	5
Limonite		5	
Pyrite			5
Tourmaline	3	5	2
Garnet	1	5	1
Zircon	1*	1*	2
Staurolite		1*	
Corundum	2		

The total weight percentage of the residue ranges from 1.8 to 9.9 of the total weight of the sample. The coarse residue ranges from 0.4 per cent to 2.8 per cent and the fine from 0.8 to 9.5 per cent of the limestone sample. The color of the residue was yellow-brown, except for PfpW1 which was medium gray.

The light mineral fractions were composed chiefly of quartz, chalcedony, and opal. A few grains of volcanic ash, orthoclase, microcline, and oligoclase completed the mineral frequencies of the Five Point. Quartz, orthoclase, microcline, and oligoclase grains were subrounded and contained no inclusions. In two samples were found small quantities of volcanic ash which were subangular, and contained no inclusions. The authigenic minerals were chalcedony and opal. Both minerals show evidence of an organic origin. Probably some of the opal had crystallized to chalcedony (Tarr, 1926). No evidence of secondary growth of the quartz and feldspar was found. A higher percentage of quartz was present in PfpF13 possibly because the sample contained a greater quantity of silt.

Muscovite was the predominate mineral in the heavy fractions, and biotite, chlorite, ilmenite, leucoxene, limonite, pyrite, tourmaline, garnet, zircon, staurolite, and corundum were minor constituents. Again a high silt content in PfpF13 was emphasized by a higher frequency of biotite, chlorite, leucoxene, limonite, tourmaline, garnet, and staurolite. The greater quantity of these minerals reduced the percentage of muscovite in the one sample. Pyrite was the only authigenic mineral in the heavies and was euhedral. The tourmaline was brown, and euhedral to subhedral; the garnet was pink to colorless, and angular; and the zircon was colorless, very small, and anhedral. The detrital silt in all the samples showed the results of prolonged transportation.

The differential thermal analysis of the fine fractions

showed illite and carbon. Although two of the samples were yellow-brown, the analyses revealed a high carbon content.

Falls City Limestone. The Falls City limestone underlies the West Branch shale and overlies the Hawxby shale.

Sample Location

Sample number	Type of outcrop	Geographic Location
PfcR10	Road ditch	NW $\frac{1}{4}$ SW $\frac{1}{4}$ sec. 8, T. 11 S., R. 9 E., Riley County
PfcR21	Road ditch	SE $\frac{1}{4}$ SE $\frac{1}{4}$ NE $\frac{1}{4}$ sec. 9, T. 11 S., R. 9 E., Riley County
PfcP10	Stream bank	SW $\frac{1}{4}$ NW $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 8, T. 9 S., R. 9 E., Pottawatomie County

Lithologic Description. The Falls City limestone is soft, porous, has a fibrous texture, and is fossiliferous. It is gray-brown and weathers tan. Limestone beds are argillaceous and commonly are molluscan with some bryozoans and brachiopods. It contains thin chalc partings and a platy zone near the base. The average thickness of the Falls City is about 2.5 feet. The formation forms a small and barely discernible hillside ridge.

Mineralogy

Mineral	PfcR10	PfcR21	PfcP10
Light Fraction			
Quartz	8-	5	5
Chalcedony	6	8	8
Opal		3	4
Volcanic ash			
Orthoclase	5	3	1
Microcline	1*	1*	
Oligoclase		1*	

Mineral	PfcR10	PfcR21	PfcP10
Heavy fraction			
Muscovite	8+	1	8
Chlorite	1	1*	
Ilmenite	1*		
Leucoxene	4	1	4
Pyrite			4
Celestite		8+	
Tourmaline	3		3
Garnet			3
Zircon	1		3
Corundum			2

Among all the limestones included in this study the insoluble residue of the Falls City showed the greatest range in weight percentage (from 0.9 to 24.0 of the total weight of the limestone sample). The coarse residue ranged from 0.2 to 3.9 per cent and the fine residue from 0.7 to 20.1 per cent of the total weight of the sample. The color of the residue was gray to blue-gray.

The light mineral fraction was dominated by quartz and chalcedony and minor percentages of opal, orthoclase, and traces of microcline and oligoclase. The quartz was detrital, and in PfcR9 it completely "masked" the chalcedony. The chalcedony in all samples appeared to have formed from the crystallization of organic opal. Many grains of chalcedony were silicified tests of ostracods and foraminifera and were diagnostic of the Falls City limestone. The quartz, orthoclase, microcline, and oligoclase were allogenic, subrounded, contained no inclusions, and showed no secondary growth.

Detrital muscovite was the leading mineral in the heavy fraction, except in PfcR21 where authigenic celestite comprised

97 per cent of the sample. The optical properties of the celestite were: biaxial positive, length slow, low birefringence, cleavage in two directions at right angles, alpha index - 1.622, beta index - 1.624, gamma index - 1.631, and mineral grains badly altered or coated with clay. Minor quantities of ilmenite, leucoxene, pyrite, tourmaline, garnet, zircon, and staurolite were also found. The pyrite in PfcP10 was authigenic and euhedral to angular.

The fine residue was composed of illite and carbon.

Aspinwall Limestone. The Aspinwall limestone underlies the Hawxby shale and overlies the Towle shale. The Aspinwall is the oldest limestone in the Admire group and the Permian System.

Sample Locations

Sample number	Type of outcrop	Geographic location
PaR10	Road ditch	NW $\frac{1}{4}$ SW $\frac{1}{4}$ sec. 8, T. 11 S., R. 9 E., Riley County
PaR19	Stream bank	NW $\frac{1}{4}$ NE $\frac{1}{4}$ sec. 31, T. 10 S., R. 9 E., Riley County
PaP5	Road ditch	SW $\frac{1}{4}$ SW $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 32, T. 8 S., R. 10 E., Pottawatomie County
PaP15	Road ditch	SW $\frac{1}{4}$ SE $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 6, T. 8 S., R. 11 E., Pottawatomie County
PaW6	Road ditch	NE $\frac{1}{4}$ SE $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 12, T. 12 S., R. 12 E., Wabaunsee County

Lithologic Description. The Aspinwall limestone is hard, massive, and fossiliferous. It is yellow-brown and weathers yellow-gray. Limonite stains, nodules, clay zones, and clay balls are distributed throughout the limestone. The average thickness of the Aspinwall is about two feet; it forms a small

hillside bench.

Mineralogy. The total weight percentage of the insoluble residue ranged from 3.0 to 29.4 of the total weight of the sample. The coarse residue ranged from 0.4 to 17.1 per cent, and the fine from 2.6 to 16.1 per cent of the total weight of the sample. The variance in lithology of the Aspinwall can be seen in the field and explains the difference in weight percentage among the five samples. The color of the residue was yellow-brown.

Mineralogy

Mineral	PaR10	PaR19	PaP5	PaP15	PaW6
Light Fraction					
Quartz	8	7+	8	8	8
Chalcedony	5	7	5	4	4
Volcanic ash	1*				
Orthoclase	5	3	4	6-	5
Microcline	1		1	2	1
Oligoclase			1*		
Coated grains	1	1	1	1*	
Heavy Fraction					
Muscovite	8-	7+	8-	7+	8
Biotite	3	4	3	3	5
Chlorite	1		1		
Ilmenite	1*	1*	1*	1*	1*
Leucoxene	5	6	6-	6+	5
Magnetite		1*	1*		
Hematite		1*	1		1*
Limonite	5	5	5	4	1*
Pyrite		1*			
Tourmaline	4	4	4	3	2
Garnet	4	3	3	4	1*
Zircon	1*	1*	3	3	1*
Staurolite		1*		1*	

The most significant feature of the Aspinwall was the high percentage of quartz sand in the residues. The limestone contained more impurities than did any other formation investigated.

Although the weight percentage of the insoluble residue varied considerably, the mineral frequency remained almost constant. Quartz was the dominant light mineral. Chalcedony, orthoclase, microcline, oligoclase, and volcanic ash completed the mineral assemblage of the light fraction. Authigenic chalcedony in the form of silicified ostracods was found in all samples. The concentration of chalcedony was higher in PaR19 because of this sample's lack of silt. Even though all samples were boiled in concentrated hydrochloric acid for 30 minutes, the mineral grains displayed an abundance of limonite-coated grains. The grains of the silt fraction were subrounded, and the feldspars were partially altered. One grain of isotropic volcanic ash which contained no inclusions was discovered in PaR10.

The five samples of the heavy fraction were remarkably similar. The relatively higher percentages of muscovite, biotite, leucoxene, limonite, tourmaline, garnet, and zircon were indicative of the Aspinwall. Muscovite in all cases comprised over half of each sample. Most of the grains were equidimensional, but some showed a high degree of rounding. A relatively high percentage of leucoxene and limonite suggests that an abundance of ilmenite was present in the source area. Tourmaline, garnet, and zircon were abundant in the Aspinwall, and they showed evidence of transportation. A trace of authigenic euhedral pyrite was found in PaR19.

The clay mineral in the fine fraction was illite; no carbon was found.

