by

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#### INTRODUCTION

The purpose of the investigation was to examine the limestones and shales and to investigate the cherts in the Manhattan, Kansas, area to determine some of the minor petrographic constituents of these rooks. Recent investigation has shown the presence of volcanic glass shards in the chert zones of the Florence, Schroyer and Threemile limestone formations. It was hoped to supplement this finding and to determine whether or not the glass shards are present in the limestones and shales above and below these layers and to determine, if present, their effect on the type rock in which they are present.

#### REVIEW OF THE IMPORTANT LITERATURE

# Origin of Chert

Much work has been done to determine the origin of chert.

The problem consists both of the origin of the siliceous material for the formation of the chert and the method or methods by which it was incorporated within the rock strata.

Keller (1941) attributes the formation of the Rex chort (Permian) to primary origin with the source of silica being derived from the weathering of land surfaces and transported to the sea by stream action. The silica on reaching the sea was deposited directly on the sea floor. Keller points out the great amount of silica now being carried by streams as evidence for his theory.

An alteration that consisted largely of a rearrangement of the silica of an original distomaceous deposit is given for the origin of most of the porcelaneous and cherty rocks of the Monterey (Miocene) formation by Bramlette (1946).

Tarr (1917) concluded that the chert in the Burlington limestone was formed from colloidal silica, derived in most part from streams which contributed it to the sea. It was deposited on the sea floor through the action of electrolytes.

It has been suggested by Shrock (1948) that siliceous rocks such as chert and radiolarites might immediately succeed deposits of water-laid tuffs and ash, inasmuch as, during and

immediately efter volcanic activity, there is much readily soluble silica available to streams for transport to the sea.

Twenhofel (1919) listed several suggested theories on the origin of the ohert in the Wreford and Forsker limestones. He concluded that the ohert was partly or wholly the result of replacement of unconsolidated limestone. The silica is believed to be 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 preservation of clastic limestone structures is given by Folk (1949) as indication that the Beekmantown cherts originated by replacement.

It is beyond the scope of this thesis to review all the previous work done on the chert problem. The reader is referred to the latest work done by Pettijohn (1949) in which he has given a thorough treatment of the work done and theories advanced.

In summarizing the theories presented by other workers on the origin of chert, Pettijohn outlined stages of silica deposition and sources of silica in sedimentary deposits as follows:

I. Syngenetic silica
A. Clastic quartz
B. Chemical silica

- 1. Bio-chemical precipitate
- Chemical precipitate
   Magmatic precipitate
- II. Penecontemporaneous silica

III. Epigenetic silica

A. Precipitation in zone of cementing
B. Precipitation in zone of weathering

In reviewing the literature, it seems likely that several theories thus far advanced are substantiated at least in part by the findings made by the authors for their particular localities.

#### Volcanic Glass

Volcanic glass is the term applied to the ejected material formed as a result of explosive volcanic eruptions. Due to its minute size and fineness the particles may be transported through the air and achieve world-wide distribution. The coarser material comes to rest in the immediate vicinity of the volcanic vents.

After transportation and deposition in the water the fine ash settles to the bottom and becomes mixed with the sediment accommulating on the sea floor. As a result of world-wide distribution it is doubtful that traces of volcanic glass are absent from any sub-aqueous or sub-aerial sediment, although the quantity may be insufficient to effect the sediments in which it is found.

Work of the "Challenger Expedition" Twenhofel (1939) has shown that terrigenous and volcanic sediments are present over the entire bottom of the deep oceans, but in many places they are more or less masked by organic sediments.

Many deposits of ash have accumulated in recognizable layers throughout the geologic section. There may be relatively pure deposits far removed from the volcances that produced them. This gives rise to the idea of transportation and deposition of the ash far from the volcanic source. The ash beds of Kansas and Nebraska (Plicene) are good examples of these deposits.

Volcanic glass is characterized by its isotropic character, its low indices of refraction (usually 1.50 to 1.52), its shape, and its colorless appearance under the petrographic microscope.

The glass fragments are termed shards due to the curved spicule-like form. The shards may contain inclusions of air, gas, or minerals associated with the cooling of the lava from which it was originally formed.

In time, the glass undergoes alteration and becomes devitrified. The formation of a bentonitic clay seam or bed results from the conversion of the ash bed in marine water.

Ross and Hendricks (1945) present this definition of bentonites:

Bentonite is a rock composed essentially of a crystalline claylike mineral formed by the devitrification and the accompanying chemical alteration of a glassy igneous material, usually a tuff or volcanic ash. It (bentonite) often contains variable proportions of accessory crystal grains that were originally phenocrysts in the volcanic glass. These are feldspar (commonly orthoclass and cligoclass), biotite, quartz, pyroxenes, zircon, and various other minerals typical of volcanic rocks. The characteristic cley mineral has a micaceous habit and facile cleavage, high birefringence and a texture inherited from volcanic turf or ash, and it is usually the mineral montmorillonite but less often beidellite.

According to Twenhofel (1939) the bentonites have been generally assumed to have been produced by decomposition of volcanic ash; and acid ash is generally assumed to have been the original form. However, since montmorillonites are formed by the decomposition of many substances the presence of this clay mineral in itself does not prove a shower of volcanic ash. Demonstration of the volcanic origin of a rock identified as bentonite must rest on the presence of glass relect structures and minerals characteristic of volcanic rocks.

# Clays in General

Clay, as the rock term implies, is a hydrous aluminum silicate of exceedingly fine grain. The chemical composition varies within very wide limits. It is a product of weathering of a wide variety of rocks and plays an important role in soils and is the dominant material of shales.

The study of clays has been carried on extensively the past twenty-five years but, it was not until recent years, after the development of new techniques such as X-ray diffraction, that the data could be evaluated.

