GEOCHRONOLOGY AND CLAY MINERALOGY OF THE ESKRIDGE SHALE NEAR MANHATTAN, KANSAS

by 45

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INTRODUCTION

Purpose of Investigation

In this investigation I have attempted to apply the Kb-Sr whole rock geochronological method to the dating of sedimentary rocks. The Eskridge Shale was suitable for this study because its age has been approximately . determined paleontologically and many fresh exposures are available.

Area of Investigation

The samples of the Eskridge Shale were collected from four different locations in the vicinity of Manhattan, Kansas. Three sets of samples came from the road cuts on the highways near Manhattan, and one set from an exposure in Sunset Zoo. The exact locations of sampling sites are plotted in Figure 1.

LITERATURE REVIEW

Eskridge Shale

The Eskridge Shale was first named by Prosser (1905) for exposures near Eskridge, Wabaunsee County, Kansas. It is also in southeastern Nebraska, eastern Kansas, and north central Oklahoma. It is classified stratigraphically by the Kansas Geological Survey (Moore et al., 1944) as Lower Permian. It belongs to the Council Grove Group of the Gearian Series. It is overlain by the Cottonwood Limestone Member of the Beattie Limestone and underlain by the Neva Limestone Member of the Grenola Formation. Figure 2 represents a generalized section of the Eskridge Shale and its subdivisions. The

EXPLANATION OF FIGURE 1

Locations of sampling sites of the Eskridge Shale.

FIGURE 1



EC:	sec.12,	T.105,	R.7E
ES:	sec.l3,	T.105,	R.7E
ET:	sec.26,	T.115,	R.8E
EW:	sec.24,	T.105,	R.7E



EXPLANATION OF FIGURE 2

A generalized section of the Eskridge Shale and its subdivisions (Mudge and Yochelson, 1959).

FIGURE 2



Eskridge Shale consists of variegated shales with some thin limestone layers. lts thickness varies from 41 feet in northern Kansas to 22.5 feet in southern Kansas (Wells, 1950). The upper third of the Eskridge Shale is generally gray or gray-green and the lower third is more variegated in color. Individual layers of shale cannot be correlated easily due to lack of adequate sections. Even in the Manhattan area where complete sections are found. correlation is difficult. Lithologic variations occur laterally and in different directions. Some of the beds, however, persist over long distances. According to Wells (1950) the Eskridge Shale was deposited in shallow marine water. On the other hand Laporte (1962) and Imbrie et al. (1959) believed that the Eskridge Shale was deposited in a non-marine environment. Thin coal beds found locally in the Eskridge Shale is interpreted by Laporte (1962) to suggest cyclic sedimentation which is believed by Moore (1959) to be very typical of the Pennsylvanian and Permian rocks in the northern Midcontinent region. Mudge and Yochelson (1959) also believe in the cyclic sedimentation nature of the Pennsylvanian and Permian rocks in Kansas.

Previous studies of the Eskridge Shale by Asmussen (1958), Hargadine (1959), and McPherron (1956) showed that the Eskridge Shale in general contains an abundance of illite, subordinate chlorite, montmorillonite-illite, montmorillonite-chlorite, chlorite-montmorillonite, and montmorillonitechlorite-illite mixed layer clay minerals.

The Eskridge Shale contains an abundance of chalcedony and quartz, minor orthoclase and microcline, and some muscovite, biotite, magnetite, hematite, zircon and topaz (Waterman, 1951), and pelecypods, some gastropods, ostracods, wood fragments, leaves and locally found shark teeth (Mudge and Yochelson, 1959).

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Polytypes

Folytypes of a mineral are those forms having the same composition but different structures. In micas polytypes result because the sub-cell has monoclinic symmetry, and the surface of the sub-cell has hexagonal or pseudohexagonal symmetry. The simplest structures are believed to be the 1M, 1Md, $2M_1$, $2M_2$, 3T, 20 and 6M polytypes (Smith and Yoder, 1956). These polytypes occur in nature under certain temperature and pressure conditions. For example 1M and 1Md are low temperature polytypes whereas 2M is a high temperature polytype. In addition, with metamorphism 1Md converts to 1M which in turn converts to $2M_1$. The fact that the polytypes form under certain environmental conditions has been proved by forming them synthetically in the laboratory under controlled temperature and pressure. However there are other factors that control polytypes such as composition as suggested by Radoslovich (1963).