Pennsylvanian System

Brownville Limestone. The Brownville is the youngest limestone in the Richardson subgroup and the Wabaunsee group of the Pennsylvanian System in Kansas. It underlies the Towle shale of Permian Age and overlies the Pony Creek shale of the Pennsylvanian.

Sample Locations

Sample number	Type of outcrop	Geographic location
CbP9	Stream bank	SW $\frac{1}{4}$ NE $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 4, T. 9 S., R. 9 E., Pottawatomie County
CbP15	Road ditch	SW $\frac{1}{4}$ SE $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 6, T. 8 S., R. 11 E., Pottawatomie County
CbW8	Road cut	NE $\frac{1}{4}$ NE $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 32, T. 12 S., R. 13 E., Wabaunsee County
CbW10	Road ditch	W $\frac{1}{2}$ NW $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 8, T. 13 S., R. 13 E., Wabaunsee County
CbW13	Stream bank	Center of sec. 29, T. 11 S., R. 13 E., Wabaunsee County

Lithologic Description. The Brownville limestone is medium hard and slightly argillaceous. It is tan to brown and weathers light gray. This limestone is blocky and weathers to nodules. Crinoid columnals, Chonetes and Marginifera are found in abundance. The average thickness of the Brownville is about two feet.

Mineralogy

Mineral	CbP9	CbP15	CbW8	CbW10	CbW13
Light Fraction					
Quartz	2	1	1	1*	3
Chalcedony	8+	8	8	8+	4
Opal	4	5	5	4	8+
Volcanic ash	1*	1*	1	1	1*
Orthoclase	1*		1*	1*	
Carbon					1*

Mineral	CbP9	CbP15	CbW8	CbW10	CbW13
Heavy Fraction					
Muscovite	8	6	8+	4	7+
Biotite			1*		1
Chlorite			1*		1
Ilmenite	1*				5
Leucoxene	5	4	3		5
Magnetite	1*				
Limonite	1				4
Pyrite		4	1	8+	
Celestite	1*	8-	1*	1*	6
Tourmaline	3	1*	1*	1*	2
Garnet	2	1*	1		3
Zircon	2		1		2

The total weight percentage of the Brownville ranged from 10.98 to 21.5 of the total weight of the sample. The coarse fraction ranged from 0.08 to 1.17 per cent and the fine from 10.9 to 21.4 per cent of the total weight of the sample. The color of the residue varied from yellow-brown to tan.

The light mineral fraction was characterized by a high concentration of chalcedony and opal, and by a very low percentage of quartz. Sponge spicules, originally opal, have crystallized to chalcedony, and many foraminifera have been replaced by silica. Traces of volcanic ash in all samples suggested that some of the silica used by these organisms may have been derived from the ash dissolving in sea water. A few grains of quartz in CbP9 were subhedral and may have formed from chalcedony. Quartz and orthoclase were allogenic and were scarce in the Brownville.

Muscovite was common in the heavy fraction, but its percentage was reduced by the occurrence of authigenic pyrite and celestite in three samples. The percentage of muscovite was highest where celestite and pyrite were absent, or nearly so. Authigenic

minerals in the heavies were indicated by the weight percentage of the coarse residue. Authigenic euhedral pyrite in CbW10 made up 96 per cent of the heavy fraction; the highest percentage of chalcedony was found in the light fraction of this sample.

Tourmaline, garnet, and zircon were found in small amounts, their percentages inversely related to the percentages of pyrite and celestite. Other minor constituents were biotite, chlorite, ilmenite, leucoxene, magnetite, and limonite. In CbW13 ilmenite and leucoxene comprised 18 per cent of the "heavies".

A differential thermal analysis revealed illite in the fine residue. No carbon was found except possibly in CbW13.

Caneyville Limestone. The Caneyville limestone underlies the Pony Creek shale and overlies the French Creek shale.

Sample Locations

Sample number	Type of outcrop	Geographic location
CcvP9	Stream bank	SW $\frac{1}{4}$ NE $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 4, T. 19 S., R. 9 E., Pottawatomie County
CcvP15	Road ditch	SW $\frac{1}{4}$ SE $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 6, T. 8 S., R. 11 E., Pottawatomie County
CcvW10	Road ditch	W $\frac{1}{2}$ NW $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 8, T. 13 S., R. 13 E., Wabaunsee County
CcvGR20) CcvNR20)	Stream bank	SE $\frac{1}{4}$ SW $\frac{1}{4}$ sec. 6, T. 11 S., R. 9 E., Riley County
CcvGW13) CcvNW13)	Stream bank	Center of sec. 29, T. 11 S., R. 13 E., Wabaunsee County

Lithologic Description. The Caneyville limestone consists of an upper limestone (Grayhorse member) and a lower limestone (Nebraska City member) separated by a shale. The Grayhorse limestone is hard, tan to brown, and weathers tan-gray. It is massive

and weathers blocky. Limonite nodules, stains, and fossil fragments are abundant. A few clay balls are found. Its average thickness is two feet. The intervening shale is thin-bedded, calcareous, and gray. The Nebraska City member is hard, platy, and argillaceous. It is dark gray, weathers tan-gray, and has an average thickness of about one foot. The total thickness of the Caneyville limestone is about 9.5 feet.

Mineralogy. Three composite samples of the Caneyville were taken and discussed together. Two samples each of the Grayhorse and Nebraska City members were taken so that each member could be analyzed separately.

Composite Samples of Caneyville

Mineral	CcvP9	CcvP15	CcvW10
Light Fraction			
Quartz	5	7	6
Chalcedony	7	7-	7
Opal		3	7
Volcanic ash		3	
Orthoclase		4	3
Microcline		1*	
Oligoclase		1*	
Carbon	7+	6	
Heavy Fraction			
Muscovite	1*	8+	7
Biotite		2	1*
Chlorite		2	6-
Ilmenite			2
Leucoxene		2	6
Limonite			6-
Pyrite	2	4	
Celestite	8+		
Tourmaline		1*	5
Garnet		4	2
Zircon		1*	2
Staurolite			1*

The total weight percentage of the Caneyville residue ranged from 3.93 to 14.18 of the total weight of the sample. The coarse

residue ranged from 0.17 to 7.68 per cent and the fine from 3.6 to 10.4 per cent of the total composition of the sample. The color varied from tan-gray to dark gray and was indicative of the high carbon content in the limestone.

The light mineral fraction was composed chiefly of quartz, chalcedony, opal, and carbon. Minor percentages of volcanic ash, orthoclase, microcline, and oligoclase completed the mineral assemblage. The quartz and feldspars were detrital, sub-rounded, and contained no inclusions. The volcanic ash was sub-angular, and showed no evidence of devitrification. The chalcedony, opal, and carbon were authigenic and were of organic origin.

The mineral percentages of the heavy fraction varied considerably. Muscovite appeared dominant in two samples, but was "masked" by celestite in the third sample (CcvP9). The micas, tourmaline, garnet, zircon, and staurolite were allogenic and were euhedral to anhedral. Ilmenite, leucoxene, and limonite comprised 33 per cent of the "heavies" in CcvW10. Celestite made up 99 per cent of the "heavies" in CcvP9. This mineral is authigenic and has certain geochemical relationships that have been discussed on page 59. Small amounts of authigenic pyrite were found which were euhedral to subhedral.

A differential thermal analysis of the fine residue revealed illite and a high concentration of carbon.

The samples of the Grayhorse and Nebraska City limestone members of the Caneyville at R20 showed almost equal weight percentages of coarse residue (26.71 per cent for the Grayhorse and

26.67 per cent for the Nebraska City). However, the amount of coarse and fine residue varied a great deal. The percentage of coarse residue in CcvgR20 was 15.81 per cent; in CcvnR20 the amount was 0.97 per cent. The fine residue of CcvgR20 was 10.9 and 25.7 per cent of CcvnR20. The variance of weight percentage of the two members at location W13 was greater. The percentage of residue of CcvgW13 was 6.35 and 9.55 in CcvnW13. The coarse and fine residue in CcvgW13 was 0.95 and 5.4 per cent respectively, and the coarse and fine residue in CcvnW13 was 2.35 and 7.2 per cent. The color of the Grayhorse residue was light gray, and the color of the Nebraska City was medium to dark gray.

Samples of Grayhorse and Nebraska City Members

	Grayhorse		Nebraska City	
	CcvgR20	CcvgW13	CcvnR20	CcvnW13
Mineral				
Light Fraction				
Quartz	8-	7	3	4
Chalcedony	4	6-	8+	6+
Opal			1*	1*
Volcanic ash	1*		2	
Orthoclase	6	7	2	2
Microcline	4			1*
Oligoclase	2	2		
Carbon				8-
Heavy Fraction				
Muscovite	6-	8	1*	3
Biotite	3	1*	1*	
Chlorite	4	2	3	
Ilmenite	1*	1*		
Leucoxene	7+	5	1*	
Limonite	1*			
Pyrite	1*	1*	8+	8+
Celestite	5		1*	3
Tourmaline	4	2		
Garnet	2	2		
Zircon		1*		

The dominant minerals in the Grayhorse limestone member were quartz, chalcedony, and orthoclase. Almost equal percentages of detrital quartz and orthoclase were found in CcvgW13. In CcvgR20 the amount of orthoclase was overshadowed by quartz; the concentration of silt in this sample was very large. The lower concentration of authigenic chalcedony was probably also due to the high silt content in CcvgR20. The chief light minerals in the Nebraska City were authigenic chalcedony and carbon. In CcvgR20 one per cent of volcanic ash was found. Detrital quartz was scarce in both samples. The chalcedony and carbon show evidence of an organic origin.