Clay mineralogists recognize three groups of clays but, this paper is concerned only with the illite and montmorillonite groups.

The name montmorillonite was proposed by A. A. Damour and Salvetat---- in 1847 for a clay material sampled near Montmorillon, France.

The clay minerals of this group are, according to Ross and Hendricks (1945), stable over a rather wide range of temperature; they have been synthesized at temperatures up to at least 200°C and they have been formed by purely weathering process, as well as by low temperature hydrothermal process. They list the following important modes of occurrence for montmorillonite: (1) in soils, either as the dominant minerals of the clay fraction or in association with other clay minerals; (2) as bentonites; (3) in pegmatite veins as an alteration product of other minerals; (4) in mineral veins, both as vein minerals and as gouge clays; and (5) as one of the dominant minerals in water laid shales.

Ross and Hendricks (1945) also stated that experiments on synthesis indicate that the formation of montmorillenite is favored by alkaline conditions or by the presence of salts of alkalies and alkaline earths, in particular by magnesium, which is commonly an essential constituent of these minerals.

Grim (1953) states:

Analysis of many ancient sediments in the authors labratory from the United States and elsewhere have shown that montmorillonite is generally absent in sediments older than Mesozoic. Except for a few beds of probable bentonitic origin, montmorillonite has not been reported in the older sediments. This point is of particular importance, for montmorillonite is abundant in many Mesozoic and Genozoic sediments, in Recent marine sediments and in present-day weethering products.

Grim attributes the absence of montmorillonite from ancient materials to alteration of montmorillonite to a mica-type of mineral due to metamorphic processes or to the presence at times in the geologic past of conditions which were unfavorable to the persistence of montmorillonite.

The term illite was proposed by Grim, Bray and Bradley in 1937 as a general term for the mica-like clay minerals.

Studies by Grim (1953) have shown that illite is a common mineral on the sea floor today and develops largely from the alteration of the montmorillonite of the source material being carried to the sea.

Krumbein and Sloss (1951) stated that the dominant clay mineral in most marine shales is illite and it is probably formed mainly by post-depositional changes of some source clay mineral such as montmorillonite.

#### FIELD PROCEDURE

The collection area included that of the recent investigation in which the volcanic glass was discovered. All samples were of the "spot" type and sampling was done at definite intervals within the formation. This type of sampling would show best the changes in mineral and clay composition within a single rock unit.

Samples were collected in Section 33, RSE T105, Section 21, RSE, T115, in Riley county and Sections 28 and 29, RSE, T115, of

# EXPLANATION OF PLATE I

Generalized stratigraphic section showing location of samples.

# PLATE I

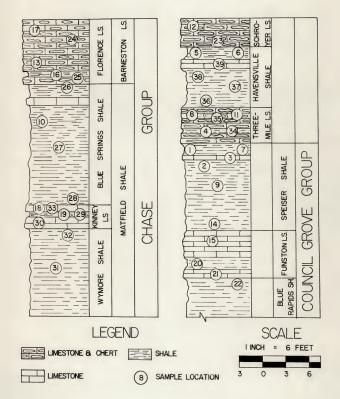


Table 1. Location of sampled units and their characteristics.

	: Location in geologic : section	At contact with over- lying Thresmile line-	At contact with over-	In Spelser shale.	Speiser shale. Shale zone in Three-	At contact with over-	stone. At contact with ever-	At contact with over- lying Threemile lime- stone.	At contact with over- lying Havensville shale.
	: Rook type : Geographic location	Rd Cut K13 SNNW Sec 33 RGE TIOS Riley	. ор	op	do	Rd Cut K13 SENE Sec 32 RSE T10S R11ey	op	Rd Cut X13 SWNF Sec 33 RSE T10S Riley county	op op
	: Rook type	shale	do	limestone	shale	do	op	op .	Limestone
The second second second	Porms tion or member	Spelser	do	do	Threemile limestone	Havensville shale	o p	Speiser	Threamile
The Party of the P	sample :	н	CV	~	4	10	•	7	10

Table 1. (Cont.).

Sample	Sample : Formation or :	: Rook type	: Geographic location	: section in geologic : section
•	Speiser	shele	Rd Cut K13 SWNW Sec 33 RSE TLOS Riley county	Middle of Speiser shale unit.
10	Blue Springs shale	do	nd Cut Kl3 SWSW Sec 28 ASK TllS Geary county	Eight feet below con- tact with overlying Florence limestone.
я	Threemile	limestone	Rd Cut K13 SWSW Sec 21 RSE T11S R11ey county	At contact with over- lying Havensville shale.
12	Schroyer	do	qo	Chert zone near top of Schroyer limestone.
23	Florence	qo	Rd Cut K13 SWSW Sec 29 RSE T11S Geary county	Lower zone of Florence limestone.
#	Speiser	shale	Rd Cut X13 SWNW Sec 33 RSE TLOS Riley county	At contect with under- lying Funston limestone.
15	Funston Limestone	limestone	do	Uppermost limestone unit in Funston lime-stone.
97	Florence	shale	Rock quarry SESE Sec 32 RSE T113 Geary county	Shale zone in Florence limestone.

Table 1. (Cont.).