Rb-Sr Method in the Geochronology of Sedimentary Rocks

The use of radioactive dating methods in geology has increased considerably in the last two decades, and some excellent results have been obtained. The Rb-Sr method is one of these methods and has been very successful. That Rb is naturally radioactive was first observed by Thompson in 1905, but it was not until 1937 that the radioactivity originating from Rb was identified (see discussion in Hamilton, 1965). Of the two isotopes of Rb, Rb^{85} and Rb^{87} , it is the Rb^{87} that decays by beta emission to yield Sr^{87} , and this forms the basis of the Rb-Sr method. Table 1 from Hamilton (1965) gives the isotopic abundances for common rubidium and strontium.

EXPLANATION OF TABLE 1

Isotopic abundances of common Rb and Sr (Hamilton, 1965).

TABLE 1

Lsotope	Abundance (%)	Reference
Rb ⁸⁷	27.85	Nier (1950a)
Rb ⁸⁵	72.15	
Sr ⁸⁸	82.56	Bainbridge and Nier (1950)
Sr ⁸⁷	7.02	
Sr ⁸⁴	0.56	****
Sr ⁸⁶	9.86	

The basic equation used in the Rb-Sr method is:

$$sr^{87} = Rb^{87} (e^{\lambda t} - 1)$$
 (1)

where ${}^{*}Sr^{87}$ is the number of daughter nuclei at time t due to the decay of ${
m Rb}^{87}$, ${
m Rb}^{87}$ the number of parent nuclei at time t, and λ is the decay constant of ${
m Rb}^{87}$. If a system contains non-radiogenic Sr the following holds:

$$Sr^{87} = Sr_0^{87} + Rb^{87} (e^{\lambda t} - 1)$$
 (2)

Because it is easier to measure isotopic ratios rather than the absolute amounts of each isotope we divide both sides of the equation by the abundance of Sr^{86} and get:

$$(\mathrm{Sr}^{87}/\mathrm{Sr}^{86}) = (\mathrm{Sr}^{87}/\mathrm{Sr}^{86})_0 + (\mathrm{Rb}^{87}/\mathrm{Sr}^{86}) (\mathrm{e}^{\mathrm{At}} - 1)$$
 (3)

Here $e^{\lambda t} - 1 = \lambda t$ when $\lambda t \ll 1$, so Equation 3 becomes:

$$(\mathrm{Sr}^{87}/\mathrm{Sr}^{86}) = (\mathrm{Sr}^{87}/\mathrm{Sr}^{86})_0 + (\mathrm{Rb}^{87}/\mathrm{Sr}^{86})$$
 At (4)

A further simplification of the Equation 4 can be made in the form of a function $\theta = At$:

$$\theta = \frac{(sr^{87}/sr^{86}) - (sr^{87}/sr^{86})_0}{Rb^{87}/sr^{86}}$$
(5)

When $\mathrm{Sr}^{87}/\mathrm{Sr}^{86}$ is plotted as ordinate and Rb $^{87}/\mathrm{Sr}^{86}$ as abscissa, as suggested by Nicolaysen (1961), Equation 5 defines a straight line called an <u>isochron</u>, and all samples of same age and initial $\mathrm{Sr}^{87}/\mathrm{Sr}^{86}$ fall on this isochron. The age t can be calculated by dividing the slope of the isochron by λ . This method was used in this investigation for it is quick and accurate and yields an accurate initial $\mathrm{Sr}^{87}/\mathrm{Sr}^{86}$ ratio. The $\mathrm{Rb}^{87}/\mathrm{Sr}^{86}$ ratio is not measured directly but can be calculated from the following relation:

$$(Rb^{87}/Sr^{86})_{atomic} = k(Rb/Sr)_{weight}$$

$$k = \frac{(At. weight Sr) (Rb^{87}/Rb)_{at.}}{(At. weight Rb) (Sr^{87}/Sr)_{at.}}$$