In the heavy fraction of the two members a great variance of minerals and their quantity was found. The Grayhorse contained an abundance of muscovite, biotite, chlorite, and leucoxene. The high silt content in CcvgR20 was again shown by an unusually high percentage of leucoxene, tourmaline, garnet, and zircon. Both samples had some pyrite, and CcvgR20 had 12 per cent celestite. The heavy fraction of both Nebraska City samples showed more than 96 per cent of the grains to be euhedral, authigenic pyrite with traces of celestite and the micas. Chalcedony, carbon, and pyrite in the Nebraska City yielded strong evidence that at the time of deposition a reducing environment existed.

The analysis of the fine fraction of both Grayhorse and Nebraska City members of the Caneyville limestone revealed illite and carbon.

Jim Creek Limestone. The Jim Creek limestone underlies the French Creek shale and overlies the Friedrich shale.

Sample Locations

Sample number	Type of outcrop	Geographic location
CjcR8	Stream bank	NW $\frac{1}{4}$ NE $\frac{1}{4}$ sec. 9, T. 11 S., R. 9 E., Riley County
CjcR20	Stream bank	SE $\frac{1}{4}$ SW $\frac{1}{4}$ sec. 6, T. 11 S., R. 9 E., Riley County
CjcW8	Road cut	NE $\frac{1}{4}$ NE $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 32, T. 11 S., R. 13 E., Wabaunsee County

Lithologic Description. The Jim Creek limestone is hard and dense. It is bluish-gray and weathers gray. The unweathered limestone is massive, but it weathers into blocks which further decompose into small chips. Brachiopods and crinoid columns were found, and the average thickness of the limestone is about 1.5 feet.

Mineralogy

Mineral	CjcR8	CjcR20	CjcW8
Light Fraction			
Quartz	6+	7+	6+
Chalcedony	7+	7+	8-
Opal	6+	2	2
Volcanic ash		1*	
Orthoclase	5	4	3
Oligoclase		1*	
Carbon		1*	1*
Heavy Fraction			
Muscovite	7+	6-	1
Biotite	4	1*	
Chlorite	1	1	1*
Ilmenite	2		
Leucocxene	6		
Pyrite		8	8+
Celestite	2	1*	
Tourmaline	5		1*
Garnet	2		
Zircon	1	1*	1*

The total residue of the Jim Creek limestone ranged from 9.2 to 10.37 per cent of the total weight of the sample. The weight of the coarse residue ranged from 0.17 to 0.59 per cent and the fine from 8.7 to 10.2 per cent of the total weight of the sample. The color of the residue was medium gray.

The light fraction of the limestone was characterized by large amounts of quartz and chalcedony, and minor amounts of opal, orthoclase, and carbon. CjcR20 contained traces of volcanic ash and oligoclase. Some of the opal had begun to crystallize to chalcedony and some of the chalcedony had indices of refraction higher than 1.54 which suggests that the silica was originally precipitated as opal, subsequently crystallized to chalcedony, and then to quartz. Most of the silica was probably of organic origin, but volcanic ash may have enriched the concentration of silica in the sea water. The quartz was detrital, subrounded, and contained no inclusions. The orthoclase also showed results of transportation. The grains were subangular, and the grain surface was partially altered to kaolin.

The heavy mineral fraction was comprised of muscovite, biotite, chlorite, ilmenite, leucoxene, pyrite, celestite, tourmaline, garnet, and zircon. In CjcR20 and CjcW8 pyrite was the most abundant mineral. The grains were euhedral to anhedral; some were replacements of lace and twig-like bryozoans. The pyrite was authigenic and where found, the variety and quantity of other minerals was reduced. Small quantities of authigenic celestite were found in CjcR8 and CjcW8. In CjcR8 only celestite

was authigenic, so that the percentages of micas, ilmenite, leucoxene, tourmaline, garnet and zircon were greatest. The tourmaline was brown, angular to rounded; the garnet was colorless to pink, and angular; the zircon was colorless, and euhedral to anhedral.

Illite and carbon were found in the fine residue.

Grandhaven Limestone. The Grandhaven limestone underlies the Friedrich shale and overlies the Dry shale.

Sample Locations

Sample number	Type of outcrop	Geographic location
CgR11	Road ditch	SW $\frac{1}{4}$ SE $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 9, T. 11 S., R. 9 E., Riley County
CgR18	Road cut	SE $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 6, T. 11 S., R. 9 E., Riley County
CgW9	Road ditch	NE $\frac{1}{4}$ NW $\frac{1}{4}$ SW $\frac{1}{4}$ sec. 34, T. 12 S., R. 13 E., Wabaunsee County

Lithologic Description. The Grandhaven limestone consists of two limestone members which are separated by a shale. The limestones are hard, dense, and somewhat argillaceous. They are brown to gray and weather light brown to light gray. Both limestones are massive and usually weather to irregular blocks or small plates. The intervening shale bed is usually clayey, calcareous, and gray-green. Brachiopods, crinoid columnals, and fusulinids are found in the limestone. Its average thickness is about two feet.

Mineralogy

Mineral	CgR11	CgR18	CgW9
Light Fraction			
Quartz	1	6-	4
Chalcedony	8+	8-	8
Opal	3	3	5
Volcanic ash	1*	1*	1*
Orthoclase		3	1
Microcline		1*	
Carbon		6-	1*
Heavy Fraction			
Muscovite	7+	6-	5
Biotite	1*	1*	
Chlorite		4	
Ilmenite	1*	1*	
Leucoxene	7-	5	
Pyrite	3	5	8
Celestite	1*	7+	3
Tourmaline	4	3	1*
Garnet	3	1*	
Zircon	2	2	1*

The total weight percentage of the insoluble residue ranged from 7.69 to 11.7 of the total weight of the sample. The coarse residue ranged from 0.09 to 1.5 per cent and the fine from 7.6 to 10.8 per cent of the total weight of the sample. The color of the residue was light gray to dark gray.

Chalcedony was the dominant mineral in the light fraction, and quartz, opal, volcanic ash, orthoclase, microcline, and carbon completed the mineral assemblage. In all the samples were found traces of volcanic ash that contained no inclusions. The opal and chalcedony showed more evidence supporting the theory that opal crystallizes to chalcedony and then to quartz. The opal was not completely isotropic, and the index of refraction of some of the chalcedony was very close to that of quartz. Quartz, orthoclase, and microcline were allogenic, subrounded,

and contained no inclusions. Although the samples were treated with hydrogen peroxide, carbon was found in two of the samples.

The heavy mineral fraction contained muscovite, biotite, chlorite, ilmenite, leucoxene, pyrite, celestite, tourmaline, garnet, and zircon. The greatest concentration of the micas, leucoxene, tourmaline, garnet, and zircon was found in CgR11 where only a small quantity of authigenic pyrite and celestite occurred. In CgR18 an abundance of celestite and pyrite were found, and the quantity of silt was less. The celestite was found as fibrous fragments, had good cleavage, and was slightly altered or coated with clay; the pyrite was authigenic and euhedral. In CgW9 pyrite comprised 86 per cent of the heavy fraction and celestite comprised 2 per cent, whereas the percentages of the micas, tourmaline, garnet, and zircon were small.

The differential thermal analysis showed illite and a high carbon content in the fine residue of the Grandhaven limestone.

Dover Limestone. The Dover limestone underlies the Dry shale and overlies the Langdon shale.

Sample Locations

Sample number	Type of outcrop	Geographic location
CdP8	Road ditch	NW $\frac{1}{4}$ NE $\frac{1}{4}$ NE $\frac{1}{4}$ sec. 28, T. 8 S., R. 10 E., Pottawatomie County
CdP14	Stream bank	NE $\frac{1}{4}$ NE $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 7, T. 9 S., R. 11 E., Pottawatomie County
CdW12	Road cut	SW $\frac{1}{4}$ SW $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 28, T. 11 S., R. 13 E., Wabaunsee County

Lithologic Description. The Dover limestone is usually soft and argillaceous in the upper and lower parts, but is quite hard and dense in the middle. This limestone is gray-green to gray and weathers light gray. Weathered surfaces are usually covered with small plates and nodules, and iron stains may be found on joint planes. Large fusulinids are very abundant throughout the formation. The average thickness of the Dover limestone is about three feet.