: Location in geologic location : section	y SESE See Top section in 13 Geary Florence limestone.	nd Cut US40 See 28 At contact with over- NSE TALS Geary county lying Blue Springs shale.	Shale zone between two limestone units of Kinney limestone.	TIOS RILEY   Numerical Superior Constitution of Superior	Lower linestone unit of Funston limestone.	At contact with over- lying lower Funston limestone.	El3 SWSW 300 At contact with under- Tils Riley lying Hevensville shale.	Rd Cut US40 Sec 28 Near top of Florence RSE Tils Geary County limestone section.
: Geographic location	Rock querry 32 RSE T113 county	Rd Cut US40 See 28	9	nd Cut K13 SHNW Se 33 R&E T10S Riley county	op	do	Rd Cut Kl 21 R&E Tl county	Rd Cut US RSE TILS
: Rock type	limestone	do	shale	op	limestone	shale	limestone	do
Formation or member	Florance	Kinney	do	Funston	do	Blue Rapids	Schroyer	Florence
Sample :	17	18	19	50	27	22	23	क्र

Sample	: cormetton or	: Rock type	: Geographic location :	: cocation in geologic : section
25	Florence	1imestone	Rd Cut US40 Sec 28 RSE Tll3 Geary county	At contact with under- lying Blue Springs shale.
56	Blue Springs shale	shale	do	At contact with over- lying Florence lime- stone.
27	do	do	do	Middle of Blue Springs shale section.
40	do	do	do	At contact with under- lying Kinney limestone.
29	Kinney	qo	do	Shale zone between two limestone units of Kinney limestone.
30	qo	limestone	do	Lower limestone unit in Kinney limestone.
31	Wymore	shale	d do	Middle of Wynore shale section.
32	90	do	do	At contact with over- lying Kinney limestone.
33	Kinney	limestone	do	At contact with over- lying Blue Springs shale.

Table 1. (Conol.).

ample	Sample : Formation or :	Rook type	: Rook type : Geographic location	: location in geologic
35	Threemile	shale	Ed Cut Kl3 SWSW Sec 21 RGE TILS Riley county	Three feet above contact with underlying Speiser shale.
35	do O	limestone	do	Near top of Threemile limestone section.
36	Eavensville shale	shale	00	At contact with under- lying Threemile lime- stone.
37	do	qo	do	Middle of Havensville shale section.
90	do	do	qo	Two feet below con- tact with overlying Havensville limestone.
39	do	limestone	do	Limestone unit in upper Havensville shale section.

Geary county, Kansas. All samples collected were shale, limestone and chert of the Chase and Council Grove Groups, and of the Barneston, Matfield, Wreford, Speiser, Funston and Blue Rapids formations.

In order to obtain samples near contacts with overlying and underlying layers and to insure proper location in the geologic section, all samples for this study were collected in road outs and walls of recent quarry excavations and, wherever possible, were collected where overlying and underlying numbers were present.

Samples sixteen through nineteen and twenty-four through thirty-three were obtained from the wells of recent quarry operations and newly made road cuts. The remainder of the sampling was done in road cuts but, in all cases, fresh samples free from weathering were collected.

# LABRATORY PROCEDURE

#### Limestone

The sample was first dried in a thermostatically controlled oven. A portion of each of the limestone samples was then crushed in a mechanical rock breaking machine which caused the sample to be broken into particles of less than five millimeters. The purpose for this was to obtain a larger surface area and thereby facilitate a more rapid rate of digestion by the concentrated hydrochloric acid during the digesting process.

After crushing, 800 grams of the rock was divided into four parts and placed in four separate glass containers. Concentrated hydrochloric acid was added to climinate the carbonates in the sample. It was found that by splitting the original 800 gram sample into four parts of 200 grams, the process of digestion was speeded up and less acid was used in the process.

After the digesting activity ceased the samples were washed and decanted several times with water to remove the acid and soluble material. The sample was then wet selved using U.S. Standard sieve sizes 200, 230 and 270. The material caught on the 200 sieve, in all cases, was saved as it was thought that it might be of some significance to the investigation at a later time. The material collected on the 230 sieve was boiled in an 18 percent solution of hydrochloric acid for 30 minutes to remove the iron exide coatings from the mineral grains. The sample was then washed and decanted several times.

After drying in a temperature controlled oven, a heavy mineral separation was made using bromoform with a specific gravity of greater than 2.62 as the separating medium. The 230 size fraction was heated before being placed in the bromoform in order to remove all moisture. The material was allowed

to stand from eight to twelve hours in the bromoform and was agitated several times before the separation was made. This procedure was used as it was found that better separation was obtained in previous work done with detrital grains by this method.

Upon completion of the mineral separation each fraction was washed with alcohol several times and again with water to remove the alcohol adhering to the mineral grains.

Detrited slides of the heavy and of the light fractions were made of each sample using Canadian balsem with an index of refraction of 1.437 as the mounting medium. Those detrital grains which floated in the bromoform during the separation were labeled "lights" while those sinking to the bottom of the solution were labeled "heavies".

The material passing through the 270 sieve size was allowed to settle and the clay suspension was separated. After drying in the temperature controlled oven, a standard differential thermal analysis study was made of each of the clays from the limestone samples to determine the changes, if any, within the same formation and to determine the relationships, of the type slay and the presence or absence of volcanic glass in the heavy and light fraction of the same sample. It was thought that the light and heavy mineral assemblages present might have some significant bearing on the type clay present.

The material retained on the 200 sieve was examined for the presence of volcanic glass with a binocular microscope to determine if there was any significance of the type of fossils, or detrital grains of the larger fraction with reference to the heavy and light fraction of the same sample.

Thin sections were made of the limestone and of the limestone-chert contacts to determine the presence or absence of volcanic glass and to find any indications of alteration and paragensis.

#### Chert

The samples studied consisted of thin sections of the limestone-chert zones of the Florence, Schroyer and Threemile formations which were examined with the petrographic microscope.

# Shale

The shale samples were first dried in the thermostatically controlled oven. They were then broken down by the mechanical rock breaker in order to facilitate the dispersion of the rock sample. To 200 grams of the sample was added 80 milliliters of a sodium silicate solution to disperse the shale. A portion of the remaining space in the 400 milliliter bottle was filled with de-ionized water which provided a liquid medium for further disaggregading the dispersion of the shale samples. The samples were then placed in a mechanical shaker for six to eight hours

to facilitate dispersion of the shale.