where

k is directly proportional to $\mathrm{Sr}^{87}/\mathrm{Sr}^{86}$ ratio and can be tabulated from a plot of $\mathrm{Sr}^{87}/\mathrm{Sr}^{86}$ versus k. Therefore the final form of Equation 4 is:

$$t = \frac{(Sr^{87}/Sr^{86}) - (Sr^{87}/Sr^{86})_{\mu}}{(Rb/Sr)_{\mu t} k}$$

One of the errors in using this method as in any other radioactive dating method results from the different values of the decay constant chosen by different workers. Glendenin (1961) calculated an average value of 1.47×10^{-11} years⁻¹ which corresponds to a half life of 47 billion years. The other commonly used value is 1.39×10^{-11} years⁻¹ that is equivalent to a half life of 50 billion years (Aldrich et al., 1956). Fifty billion years has been used as the half life of Rb^{67} for this study in order to be consistent with other data reported from the Kansas State University Geochronology laboratory. Aside from the uncertainties in the decay constant, the accuracy of the age obtained by the Rb-Sr method depends on whether the rock remained a closed system. Addition or subtraction of Rb, Sr, or radiogenic Sr can cause high or low ages. Previous work in Australia of dating two shale units gave reasonable ages but a third unit (Compston and Pidgeon, 1962) yielded discordant results attributed to detrital micas that caused large variations in Sr⁸⁷/Sr⁸⁶ ratios. Rb-Sr ages obtained for 20 shales from the Middle Devonian Hamilton Group of New York and Pennsylvania yielded an age up to 15 per cent greater than that accepted for Middle Devonian time (Whitney and Hurley, 1964). This error is attributed to the radiogenic Sr in detrital minerals. Whitney and Hurley (1964) worked with whole rock samples of shale from an area that had never undergone deep burial or intense deformation, and concluded that these factors minimize the errors caused by phase changes during diagenesis and the loss of radiogenic Sr during heating that affect age determinations on mineral separates. Their work on glauconites has resulted in lower ages (10-20%). The major cause for this is thought by them to be the loss of radiogenic Sr due to diagenetic modifications and diffusion during deep burial and heating. Allsop and Kolbe (1965) worked with the Malmesbury sediments in South Africa and found no variations of the initial Sr⁸⁷/Sr⁸⁶ ratio. The isochron they obtained showed good linearity. Therefore these authors concluded the following:

(1) The sediments all came from a single young source area with no addition or subtraction of Rb or Sr. Because no source area of the required age was found, there must have been some chemical exchange with the surrounding medium.

(2) The minerals that contain the most Rb and Sr are probably authigenic even though there were large amounts of clastic feldspars and micas.

(3) Homogenization of the Sr isotopes is probably the cause of the average ratios found for the whole rock. Either diagenesis or metamorphism, the former being the more likely, may have caused the homogenization.

Bofinger and Compston (1967) worked with the Hamilton group of New York and Pennsylvania and found:

(1) That the apparent ages obtained are in fact minima, regardless of the age of the provenance;

(2) that the provenance is not reflected in the apparent age but is reflected in the initial $\rm Sr^{87}/\rm Sr^{86}$ value of any particular isochron;

(3) that this initial $\mathrm{Sr}^{87}/\mathrm{Sr}^{86}$ is predictable in terms of the provenance and that for a common provenance the younger sediments have higher values than the underlying material:

(4) that major variations in the provenance material throughout a single sedimentary unit will be shown by variations in the initial $\mathrm{Sr}^{87}/\mathrm{Sr}^{86}$ while the apparent age remains constant."

It was mentioned above that loss or gain of radiogenic Sr produces errors in the age. Working with shales, Whitney and Hurley (1964) concluded that Sr might be depleted in detrital material during the sedimentary cycle. This might be due to preferential leaching of Sr during weathering and transportation, or Rb fixation (with K) as interlayer cations in "degraded" illite or muscovite or Rb absorption on clay particles. The detrital material in shales may also be derived from a younger source area.