Mineralogy

Mineral	CdP8	CdP14	CdW12
Light Fraction			
Quartz	8-	7	4
Chalcedony	6	7+	8+
Opal	1	1*	1*
Volcanic ash	2	2	2
Orthoclase	6-	5	1
Microcline	1*	1	1*
Oligoclase		1*	
Heavy Fraction			
Muscovite	8-	7+	8-
Biotite	1	3	1*
Chlorite	1*		5
Ilmenite	1	1*	5
Leucoxene	6	7-	5
Pyrite	1		
Tourmaline	4	5	1
Garnet	1	5	1
Zircon	2	1	4
Staurolite	1*	1*	

The total weight percentage of the insoluble residue of the Dover limestone ranged from 6.19 to 15.13 of the total weight of the sample. The range of the coarse fraction was from 0.69 to 0.83 per cent and the fine from 5.4 to 14.3 per cent of the total weight of the sample. The percentage of coarse residue remained almost constant and is a diagnostic feature of the Dover.

The color of the residue was tan to light gray.

The quantity of silt in the light fraction decreased toward the southeast, and the quantity of authigenic chalcedony increased. The main constituents of the light fraction were quartz and chalcedony, and minor amounts of opal, volcanic ash, orthoclase, microcline and oligoclase. Shards of volcanic ash were found in all samples of the Dover, and the percentage appeared to be unrelated to the percentages of allogenic or authigenic minerals. The chalcedony and opal were authigenic and were found in all samples. The quartz and feldspars were sub-rounded, relatively unaltered, contained no inclusions, and exhibited no secondary growth.

The heavy mineral fraction was characterized by almost a complete absence of authigenic pyrite and celestite. The dominant minerals were muscovite and leucoxene. Approximately one-half to one-third of the grains of muscovite contained inclusions of iron ores and were partially altered to clay and sericite; the other grains were equidimensional and clear. The tourmaline was brown (except for two blue grains in CdP8) and either euhedral or well rounded, which suggested that some of the grains had been reworked from older sediments. The garnet was colorless to pink, and angular. The zircon was colorless and anhedral, and the staurolite was yellow and anhedral. Globular white leucoxene and ilmenite were found in all samples; in CdW12 the proportion was almost 1:1.

Illite occurred in all samples of the fine residue, and in

two samples carbon was found.

Maple Hill Limestone. The Maple Hill is the oldest limestone of the Richardson subgroup and the Wabaunsee group of the Pennsylvanian System in Kansas. It underlies the Langdon shale and overlies the Pierson Point shale.

Sample Locations

Sample number	Type of outcrop	Geographic location
CmhP18	Road ditch	NW $\frac{1}{4}$ NE $\frac{1}{4}$ NE $\frac{1}{4}$ sec. 29, T. 7 S., R. 11 E., Pottawatomie County
CmhP22	Road ditch	NW $\frac{1}{4}$ NW $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 5, T. 6 S., R. 11 E., Pottawatomie County
CmhW4	Stream bank	SW $\frac{1}{4}$ SW $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 25, T. 11 S., R. 12 E., Wabaunsee County

Lithologic Description. The Maple Hill limestone is gray to gray-brown and weathers tan. It is hard, massive, and the upper part weathers into irregular plates. This limestone tends to fracture at an angle of nearly 30 degrees from the vertical plane. Limonite stains are found often on weathered surfaces. Fusulinids, crinoid columnals, and brachiopod fragments can be recognized in this limestone. The average thickness of the Maple Hill limestone is about 1.5 feet.

Mineralogy

Mineral	CmhP18	CmhP22	CmhW4
Light Fraction			
Quartz	6	7	8-
Chalcedony	8	7+	6
Opal	1		
Volcanic ash	1		1
Orthoclase	2	4	4
Microcline		1	1*
Oligoclase		1	
Carbon		5	5

Mineral	GmhP18	GmhP22	GmhW4
Heavy Fraction			
Muscovite	8-	8-	7
Biotite	1		1
Chlorite	4		1
Ilmenite	1*	1*	
Leucoxene	5	5	1
Limonite	1		
Pyrite	2	1	8-
Celestite	6-	6-	1*
Tourmaline	2	1	1
Garnet	2		1
Zircon		1	1*

The total weight percentage of the insoluble residue of the Maple Hill limestone ranged from 4.48 to 9.25 of the total weight of the sample. The coarse residue ranged from 0.08 to 1.05 percent and the fine from 4.4 to 8.2 per cent of the total weight of the sample. The color of the residue was medium gray.

The light fraction of the coarse residue was characterized by an abundance of quartz and chalcedony. Other minerals found were opal, volcanic ash, orthoclase, microcline, and carbon. The silica of the chalcedony and opal was probably of organic origin; this was suggested by an abundance of carbon in all samples. Volcanic ash may have contributed some additional silica when it dissolved in sea water. The quartz and feldspars were subrounded, contained no inclusions, and showed no secondary growth.

In the heavy fraction muscovite, biotite, chlorite, ilmenite, leucoxene, limonite, pyrite, celestite, tourmaline, garnet, and zircon were found. Celestite and pyrite occurred together in all samples. The celestite was fibrous and either altered or coated with clay on the surface. The pyrite was euhedral to anhedral and was very abundant in GmhW4. The tourmaline, garnet,

and zircon showed marked evidence of having been transported. All grains exhibited some degree of angularity, but no evidence of having been reworked from previous sediments. The mica grains were equidimensional and contained no inclusions. The leucoxene was globular and white.

The differential thermal analysis of the fine residue of the Maple Hill limestone revealed illite and carbon.

Authigenic and Biogenic Substances of the Limestones Studied

Illite. A differential thermal analysis of the fine residue from each limestone sample showed curves having a large endothermic peak at approximately 630 degrees centigrade. From this analysis it was concluded that illite was the dominant clay mineral in the limestones investigated in this report. Illite belongs to a clay group which has the general formula $(\text{OH})_4\text{K}_y(\text{Al}_4 \cdot \text{Fe}_4 \cdot \text{Mg}_4 \cdot \text{Mg}_6) \text{Si}_{8-y} \cdot \text{Al}_y \text{O}_{20}$ in which y varies from 1 to 1.5. Although it contains less potash and more water than the micas, illite is closely related to the white micas. Pettijohn (1949), p. 102, stated that "a microscopic study of clays and shales composed largely of illite shows green flaky masses of material with the optical properties of the chlorites". Grim (1939), p. 469, believes that the clay minerals are monoclinic in form and that they are characterized by a pronounced basal cleavage.

The occurrence of illite is widespread; it is found in present day soils and is very common in recent marine sediments

and also in ancient sediments. Pettijohn (1949), p. 105, emphasizes the reciprocal relationship between illite and montmorillonite; where one is abundant, the other is rare. In the many ancient sediments from the United States and elsewhere which Grim (1953), p. 356, has analyzed, he has found that illite is very abundant and that montmorillonite is usually absent in sediments older than Mesozoic. However, in an analysis of many Mesozoic and Cenozoic sediments, recent marine sediments, and present day weathering products illite was found in small quantities but montmorillonite was very abundant. Grim (1939), p. 484, said that illite appears to alter easily and is not likely to be a constituent of residual deposits. Furthermore, montmorillonite can alter to illite and Grim (1953), p. 356, postulated that

in the course of geologic time, montmorillonite would probably slowly pick up potassium and magnesium from ground waters, which might in turn obtain such constituents from the disintegration of ferromagnesian minerals and feldspars. The adsorption of potassium and magnesium would favor a shift to a mica type of mineral. Thus in the course of time, because of dehydration due to compaction, montmorillonite would tend to be altered in the direction of the micas.

The origin of illite is not fully understood. According to Grim (1939), p. 487, illite may appear as an intermediate product during the process in which feldspar is weathered to kaolinite. Illite shows an instability when exposed to weathering processes and therefore is probably not the product of them.

On the basis of the investigation recorded in this thesis, the author concludes that the illite in these Pennsylvanian and

Permian limestones developed after the sediments were deposited in a shallow inland sea. Tait (1952), p. 62, records the pH values as ranging from about 7.9 to 8.4. According to Grim (1953), p. 351,

The marine environment is alkaline; there is no leaching; and the water contains a good deal of dissolved calcium. These environmental conditions favor the formation of montmorillonite, illite, or chloritic clay minerals rather than kaolinite.

The writer of this thesis believes that montmorillonite was originally deposited with calcium-rich sediments on the sea floor. During compaction and dehydration potassium-bearing sea water reacted with the montmorillonite. The potassium became fixed in the clay lattice, thus linking the structural sheets together. In this position the potassium could not easily be replaced. According to Pettijohn (1949), p. 503, the fixation of potassium in the clay lattice explains why this element, unlike sodium, does not accumulate in the oceans.

The differential thermal analysis of the samples did not indicate any montmorillonite, but it must be emphasized that this does not exclude the possibility of this mineral being present. Rowland (1955), p. 156, states that where the order of stacking and the organization of the crystals is poor, as is the case in most sediments containing montmorillonite, the peak of the middle endothermic curve occurs at approximately 600 degrees centigrade. This is the same temperature at which members of the illite group also lose their hydroxyls. In sediments which contain both illite and montmorillonite, it is almost

impossible to distinguish these two minerals by means of differential thermal curves alone. In order to establish finally whether montmorillonite is present, an X-ray diffraction analysis should be made.