After the sample had been dispersed it was wet sieved using sieve sizes 200, 230 and 270 (U.S. Standard sizes). The material retained on the 200 sieve, after it was dried in the oven, was saved for the binocular microscope study. The material caught on the 230 sieve was treated with a solution of hydrochloric acid to eliminate the carbonates and was then boiled 30 minutes in a 18 percent solution of hydrochloric acid to eliminate the iron oxide coatings from the mineral grains.

Pollowing washing, decenting, and drying, a heavy mineral separation was made. The 230 size fraction was heated prior to placing it in the bromoform solution and allowed to stand from eight to twelve hours in the bromoform before the separation was completed. Several agitations of the sample were made to insure a good separation and to prevent the heavies from adhering to the side of the glass funnel.

The light and heavy portions were then washed with alcohol several times and again with water to remove the alcohol surrounding the mineral grains. Several detrital slides were made of each fraction using Canadian balsam, with an index of refraction of 1.437, as the mounting medium.

The clay fraction was allowed to settle and was separated off, treated with a one normal solution of hydrochloric acid to remove any carbonates and allowed to dry in the oven. Differential thermal analysis of the shale samples were made.

#### METHODS OF STUDY

The methods of study consisted of (1) detrital grain and thin section study with the standard petrographic microscope; (2) clay mineral examination by use of the differential thermal analysis machine and the benzidine staining method; (3) study of the larger fractions of the detrital grains with the binocular microscope and (4) use of the oil immersion method of study of the detrital grains whenever applicable.

#### STUDY PROCEDURE

# Thin Section Study

A thin section study of the limestone and limestoneohert zones of the Florence, Schroyer, Threemile and Kinney formations was made by use of the standard petrographic microscope. The examination was for the purpose of determining the presence or absence of volcanic glass and preceded the other methods of study.

Earlier work on the Florence, Schroyer and Threemile limestones has shown the presence of glass shards in the chart and the limestone-chart contacts. This study was made to supplement that finding and to determine the presence or absence of "ash" in the non-cherty zones of these formations and the limestone formations in which there is absent.

### Detrital Grain Study

An examination was first made of the lights in each mineral sample to determine the presence of glass shards. An analysis of the minerals present and a mineral count was made. The mineral count consisted of counting one-hundred grains in successive traverses across the glass slide and then recording the total as a percentage value.

For the same sample the heavy fraction slides were observed noting the presence of glass, the type, shape, size, and the abundance of the minerals present. A mineral count was made by successive traverses across the slide and the minerals present listed as percentage values.

# Oil Immersion Method

The oil immersion method was employed in the determination of some minerals. This method consists of placing a small amount of the sample to be studied in oils having different indices of refraction and thereby determining whether the mineral had a higher or lower index than the medium in which it was immersed. The index of the mineral was then listed as greater than or less than the index of the immersion oil used.

# Clay Mineral Study

Differential Thermal Analysis. This method was used very effectively in the examination of the clay fraction. It consisted of heating the clay sample with an inert material (Alundum (Al<sub>2</sub>O<sub>3</sub>)) at a uniform rate in a furnace. The graph of the clay sample depicts the exothermic and endothermic reactions within the clay. By means of comparisons of the temperature curve to these reactions of known clay minerals, the type or types of clay can be ascertained.

A more thorough explanation of the use of the differential thermal apparatus is given by Grim (1953).

Benzidine Staining Method. Hendericks and Alexander (1940) give several clay staining methods for the determination of

the presence of montmorillonite.

A benzidine staining test was made of the clay fractions of each sample studied in this investigation to help in the determination of the type clay present. The method consisted of adding a few milliliters of a solution of benzidine to the clay sample and recording the change in color that took place.

Montmorillonite reacts with the benzidine forming a blue color. Organic matter will also give a blue color and hence must be absent from the sample.

Binocular Microscope Examination

The fraction of each sample caught during the sieving

process on the 200 size sieve was examined by use of the binocular microscope. The presence or absence of volcanic glass, fossils and mineral grains was determined. It was thought that there might be some correlation of the larger grains with the minerals found in the less than 200 mesh fraction.

# INFORMATION GAINED BY THIS INVESTIGATION

# Presence of Volcanic Glass

This investigation was concerned with the presence or absence of volcenic glass in the limestone and shale zones above and below the zones from which volcanic glass had already been reported.

An examination of the thin sections prepared of the Florence, Schroyer, Threemile and Kinney limestone did not reveal the presence of glass although the light fraction of the insoluble residue showed that glass was present in all but the Kinney limestone. Not being able to find glass in the thin sections is probably due to two factors, the abundant fossil fragments and the small size of the glass shards.

During the examination of the light fraction of the mineral samples, isotropic material was observed in samples & (Threemile), 12 (Sohroyer), 17 (Florence), 23 (Sohroyer),

24 (Florence), 25 (Florence), and 35 (Threemile) making up a very small portion of the total mineral count. The isotropic material was colorless, in the form of shard-shaped particles and had a low index of refraction. Fortions of the remaining lights from each of these samples were examined for the presence of more shard particles and to determine the indices of refraction of the grains. For the particles observed the index of refraction was greater than 1.51 but less than 1.52. The light fraction of these samples was then re-separated in a solution of bromoform adjusted to a specific gravity of 2.45. It was believed that, should the isotropic particles be opal, this would create a definite separation between opal which would float and quartz which would sink to the bottom.

Opal did not ap ear in the light fraction of the second separation which confirmed the belief of the author that it was absent. Nor did opal appear in subsequent clay tests or the examination of the larger fraction of the detrital minerals.

On the basis of their isotropic character, shard-like shape, low index of refraction (less than 1.52) and the presence of mineral inclusions within some of them, these isotropic particles were determined as volcanic glass shards.

# Mineral Analysis

The next step of the investigation involved the mineral determination and count of both the light and heavy fraction of all samples. It was thought that there may be a definite mineral suite which would be characteristic of the rocks showing ash and different from similar rocks lacking ash.

This was found to be true. The ash was absent from all the shale samples although montmorillonite was found in four of the samples. These montmorillonite zones may represent altered ash falls. All the limestone samples lacking chart also lacked ash while those limestone samples containing chart, with the exception of samples 11 and 13, showed the presence of ash, and samples taken both above and below 11 and 13 showed ash.

Table 2 lists the mineral and clay analysis of the samples studied. Due to the small crop of mineral grains in the heavies in most of the limestones, the value given is the actual mineral count. The other samples, in which 100 mineral grains were counted, are given as percentage values.

The light fraction for all the limestone samples consisted of chalcedony, orthoclase, plagicclase and microcline feldspars, and quartz. In all cases chalcedony made up over 92 percent of the total light fraction. The chalcedony appeared

Table 2a. Mineral and clay analysis.

Minerals :	#13:	#17	: #1ore	#25 :	Florence 1s.
		Hea	vy Fract	ion	
Biotite Celestite Corundum Enstatite				3*	14
Fluorite Bernet Bematite	2* 5*	1* 6*	1* 3*	1*	3*
yanite Magnetite			2*		
Auscovite Pyrite Popaz Pourmalene		3*	1.	- 5*	8* 4* 2*
conted	1*	2*	7.0	1*	7* 9*
		Lig	ht Fract	ion	
halcedony icrosline rtheclase	98-	97-	99-	94-	98-
Plagicolase Junta Hass Joated	l- no	l- yes	l- yes	3- yes	1- 1- no
		Cls	y Analys	is	
Illite	I	I	1	I	I
Montmor-					

illonite

<sup>\*</sup> figure represents actual mineral arrin count. - figure represents percentage value.

Table 2b. Mineral and clay analysis.

	#26	Springs 1	#10 :	#27	springs	#28	: #18 :	#33
		He	avy Fr	action				
Biotite Gelestite Corundam Enstatite	,		1-	1" 3"			4*	
Fluorite Garnet Hematite Hornblende Kyanite	2*		3-	2* 7* 3*		2* 1*	4* 20*	24
Magnetite Muscovite Pyrite Topaz	5* 4*		92-	16* 1*		40* 1* 1*	2* 3*	
Tourmalene Ziroon Coated	1.0		1-	2*		10		3
		11	ght Fr	action				
Chalcedony Microsline	98-		35-	93-		92-	98-	97-
Orthoplase Plagioplase	1-		52-	4-		3-	1-	2-
Quartz Gleas Coated	no no		8- no	1- no		5- 20	no	no
		<u>C1</u>	ay Ana	lysis				
Illite			1	I			I	I
Montmor- illonite	М					M		

Mineyele . Sine invince sh . Sine Serings sh . . Kinney la.

<sup>\*</sup> figure represents actual mineral grain count. - figure represents percentage value.

Table 2c. Mineral and clay analysis.

Minerals	kinne #19:	y 1s.	Kinney la.	Wymor 32:	e sh.	Schro 12	yer 1s
		H	savy Fractic	200			
Biotite Celestite					3*		
Corundum Enstatite				2*			
Fluorite				2			
Carnet Hematite Hornblende Kyanite	1*	2*	6*	3*	2*	2* 3*	1*
Magnetite				58	2*		
Muscovite Pyrite Topaz	2*	4* 5*	18*	65* 4*	26* 2* 1*		
Tourmalene Zireon Conted	1.0		2*	2*	4*		1* 2*
		1.5	ight Practic	on .			
Chalcedony Microsline	96-	96-	95-	84-	73-	98-	97-
Orthoclase Plagioclase	2-	2-	3-	12-	24-	1-	1-
Quartz	2-	2-	1-	4-	3-	1-	1-
Glass Coated	no	no	no	no	no	yes	yes
		C:	lay Analysis				
Illite	I	1	r	I	I	I	I
Montmor- illonite							

<sup>\*</sup> figure represents actual mineral grain count. - figure represents percentage value.

Table 2d. Mineral and clay analysis.

	-		-	-		THE REAL PROPERTY.	-	
Minerals								Threemile 1s.
	- 2	#5 1 #6 1	#39	0	#36 : #37 :	236	1	#8 :#11 : #4

			Heavy	Fract	1 on				
Biotite Celestite Corundum Enstatite Fluorite	2*								2*
Garnet Hematite Hornblende			1° 2*	6*	2* 9*		2*	1*	8*
Kyanite			2*						
Magnetite Muscovite Pyrite	43*	2* 3* 1*		6* 2*	3*	3*			
Topaz Tourmalene								1*	1*
Zircon Coated	4*	1* 6*	1*	3*	2* 5*	1* 2*	1*	2*	1*
			Light	Fract:	lon				
Chalcedony Microcline	96-	95-	93-	90-	94-	95-	98-	96-	97-
Orthoclase Fingioclase	2-	2-	5-	6-	3-	2-	1-	2-	1-
Quartz Glass Coated	2- no	3 no	2- no	4- no	2-	3- no	l- yes	2- no	l- no
			Clay	Analyai	8				
Illite	I	I	1	1	I		I	I	I
Montmor- illonite						M			

<sup>\*</sup> figure represents actual mineral grain count.
- figure represents percentage value.

Table 2e. Mineral and clay analysis.