Pyrite. (FeS_2) Authigenic pyrite, ranging in quantity from traces to 99 per cent of the heavy mineral fraction, was distributed throughout the limestones investigated. Those samples in which pyrite made up 5 per cent or more of the heavy mineral fraction are PfpW1, PfcP10, CbP15, CbW10, CcvP15, CcvnR20, CcvnW13, CgW9, and CmhW4. Most of the pyrite was found in euhedral grains, but much pyrite also was found in CjcW8 as a replacement of lace and twig-like bryozoans. Wherever pyrite was abundant, chalcedony, carbon and sometimes celestite also comprised a large percentage of the sample. According to Pettijohn (1949), p. 346, carbon and pyrite associated with limestone indicate that the limestone was formed in a marine reducing environment. The writer of this thesis believes that the pyrite found in these limestones was formed in a shallow, stagnant, marine basin where, rarely, small amounts of fresh sea water entered. The oxygen was extracted from the water by organisms. When the oxygen was depleted, these organisms decomposed into water, carbon dioxide, and hydrogen sulfide. The pH of the sea water was lowered by an increased concentration of carbon dioxide which had been derived from the decomposition of organisms.

Sulfur was added to the sea water probably in two ways: by the decomposition of sulfoproteins and by reduction of sulphates

dissolved in the sea water. Hydrogen sulfide, formed from the union of the hydrogen and sulfur, also aided in lowering the pH of the sea water until it became slightly acidic. The hydrogen sulphide reacted with iron compounds and formed pyrite. Most of the pyrite was precipitated on the sea floor and crystallized to euhedral grains, but some of the pyrite replaced calcareous fossils. The addition to the water of carbon dioxide increased the concentration of carbonic acid; some of the limey sediment went into solution, and both silica (see later discussion on silica) and pyrite were precipitated. Most of the calcareous remains that were dissolved were replaced by silica; however, some of the remains were replaced by pyrite as is shown in Cjcw8 where pyrite has replaced some calcareous bryozoans.

The author believes that the pyrite was formed after sedimentation and before lithification of the sediment.

Silica. (SiO_2) Silica, as found in the samples of this investigation, was in the form of quartz, chalcedony, and opal. Most of the quartz found was detrital, sub-rounded, without inclusions, without secondary growth, and probably was derived from igneous rocks. However, some quartz grains were incorporated in aggregates of chalcedony and were apparently derived from recrystallization of the chalcedony.

Authigenic chalcedony was an abundant constituent of the coarse residue of the gray limestones used in this investigation. Where chalcedony was abundant, high percentages of carbon, pyrite, and, sometimes, celestite were found, also. The

optical properties of the chalcedony were: fibrous structure; negative elongation; indices, 1.531 to 1.539; and birefringence, .008. The chalcedony was found as small nodules, as replacements of calcareous fossils, and as the recrystallization of opaline sponge spicules.

Those limestone samples in which opal comprised five per cent or more of the light residue were: PfpR10, PfpW1, CbP9, CbP15, CbW8, CbW10, CbW13, CcvW10, CjcR8, and CgW9. All opal in these samples appeared as sponge spicules or fragments of sponge spicules. The opal was yellow-brown, isotropic, had a refractive index of 1.448, and contained approximately eight per cent water (Winchell, 1951, p. 251). Many of the spicules appeared to be partly anisotropic when examined between crossed nicols. This suggested that the opal was crystallizing to chalcedony.

The author believes that both the opal and chalcedony found in these limestones were derived largely from marine organisms. The replacement of calcareous organic remains and the recrystallization of siliceous sponge spicules to chalcedony occurred after deposition and during lithification. The volcanic ash which was found as mere traces in the limestones may indicate that some of the ash that fell into the sea may have been a source for a small quantity of the colloidal and dissolved silica in the sea water. It would have been possible for much of the volcanic ash that fell into the sea to have been dissolved, thereby increasing the concentration of silica in the sea water. Most of the silica, however, was brought to the sea by river water; this quantity

alone could account for all the silica found as opal and chalcedony in the limestones. The sponges extracted from the sea water some of the silica and used it to form opaline spicules (Moore, 1955, p. E 26). Where a sample contained a relatively high percentage of chalcedony and opal, a high percentage of carbon, pyrite, and, sometimes, celestite were found, also. This mineral association indicates to the author that the chalcedony was formed in a stagnant marine environment after deposition of the lime.

Let the reader consider the relationship between the pH value and the solubilities of silica and of calcium carbonate, when this relationship occurs in an environment in which the sediment is composed of limey mud and of siliceous and calcareous organic remains. (Fig. 3) At a given pH, water in contact with opal and calcite becomes saturated with silica and calcium carbonate. If the pH is increased, the saturation point of silica will be increased and the saturation point of calcite decreased. In this case, siliceous organic remains would be dissolved, and calcium carbonate would be precipitated. If the pH was lowered, silica would be precipitated and calcium carbonate and the remains of calcareous organisms would be dissolved.

Let the reader suppose that sea water with a normal pH value of 8.1 to 8.3 (Tait, 1952, p. 62) became isolated in a shallow basin and that the oxygen in the water was exhausted by organisms. Under such conditions the organisms would die and decompose to carbon dioxide and hydrogen sulfide, which would lower the pH until the sea water became slightly acidic. The saturation

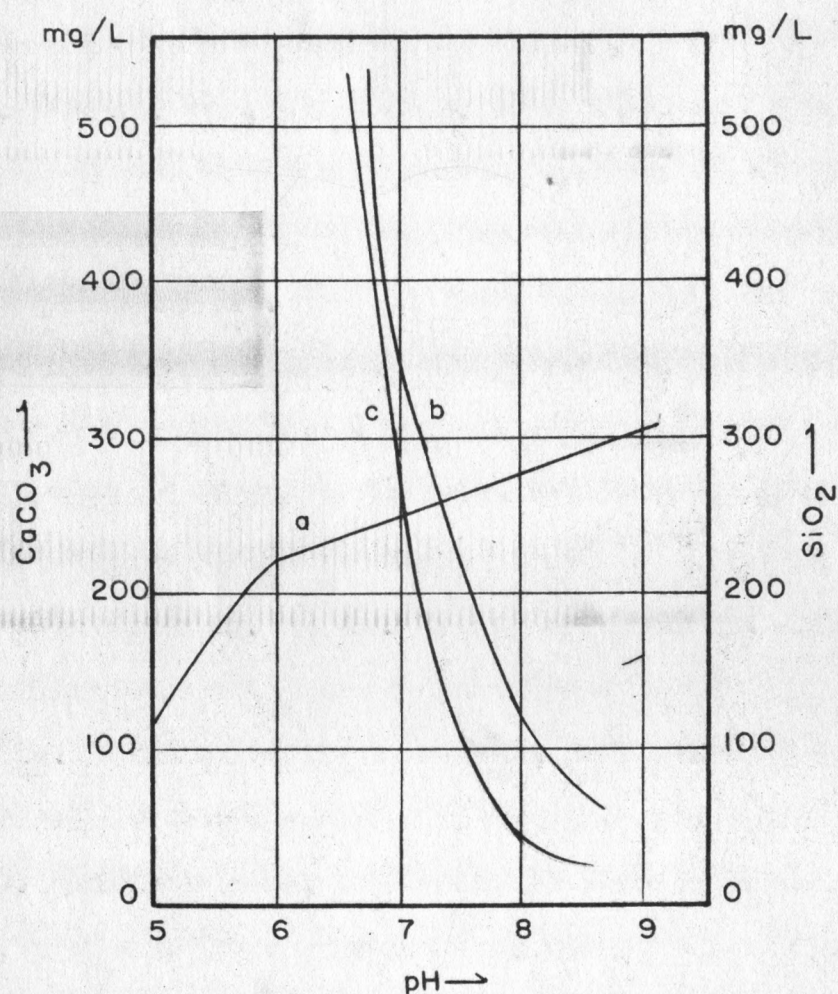


Fig. 3. The relationship between the pH value and the solubilities of (a) SiO_2 -gel, (b) CaCO_3 in pure water, and (c) CaCO_3 in sea water. (after Correns 1950).

points of calcite and opal would be changed, so that some of the limey mud and remains of calcareous organisms would be dissolved. Silica would replace the calcite, but the form of the siliceous sponge spicules would be unchanged. During the process of lithification the opal would recrystallize to chalcedony and, perhaps, subsequently to quartz (Tarr, 1926, pp. 8-12).

None of the limestones studied contained chert nodules or other megascopic forms of chert. In all the samples the percentage of chalcedony and opal in each limestone was less than one per cent. Therefore, the author inferred that the concentration of silica in the sea water was not abnormally high and that most of the silica in these limestones was derived from the solution of siliceous sponge spicules.

The replacement of the calcareous organic remains by silica was accomplished in a marine reducing environment where the pH of the sea water had been lowered by the decomposition of marine organisms.

Celestite. (SrSO_4) Authigenic celestite was found in samples PfcR21, PfcP10, CbP9, CbP15, CbW8, CbW10, CbW13, CcvP9, CcvR20, CcvnR20, CcvnW13, Cjcr8, Cjcr20, Cgr11, Cgr18, Cgw9, CmhP18, CmhP22, and CmhW4. The optical properties of the celestite were: biaxial positive, moderate 2V, alpha index - 1.622, beta index - 1.624, gamma index - 1.631, birefringence of 0.009, cleavage in two directions, fibrous, parallel extinction, positive elongation, and grains either slightly altered or coated with clay. Because of the abundance of celestite in CcvP9, thin

sections were made and examined, and the celestite was found to have occurred: (1) in what may be cavity fillings in fossils, (2) by replacement of calcareous bryozoans, and (3) as fibrous crystals disseminated throughout the matrix (Plates II, III, IV, V, and VI). These occurrences of celestite and its association with authigenic chalcedony, opal, carbon, and pyrite suggested to the author that the celestite in these limestones was formed under certain environmental conditions discussed below.

Aragonite and anhydrite are the chief carriers of strontium among minerals formed during the exogenic cycle (Rankama and Sahama, 1950, p. 480). Noll (1934), p. 507, stated that "aragonite contains up to four per cent strontium". Celestite is often associated with marine organisms which have constructed shells originally composed of aragonite. Aragonite is less stable than calcite and is often converted into calcite or goes into solution. In this process strontium is separated and is precipitated in the fossils as sulfate (Rankama and Sahama, 1950, p. 481).

It is the belief of the writer that the celestite in the limestones studied in this thesis was derived in a reducing environment from the solution of aragonite and from the recrystallization of aragonite to calcite. Perhaps the carbonates of calcium and strontium were extracted from the sea water by marine organisms during the normal deposition of lime. The calcium carbonate crystallized into aragonite which may have contained a maximum of four per cent strontium. If the sea water were

EXPLANATION OF PLATE II

Fig. 1. (X 120) An apparent cavity filling of fibrous radial celestite surrounded by calcite.
Caneyville Limestone. (Plane - polarized light.)

Fig. 2. (X 120) Cavity filling between crossed nicols.

PLATE II



Fig. 1.

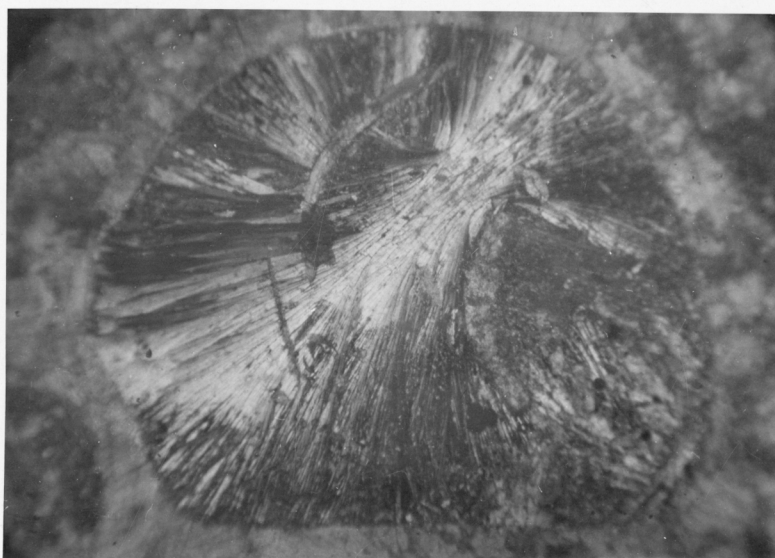


Fig. 2.

EXPLANATION OF PLATE III

Fig. 1. (X 300) Close up of Fig. 1, Plate II, showing fibrous celestite. Caneyville limestone. (Plane - polarized light.)

Fig. 2. (X 300) Close up of Fig. 2, Plate II, showing celestite. Caneyville limestone. (Crossed nicols.)

PLATE III

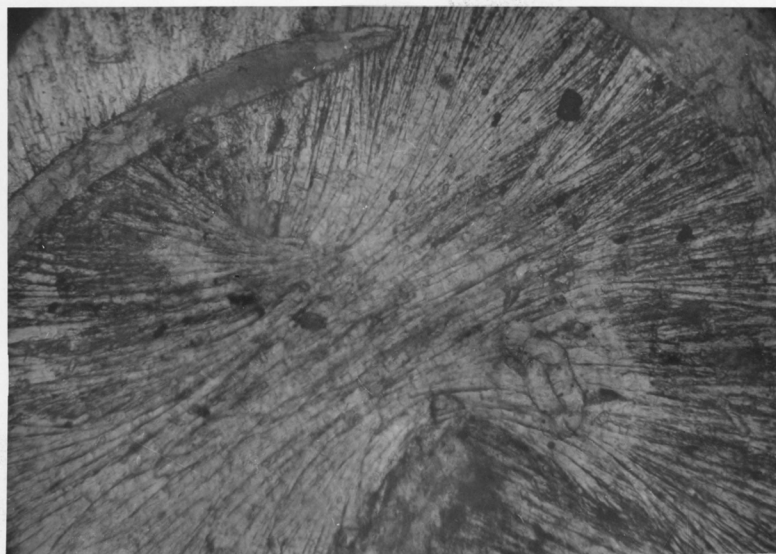


Fig. 1.



Fig. 2.

EXPLANATION OF PLATE IV

Fig. 1. (X 120) Replacement of bryozoan by fibrous celestite. Bryozoan shell fragment is surrounded by carbonaceous matter (black). Matrix composed of fine crystals of calcite and fibrous celestite. Caneyville limestone. (Plane - polarized light.)

Fig. 2. (X 300) Close up of Fig. 1. Fibrous celestite has replaced calcareous bryozoan shell fragment at left. Calcite at extreme right. (Plane - polarized light.)

PLATE IV



Fig. 1.

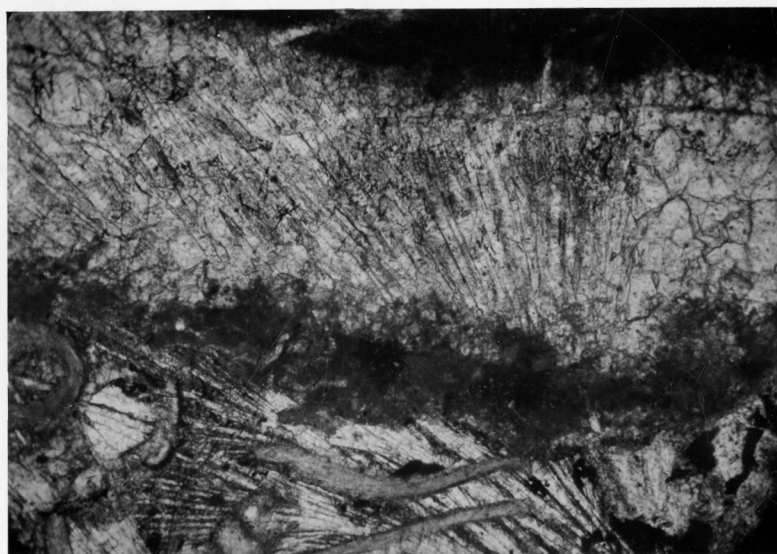


Fig. 2.

EXPLANATION OF PLATE V

Fig. 1. (X 300) Fibrous celestite in matrix.
Caneyville limestone. (Plane - polarized
light.)

Fig. 2. (X 300) Fig. 1. between crossed nicols.

PLATE V

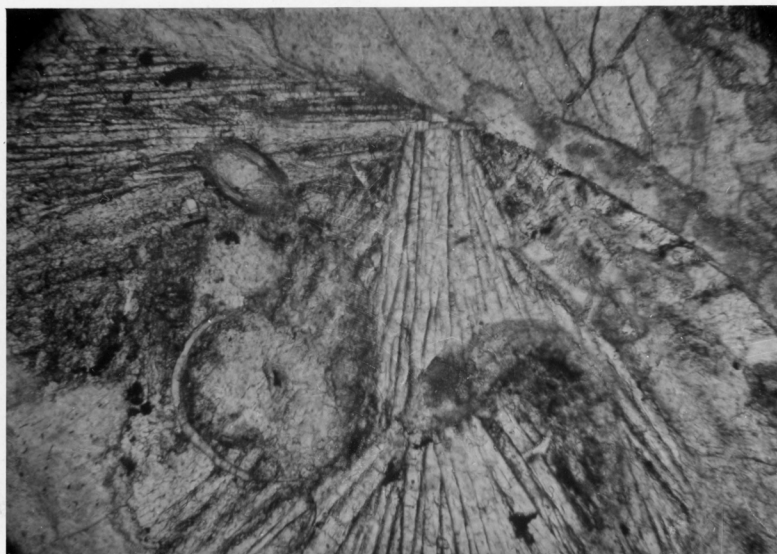


Fig. 1.