Minerals	Threemi #35 :	#34	: Spe : #1	1ser : 7:	sh. #3	Spe18 #9 :	er sh. #14
		Hes	avy Fr	actio	n		
Biotite Celestite Corundum Enstatite Fluorite Garnet Hematite Hornblende	1*	1*	2*	4* 2*		3* 1* 1*	fe.
	2* 3*	3*	6*	7*		2*	
Kyanite Magnetite			3*	5*	3*		
Muscovite		6*	12*	17*		15*	96-
Pyrite Topaz				3*	1*	4*	1-
Tourmelene Zircon Coated		1*	2*	3*	1*	1*	3-
		<u>1.1</u>	ght Fr	actic	n		
Chalcedony	93-	98-	99-	96-	98-	99-	97-
Microcline Orthoclase Plagioclase Quartz	4-	1-	1-	2-	1-		2-
	3-	1-		2-	1-	1-	1-
Glass Coated	yes	no	no	no	no	no	no
		Cl	ay Ana	lysis	1		
Illite	I	I	Ī	I	I	I	
Montmor- illonite							М

<sup>\*</sup> figure represents actual mineral grain count. - figure represents percentage value.

Table 2f. Mineral and clay analysis.

Minerals :		on ls. : #20 :	Funston 1s. #21	: Blue	Rapids sh.
		Heav	y Fraction		
Biotite Celestite Corundum Enstatite			1*		
Fluorite Garnet Hematite Hornblende Kyanite	1*	1* 5*	2*		
Megnetite Muscovite Pyrite Topaz Tourmelene	1*	3*			6*
Ziroon Conted			2*		2* 5*
		Ligh	t Fraction		
Chalcedony Microcline	100-	35*	95-		32*
Orthoclase Plagioclase Juartz		1* 1* 12*	5-		20* 10* 35*
Glass Coated	no	no	no		no
		Clay	Analysis		
Illite	I	I	I		I
Montmor- illonite					

<sup>\*</sup> figure represents actual mineral grain count. - figure re resents percentage value.

both as fossil re lace ent and mineral rains.

The plagicclass, whenever twined, was determined by the ichel-Levy method to be oligoclass.

Other heavy minerals present in the limestone were garnet, hematite, zircon, biotite, kyanite, pyrite, topaz, muscovite, corundum, fluorite and tourmaline. Only in the case of sample 30 of the Kinney limestone was there more than a trace of heavy minerals present. In this sample muscovite composed over one-half of the heavy fraction.

Sample 18, also of the Kinney limestone, contained several yellow garnets which, due to the yellow color, were thought to be of the grossularite type.

The heavies in the shale sam les were found to contain a very large number of mineral grains. Muscovite was the dominant mineral in all slides with garnet, zircon, hematite, celestite, biotite, topaz, magnetite, kyanite, hornblende, pyrite, corundum, enstatite, tourmaline and fluorite forming the accessory minerals.

The light fraction of the shale samples contained chalcedony, orthoclase, plagicelase, microcline and quartz. The chalcedony occurred both as mineral grains and fossil replacements. It was the dominant mineral in all but two shale samples and made up over 90 percent of the total light fraction in all but four samples.

In samples 31 and 32 of the 1/ ore shale, chalcedony comprised 73 and 84 percent of the total light fraction respectively with orthograms making up the remaining portion.

In Blue Springs sample 10, orthoclase exceeded chalcedony by 17 percent. Blue Papids sample 22 showed quartz exceeding chalcedony by 6 percent and orthoclase by 18 percent.

# Authigenic Feldspars

In sample 35 of the Threemile limestone, euhedral crystals were observed which proved to be authigenic feldspars.

Fig 1. Authigenic feldspar.

Fig 1. is a drawing of a authigenic feldsper. The detrital nucleus is well rounded showing evidence of transportation and wear. The alteration which has affected the nucleus may be a kaolin coating.

The evidence of rounding and alteration helps to differentiate between the nucleus and the secondary rim.

The sharp crystal boundaries of the secondary rims suggest that the growths are authigenic.

Due to the difficulty of obtaining optical properties on all the grains it is not known whether more than one feldspar type occurs as the nucleus in the authigenic grains.

Several grains on which optical properties could be determined were found to be oligoclase with an authigenic rim of orthoclase.

Johnson (1949) reported authirenic felds ars (oli oclase) from several shale units of the Permian system including the Tymore shale member.

Previous study by other workers has shown the presence of authicenic feldspars in limestones and shales throughout the world.

The presence of authigenic feldspars in a rock unit is believed by Crowley (1939) to be a criterion of marine origin.

Examination of the literature indicates leak of agreement as to when the secondary growth occurred. Some workers believe the growth took place on the sea floor prior to the lithification of the rock unit while others view the action of circulating water as the means for formation.

It is known however, that the secondary growth occurred after the descrition of the nucleus as a detrital grain.

## Examination of Clay Fractions

The clay samples were examined by the differential thermal machine. The term illite was applied to those clays whose reaction showed an endothermic peak between 100-200°C, 500-650°C, and about 900°C and an exothermic peak immediately following the third endothermic peak.

For the clays showing an initial endothermic peak at 100-250°C and a peak between 600-700°C, montmorillonite was listed.

relate II shows characteristic curves of the illite and montmorillonite clays with snaples 45 and 14 from this investigation.

Of samples studied by this method, samples 14(Speiser), 36(Havensville), 28(Blue Springs), and 26(Blue Springs) were found to be dominantly montmorillonite. All others were of the illite group.

Further tests by the clay staining method uning benzidine confirmed these results. The samples containing appreciable amounts of montmorillonite were stained blue while the illite clays were unaffected.

It must be said, however, that these two tests are not conclusive evidence of the absence of clays other than montmorillonite. Grim (1953) stated that unless the clay mineral analysis is made by a combination of differential thermal, X-ray diffraction, and chemical methods, and unless the procedures are detailed, the completeness of the results is questionable.