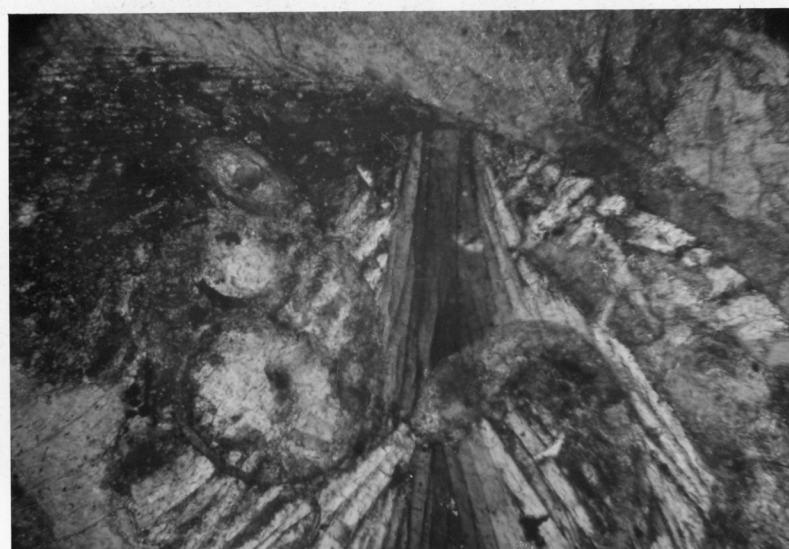
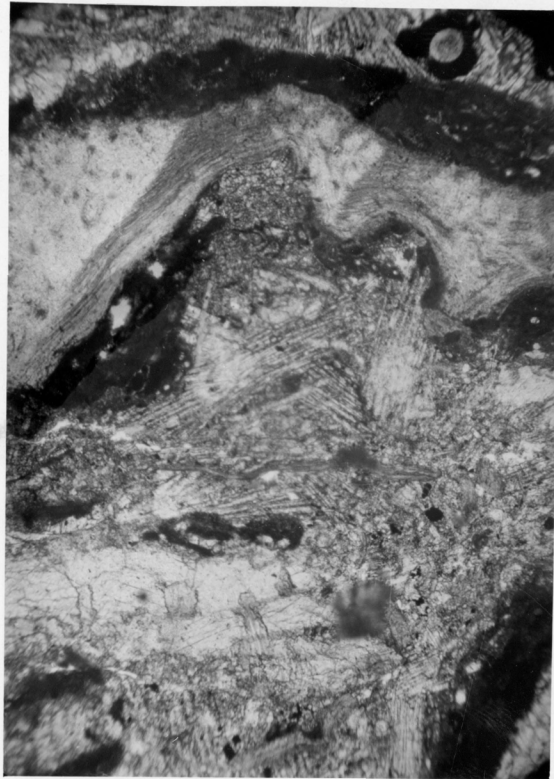


Fig. 2.

EXPLANATION OF PLATE VI

(X 120) Fibrous celestite and small calcite crystals in matrix of Caneyville limestone. Fragment of brachiopod in upper one-third of photo. (Plane - polarized light.)

PLATE VI



isolated, so that the oxygen could be exhausted by organisms, organic decomposition would produce carbon dioxide and hydrogen sulfide. These products would decrease the oxidation potential and the pH of the sea water. Calcium carbonate would dissolve, but strontium carbonate is much less soluble (Rankama and Sahama, 1950, p. 480), and probably would be converted to strontium sulfate in a reducing environment. Possibly, the strontium sulfate would be concentrated by the percolation of strontium-bearing solutions through the limey sediment. Then celestite would be precipitated from the water, filling cavities, replacing calcareous organic remains, and forming part of the matrix. Therefore, the celestite would be secondary, forming after deposition of the lime and probably during lithification. The author believes that the chalcedony, opal, carbon, pyrite, and celestite were formed at approximately the same time and under the same environmental conditions.

Carbon. Many of the limestones used in this investigation contained carbonaceous matter which was disseminated through the coarse and fine insoluble residue. The carbon was identified in the fine residue by means of the differential thermal analysis curves. The curves of the samples that contained carbon had exothermic peaks ranging from 350 to 550 degrees centigrade. In the samples in which the author thought that carbon was likely to be present, he treated the coarse residue with a 15 per cent solution of hydrogen peroxide. In the cases in which this treatment did not succeed in removing all the carbon,

the percentage of the carbon was recorded along with the other minerals of the light fraction. The optical properties were: yellow to black, translucent to opaque, isotropic, moderate relief, refractive index greater than 1.54, and no pleochrism.

The limestones that contained carbonaceous matter were the Five Point, Falls City, Brownville, Caneyville (Grayhorse and Nebraska City members), Jim Creek, Grandhaven, Dover, and Maple Hill. The color of these limestones ranged from yellow-brown to dark gray. In most of the limestones the carbon concentration was correlated with the color of the limestones; it was found that the greater the carbon content, the darker (gray) was the color. An exception was the Five Point limestone, which was yellow-brown, yet showed in a differential thermal analysis a higher percentage of carbon than did the gray Falls City limestone.

Carbon was usually associated with chalcedony, opal, pyrite, and celestite; however, the Brownville limestone was an exception. Carbon was found in CbW13 but was not found in the other samples. Perhaps the yellow-brown color of the Brownville may be explained by oxidation of pyrite during the last stages of diagenesis. Where carbon is found concentrated in the limestones, it indicates that the sediments were formed in a reducing and slightly acidic environment. A large accumulation of organic material in the absence of oxygen accounted for the carbon content.

SUMMARY

From three to five samples were taken from each limestone studied in this investigation. Each sample was taken from a different geographical location. A petrographic study of the insoluble residue of these samples revealed the average mineral characteristics of each formation. The mineral varieties and the mineral frequencies for each limestone were determined with a reasonable degree of accuracy, but the small number of samples precludes the application of these results to problems of regional mineralogical and lithological variations.

The weight percentages of insoluble residue from each sample was determined and recorded. By comparing the percentage of residue with the mineral frequency of each sample, it was possible to explain variations in mineral percentages. For example, PfpPl3 showed a higher silt content in the heavy and light fractions than did the other samples of the Five Point limestone. By comparing the mineral frequency with the percentage of residue, it was seen that the percentage of coarse residue of PfpPl3 was higher than in the other samples.

The non-carbonate mineralogy of the limestones studied was remarkably similar, and no great difference between the Permian and Pennsylvanian limestones was observed. The allogenic, or detrital, minerals in the limestones were quartz, volcanic ash, orthoclase, microcline, oligoclase, muscovite, biotite, chlorite, ilmenite, leucoxene, magnetite, hematite, limonite, tourmaline, garnet, zircon, staurolite, and corundum. All of the grains of

these minerals were somewhat rounded and eroded, indicating that the grains had been transported by water.

Illite was found to be the dominant clay mineral in the fine fraction and indicated to the author that all the limestones studied were of marine origin. Some montmorillonite may have been present in these limestones, but its presence was impossible to determine by means of the differential thermal analysis curves alone. The author believes that montmorillonite was deposited originally with the lime and was converted to illite by potassium-bearing sea water in contact with the sediment during diagenesis.

Authigenic chalcedony, carbon, pyrite, and celestite were found in most of the limestones; this indicated to the author that these minerals developed at approximately the same time and under the same environmental conditions. These minerals formed after deposition and during lithification in an environment in which the oxidation potential and the pH of the sea water had been lowered by products formed from organic decomposition.

However, the Aspinwall limestone showed characteristics slightly different from those of the other limestones studied. The samples of the Aspinwall had an unusually high concentration of silt in the coarse fraction including high percentages of quartz, feldspar, mica, iron oxide, leucoxene, tourmaline, garnet, and zircon; opal, carbon, pyrite, and celestite were absent.

Opaline sponge spicules or fragments of sponge spicules were found in many of the limestones and are believed by the author to be a source for the major quantity of silica found in the light fraction of the formations. Additional quantities of silica may have been supplied to the sea by the solution of volcanic ash and by silica transported to the sea by river water. The bulk of the silica was extracted from the sea water by organisms, but, possibly, some inorganic precipitation did occur.

Evidence was found by the author which showed that opal can recrystallize to chalcedony, and chalcedony, subsequently can recrystallize to quartz. Chalcedony and pyrite, in many cases, had replaced calcareous marine fossils, and celestite was found (1) in what may be cavity fillings in fossils, (2) as replacement of calcareous bryozoans, and (3) as fibrous crystals disseminated throughout the matrix.

It was concluded that (1) the limestones studied generally contain more than 85 per cent calcium carbonate; (2) in the insoluble residues investigated the clay fraction is much greater than is the silt fraction; (3) no significant variation in the non-carbonate mineralogy exists between the Permian and Pennsylvanian limestones studied; (4) the source area for the detrital sediments was probably a low land mass of unknown location; (5) because of the small number of samples taken from each formation, a regional correlation of the formations by the use of insoluble residues was not attempted; and (6) the limestones studied

in this thesis were formed under very similar environmental conditions.



Fig. 4. Mineral variety and mineral frequency of the limestones studied in this investigation.

NAME AND NUMBER OF SAMPLE	COMPARISON OF THE WEIGHT PERCENTAGE OF INSOLUBLE RESIDUE TO TOTAL WEIGHT OF SAMPLE			COLOR OF INSOLUBLE RESIDUE	MINERAL PERCENTAGES OF LIGHT FRACTION								MINERAL PERCENTAGES OF HEAVY FRACTION														REMARKS	
	QUARTZ	CHALCEDONY	OPAL		VOLCANIC ASH	ORTHOCLASE	MICROCLINE	OLIGOCCLASE	CARBON	COATED GRAINS	MUSCOVITE	BIOTITE	CHLORITE	ILMENITE	LEUCOXENE	MAGNETITE	HEMATITE	LIMONITE	PYRITE	CELESTITE	TOURMALINE	GARNET	ZIRCON	STAUROLITE	CORUNDUM			
																										TOTAL		COARSE
(Hamlin shale)																												
Five Point limestone R10	1.8	1.0	0.8	yellow - brown	24	44	30	1	1		tr			86			tr	8					3	1	tr		2	high carbon
Five Point limestone P13	9.8	2.8	7.0	yellow - brown	92	3			5	tr				47	1	4	tr	19			9		11	8	tr	tr		carbon, high silt content
Five Point limestone W1	9.9	0.4	9.5	medium gray	9	71	18	1	1					75			tr	10				10		2	1	2		carbon
(West Branch shale)																												
Falls City limestone R9	24.0	3.9	20.1	gray	72	19			9	tr				91		1	tr	5					2		1			carbon
Falls City limestone R21	11.1	0.2	10.9	gray	12	83	2		2	tr	tr			1		tr		1				97						carbon, lots of altered celestite
Falls City limestone P10	0.9	0.2	0.7	brown - gray	7	88	4		1					81				5			5	tr	2	2	3		2	carbon
(Hawxby shale)																												
Aspinwall limestone R10	29.4	17.1	12.3	tan	78	8		tr	12	1			1	66	2	1	tr	10			12		4	5	tr			high silt content
Aspinwall limestone R19	3.0	0.4	2.6	tan	59	38			2				1	59	4		tr	21	tr	tr	8	tr	5	2	tr	tr		small amount of residue
Aspinwall limestone P5	17.6	5.3	12.3	tan	85	10			4	1	tr		1	67	2	1	tr	14	tr	1	7		4	2	2			
Aspinwall limestone P15	22.8	9.2	13.6	tan	75	6			17	2			tr	56	3		tr	24			6		2	5	3	tr		
Aspinwall limestone W6	27.5	11.4	16.1	tan	82	5			12	1				76	11		tr	9		tr			1	tr	tr			
(Towle shale)																												
Brownville limestone P9	21.5	0.1	21.4	yellow - tan	2	93	5	tr	tr					84			tr	8			1		tr	3	2	2		trace of altered celestite, badly weathered
Brownville limestone P15	14.37	1.17	13.2	yellow - brown	1	88	11	tr						20				4				5	70	tr	tr			altered celestite
Brownville limestone W8	10.98	0.08	10.9	tan	1	89	9	1	tr					92	tr	tr		3				1	tr	tr	1	1		trace of altered celestite
Brownville limestone W10	12.75	0.65	12.1	yellow - brown	tr	94	5	1	tr					4							96	tr	tr					lots of pyrite
Brownville limestone W13	13.41	0.41	13.0	yellow - tan	3	5	92	tr				tr		46	1	1	10	8			5	tr	22	2	3	2		opal, carbon, ilmenite, and celestite
(Pony Creek shale)																												
Caneyville limestone P9	14.18	7.68	6.5	dark gray	8	38						54		tr							1	99						high carbon, chalcedony, pyrite, and celestite
Caneyville limestone P15	10.57	0.17	10.4	medium gray	39	32	2	2	4	tr	tr	21		92	1	1		1				5		tr		tr		high carbon, chalcedony, ash, and pyrite
Caneyville limestone W10	3.93	0.33	3.6	tan - gray	20	37	41		2					41	tr	13	2	18			13			7	5	1	tr	high silt, carbon, opal, and ilmenite
Grayhorse limestone R20	26.71	15.81	10.9	light gray	70	6		tr	19	4	1			15	3	6	tr	58			tr	tr	12	5	1			high silt, leucoxene, and carbon
Grayhorse limestone W13	6.35	0.95	5.4	light gray	44	13			42		1			89	tr	1	tr	7				tr		1	1	tr		high orthoclase, carbon
Nebraska City limestone R20	26.67	0.97	25.7	medium gray	3	95	tr	1	1					tr	tr	2		tr				97	tr					high chalcedony, high pyrite, and celestite
Nebraska City limestone W13	9.55	2.35	7.2	dark gray	4	27	tr		1	tr		67		2								96	2					chalcedony, high carbon, high pyrite, celestite
(French Creek shale)																												
Jim Creek limestone R8	10.37	0.17	10.2	medium gray	24	46	23		7					59	4	1	2	21					2	8	2	1		carbon, chalcedony, orthoclase, leucoxene, celestite
Jim Creek limestone R20	9.69	0.59	9.1	medium gray	49	45	1	tr	5		tr	tr		17	tr	1						81	tr			tr		high carbon, chalcedony, orthoclase, pyrite
Jim Creek limestone W8	9.2	0.50	8.7	dark gray	25	70	2		3			tr		1		tr						99		tr		tr		high carbon, chalcedony, orthoclase, pyrite
(Friedrich shale)																												
Grandhaven limestone R11	7.69	0.09	7.6	light gray	1	97	2	tr						59	tr		tr	29				2	tr	4	3	2		high carbon, chalcedony, leucoxene, pyrite, celestite
Grandhaven limestone R18	11.7	1.5	10.2	medium gray	15	63	2	tr	3	tr		16		15	tr	6	tr	11				12	52	3	tr	1		high carbon, chalcedony, leucoxene, pyrite, celestite
Grandhaven limestone W9	11.06	0.26	10.8	dark gray	4	85	10	tr	1			tr		12								86	2	tr		tr		high carbon, chalcedony, leucoxene, pyrite, celestite
(Dry shale)																												
Dover limestone P8	15.13	0.83	14.3	tan	63	18	1	2	16	tr				69	1	tr	1	21				1		4	1	2	tr	no carbon, high leucoxene, orthoclase
Dover limestone P14	6.19	0.79	5.4	light gray	38	51	tr	1	9	1	tr			49	3		tr	30						7	10	1	tr	carbon, high chalcedony, orthoclase, leucoxene, garnet
Dover limestone W12	9.49	0.69	8.8	light gray	4	92	1	2	1	tr				66	tr	7	11	10						1	1	4		carbon, high chalcedony, ilmenite, leucoxene
(Langdon shale)																												
Maple Hill limestone P18	4.48	0.08	4.4	medium gray	18	78	1	1	2					64	1	6	tr	8			1	2	14	2	2			high carbon, chalcedony, pyrite, celestite
Maple Hill limestone P22	5.84	0.24	5.6	medium gray	40	46			5	1	1	7		73			tr	9				1	15	1		1		high carbon, chalcedony, pyrite, celestite
Maple Hill limestone W4	9.25	1.05	8.2	medium gray	62	21		1	5	tr		11		35	1	1		1				60	tr	1	1	tr		high carbon, chalcedony, pyrite, celestite

Fig. 4. Mineral variety and mineral frequency of the limestones studied in this investigation.

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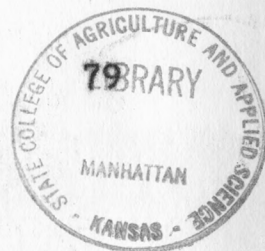
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THE NON-CARBONATE MINERALOGY OF SOME PERMIAN
AND PENNSYLVANIAN LIMESTONES

by

PAGE CHARLES TWISS

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The non-carbonate mineralogy of some Permian and Pennsylvanian limestones was determined by the examination of the insoluble residue. The limestones, from youngest to oldest, are: the Five Point, Falls City, and Aspinwall of the Admire Group (Wolfcampian Series of the Permian System), and the Brownville, Caneyville (Grayhorse and Nebraska City members), Jim Creek, Grandhaven, Dover, and Maple Hill of the Richardson subgroup (Wabaunsee Group, Virgilian Series of the Pennsylvanian System). Channel samples were taken of these limestones from exposures in Riley, Pottawatomie, and Wabaunsee Counties, in Kansas. The samples were treated with chemically pure hydrochloric acid, and the insoluble residue was divided into coarse and fine fractions by use of a 230 mesh sieve. A differential thermal analysis was made of the fine fraction, and the clay mineral was then ascertained. The light and heavy fractions of the coarse residue were separated by the use of bromoform and were then separately mounted in Canada balsam on glass slides. From their examination under the petrographic microscope, the mineral frequencies for each limestone sample was determined.

From the information gained in this study the author has made the following conclusions:

1. The insoluble residues of these limestones were remarkably similar in mineral composition, and no great mineralogical difference between the Permian and Pennsylvanian limestones was observed.

2. Because of the fossil content and because illite was found as the dominant clay mineral in these limestones, they were assumed to have formed in a marine environment.
3. Opaline sponge spicules were found in 65% of the limestone samples and are believed to be the source for most of the silica present.
4. Authigenic chalcedony, carbon, pyrite, and celestite were found in most of the samples; these substances were formed after deposition and probably during lithification. The writer believes that these minerals were formed in an environment in which the oxidation potential and the pH of the sea water had been lowered by products formed from organic decomposition.
5. The source area for the detrital constituents of these limestones was a low land mass of unknown location.