The methods of differential thermal and staining tests, although not considered conclusive, were believed significant in this study.

## EXPLANATION OF LATE II Differential Thermal Analysis (DTA) Curves

- A. DTA curve of an illite clay sample Grim (1953) p. 197 showing characteristic endothermic peaks at 100-200°C, 500-650°C and about 900°C.
- B. DTA curve of sample 45 showing characteristic illite reaction.
- DTA curve of a mentacrillenite clay sample Grim (1953) p. 198 showing characteristic endothermic peaks at 100-250°C, and between 600-700°C.
- D. DTA curve of samele 14 showing cheracteristic montmorillonite reaction.

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The determination of the clay mineral in the limestone samples was exceedingly difficult as, during the directing process to remove the carbonate matter, some of the clay minerals may have been removed. The results indicate that the clay mineral in the limestones was illite in every case.

## DISCUSSION AND CONCLUSIONS

Certain conclusions may be drawn from the data collected in this investigation. Table 3 depicts the findings in the samples studied.

Volcanic glass was found in all limestone samples conteining short except for number 11 (Florence) and 13 (Threemile).

The absence of ash in these two samples was believed due
either to the method of sampling or possibly complete devitrification of an ash fall and hence complete absence of
the ash in these zones.

In no case has ash been found in shales although parts of some shales contain montmorillonite. These parts are thou ht to represent ash falls with the ash subsequently converted to montmorillonite.

The association of ash with the chert of the Florence, Schroyer and Thresmile limestone formations is thought also to represent ash fails with some ash preserved by the secondary deposition of silica. The two cases where no ash was found in the chert of the Florence and Thresmile formations probably represents the complete devitrification of an ash

fall. It is crobable that ash falling on a muddy bothom would be converted to montmorillonite while ash falling on a limy bottom would not be, although it sight be subsequently devitrified. In other words the bund not of coloium may prevent the formation of montmorillonite when ash is devitrified.

The presence of ash in three of the four limestonechert samples of the Florence limestone examined and in two of the three Three-mile limestone samples and, the complete absence of ash in all the limestone samples in which chert was also absent, is believed simificant. It indicates that the cherts of the limestones studied are due to altered ash falls.

The complete absence of glass or relict structures in the other limestone and shale units was not taken as absolute evidence for the absence of an ash fall during the time which these units were being deposited since small amounts of glass may be completely removed by devitrification.

The presence of a montmorillonite type clay in samples 26 and 28 of the Blue Springs shale, sample 36 of the Havensville shale and sample 14 of the Speiser shale, lives rise to the possibility of an ash fall in which the glass has since been subsequently devitrified and chemically altered to montmorillonite. The presence of montmorillonite must not be taken as absolute evidence of alteration of ash for,

Table 3. Immary of sample onarecteristics.

Florence	17,24,25		Abundant	Tresent	Absent	bundant
do (shale lentil)	13	HH	Abundant	Absent	Absent	bundant bundan
Blue Springs	26,28	2	Absent	Absent	*Abu dant	(Fresent?
op	10,27	03	Absent	Absent	Absent	Abundant
Kinney	18,19,29,30,33	10	Absent	Absent	Absent	Abur ant
ymore shale	31,32	8	Absent	Absent	Absent	Abuniant
Schroyer	12,23	64	Abundant	Tresent	Absent	bund ant
Hevensville shale	5,6,37,38,39	10	Absent	Absent	Absent	bund ant
do	36	7	Absent	Absent	*Abundant	( Pr sent?
Threemile	8,35	63	Abundant	Fresent	Absent	Abund ant
do (shale	11 4,34	48	Abundant	Absent	Absent	Thundant Abundant

Table 3. (Conol.) .

Mamber or or :	formation or ; sample number; rotal number; member ; of samples ;	rotal number of samples	: Chert	: Ash	: ont or : : illouite: Illite	Illite
Speiser	1,2,7,9	4	Absent	Absent	Absent	Abund ant
do (limestone lentil)	3	нн	Absent Absent	Absent Absent	*Abundant Absent	(Tresont:)
Funston	15,21	65	Abent	Absent	Ab ont	Anuncant
do (shale lentil)	20	н	Absent	Absent	Absent	Asundant
Blue Rapids shale	22	7	Absent	Absent	Absent	Abundant

In every case the montavrillonite shale is either at the top or bottom of the shale member.

montmorillonites may be formed by the decomposition of other substances.

The samples containing illite at the major clay may be interpreted as naving no ash or an infinificant amount of ash and therefore the original clay has since been altered to illite as is normal in marine snales.

The silica of the ash may be disolved more or less completely and perhaps furnishes silica to the sedimentary layers above or below this zone of alteration. The presence of silicifica shales and limestones related to vulcanism in the geologic column throughout the world may represent illustrations of this theory.

The ash may, upon devitrification, furnish silica which may be redeposited as chert. Markley (1954) suggested a possible origin of the local chert as due to this. He (Markley) believes as falls occurred at the time in which the limestones containing chert were being deposited. He believes the glass represents as falls during normal lime deposition and the ash parhaps altered to a silica gel and incorporated in the limestone being formed. Due to compaction of these limestones, replacement of the lime or limestone by the silica occurred. The presence of glass shards within the chert we given by Markley as proof for his theory.

It seems probable that the absence of devitrification or alteration of the shard structures within the chart may be due

to the protection of the shards by the silica of the chert.

Ash, deposited at times when the sea favored the formation of shale, may have since been devitrified and is now absent or has been converted to montmorillonite. Probably the silica formed from this alteration of ash in the zones above and below the chert beds has been a factor in the growth of the chert nodules of the limestone. No evidence was found supporting this transportation of silica nor is it possible to measure the amount of ash carried to the sea during Permian times. It appears likely that volcanic ash was deposited intermittently in the sea during Permian times in this area.

The presence of a montmorillonite type clay at the top and bottom of the Blue Springs shale with an illite shale reported in the sampled horizons between and, the presence of montmorillonite at the base of the Havensville and Speiser shales, suggests a change in lithology due to the influx of volcanic material in the sea water.

It has been stated Twenhofel (1953) that normal marine deposition favors the accumulation of limestone and that the formation of other rock types in marine waters is an exception.

In every case the montmorillonite shales were at the top or bottom of the shale in which they were found. They represent changes in lithology other than just a change in the clay mineral deposited. Since disstrophism frequently accompanies vulcanism it is reasonable to expect a change in lithology to be correlated with ash falls in water shallow enough to have decrital addiments.

At those times when the water was clear enough for the deposition of lime the ash falls were altered in a different way and are now represented by chert zones.

Sample 35 of the Threemile limestone formation contained euhedral crystals which, by petrographic analysis, proved to be authigenic feldspars. The evidence of rounding and alteration helped to differentiate between the nucleus and the secondary rim of these feldspars. The nucleus was found to be oligoclase while the secondary growth was orthoclase. Authigenic feldspars have been found, by other workers, in limestones and shales throughout the world. There is still some disagreement as to the time of origin of authigenic feldspars but they probably indicate marine origin.

### RESUME OF CONCLUSIONS

- The presence of volcanic glass shards in the limestone units containing the chart substantiates the theory of the origin of chart as due to an ash fall.
- Meveral eah falls are inferred by the presence of a montmorillonite type clay in the smale zones. This type

clay may be formed from the subsequent Jevitrification of the ash.

- 3. It was found that there is a definite mineral suite which was characteristic of the rocks showing ash and different from similar rocks lacking ash.
- 4. All the limestone samples lacking chert also lacked ash while those limestone samples containing chert, with the a parent exception of samples 11 and 13, showed the presence of ash.
- 5. The presence of illite in the shale samples may represent a lack of ash or an insignificant amount of ash and therefore the original clay has been altered to illite as is normal in marine shales.
- The dominant clay mineral in all the limestone samples was illite. This indicates one of three possibilities;
- (1) a lack of ash, (2) insignificant amount of ash or (3) subsequent devitrification of the ash to form the silica present as chert in some of the limestones. The last hypothesis is the most probable for the cherty limestones.
- 7. The abundance of a montmorillonite type clay at the top and bottom of some shale units suggests a change in lithology due to the influx of volcanic material in the sea water.
- Authigenic feldspars are present in some of the local limestones.

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## MINOR PETROGRAPHIC CONSTITUENTS OF SOME PERMIAN ROCKS

by

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AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the

requirements for the degree

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Department of Geology and Geography

KANSAS STATE COLLEGE OF AGRICULTURE AND APPLIED SCIENCE The purpose of the investigation was to examine the limestones and shales and to investigate the cherts in the Manhattan, Kansas, area to determine some of the minor petrographic constituents of these rocks. Recent investigation has shown the presence of volcanic glass shards in the chert zones of the Florence, Schreyer, and Threemile limestone formations. It was hoped to supplement this finding and to determine whether or not the glass shards are present in the limestones and shales above and below these layers and to determine, if present, their effect on the type rock in which they are present.

The collection area included that of the recent investigation in which the volcanic glass was discovered. All samples were of the "spot" type and sampling was done at definite intervals within the formation.

All samples collected were shale, limestone and chert of the Chase and Council Grove Groups, and of the Barneston, Matfield, Wreford, Speiser, Funston and Blue Rapids formations.

The methods of study consisted of: (1) detrital grain and thin section study with the standard petrographic microscope; (2) clay mineral examination by use of the differential thermal analysis machine and the benzidine staining method; (3) study of the larger fractions of the detrital grains with the binocular microscope and (4) use of the oil immersion method of study of the detrital grains whenever applicable.

Volcanic glass shards were observed in samples of the Florence, Schroyer and Threemile limestone formations.

Authigenic feldspars were found in sample 35 of the Threemile limestone formation. Several grains, on which optical properties could be determined, were found to be oligoclase with an authigenic rim of orthoclase.

The dominant clay mineral in all but four samples was illite. Montmorillonite clay was found in samples of the Speiser, Havensville and Blue Springs shales at definite horizons.

Gertain conclusions were derived from the data collected in this investigation. They were the following:

- 1. The presence of volcanic glass shards in the limestone units containing the chert substantiates the theory of the origin of chert as due to an ash fall.
- Several ash falls are inferred by the presence of a montmorillonite type clay in the shale zones. This type clay may be formed from the subsequent devitrification of the ash.
- 3. It was found that there is a definite mineral suite which was characteristic of the rocks showing ash and different from similar rocks lacking ash.
- 4. All the limestone samples lacking chert also lacked ash while those limestone samples containing chert, with the apparent exception of samples 11 and 13, showed the presence of ash.

- 5. The presence of illite in the shale samples may represent a lack of ash or an insignificant amount of ash and therefore the original clay has been altered to illite as is normal in marine shales.
- 6. The dominant clay mineral in all the limestone samples was illite. This indicates one of three possibilities: (1) a lack of ash, (2) insignificant amount of ash or (3) subsequent devitrification of the ash to form the silica present as chert in some of the limestones. The last hypothesis is the most probable for the cherty limestones.
- 7. The abundance of a montmorillonite type clay at the top and bottom of some shale units suggests a change in lithology due to the influx of volcanic material in the sea water.
- 8. Authigenic feldspars are present in some of the local limestones.