The greater the time difference between the age of the source area and the time of deposition the more critical the problem of inherited Sr becomes. On the other hand detrital mineral grains may exchange Sr with that in the aqueous phase either during transport and/or deposition. Loss or gain of Rb and/or Sr during transport, deposition and/or diagenesis might mask the presence of radiogenic Sr^{87} and change the Rb/Sr of the sedimentary rock (Chaudhuri and Faure, 1967).

Dating of sedimentary rocks by the Rb-Sr method gives better results for older sediments than for younger sediments. For Precambrian sedimentary rocks, for example, the error introduced by inherited Sr is much less than that for Paleozoic or younger or sedimentary rocks (Whitney and Hurley, 1964).

Compston and Pidgeon (1962) have found that carbonaceous shales seem least contaminated with inherited radiogenic Sr. This raises the question, however, whether carbonaceous shales in general possess an extremely low content of detrital mica.

In spite of the difficulties encountered in the application of the Rb-Sr method, it is possible to obtain good results. This method is also valuable in that it provides a check against other dating methods such as the K-Ar and U-Pb methods. Its usefulness can be tested when it is applied to rocks of known age. The use and therefore the value of the Rb-Sr method is increasing rapidly, and it will be used extensively in the future.

Previous Rb-Sr geochronological studies on the Eskridge shale were done by Chaudhuri and Brookins (1967). Their data were also used in this study for comparison.

FIELD PROCEDURE

The samples were collected from exposures vertically, taking care that the weathered portions were first removed. About 300 grams of each sample were obtained from every distinguishable layer in the exposure, and the samples were labeled. The samples were described briefly in the field. These data are tabulated in the appendix.

LABORATORY PROCEDURE

Preparation of Samples for Rb-Sr Geochronology

This involves three steps: first, a preliminary determination of Rb-Sr ratios; second, preparation of samples for determination of isotopic ratios; and third, the mass spectrometry.

Preparation of Samples for X-ray Fluorescence

A portion of each sample was ground by mortar and pestle and was passed through a 100-mesh sieve. This finely ground portion was then packed tightly into the sample holder of a Norelco X-ray fluorescence-diffraction unit. The samples were run from 41 to 35 degrees 20. The instrumental settings are given below:

Target: molybdenum or tungsten	Crystal: topaz
Chart speed: 30 inches/hour	Voltage: 47 Kv
Scan speed: one degree/minute	Current: 45 Ma
Scale factor: 1000	Time constant: 2 seconds
Detector voltage: one kilovolt	Window: 13 volts
	Level: 17 volts

Runs were also made of G-1 standard to obtain the relative intensities of Rb and Sr peaks. Thus the ratios obtained for Rb and Sr of the standard were later corrected by multiplying by a correction factor. The standard G-1 was run several times after repacking between each run.

The ratios of Rb-Sr were obtained in the following manner. After the runs were complete, a base line was drawn for every run passing through three points that were determined by visual examination. This base line was made by using a French curve. The portions between the peak tops and the baseline are proportional to the relative intensities of the peaks. Therefore by measuring these distances the approximate ratios of Rb/Sr are obtained (this method is accurate to \pm 5%). A sample calculation is given in Figure 3. The ratio of Rb/Sr in standard G-1 is 0.8481. Therefore the ratios obtained for this standard in this work had to be corrected to this value. The Rb/Sr ratios of the samples were also modified by the correction

EXPLANATION OF FIGURE 3

Sample calculation of Rb-Sr ratio from X-ray fluorescence run.





Rb/Sr = 5.5 cm/8.5 cm = 0.647

A TYPICAL Rb-Sr X-RAY FLUORESCENCE RUN

factor which was the average Rb/Sr of G-1 obtained in this work divided by 0.8481. All samples were run in at least duplicate. The Rb/Sr data are given in Table 2.

Preparation of Samples for Determination of

Isotopic Ratios

The samples showing the widest range of Rb-Sr ratios were selected after X-ray fluorescence analysis. About one gram of each 100 mesh sample was put into solution in teflon beakers using a mixture of reagent HF and vycor distilled HClO,. To each beaker approximately 2-3 ml of perchloric acid and about 20 ml of hydrofluoric acid were added and the samples were dissolved with occasional stirring with teflon rods. Then the beakers were placed on a hot plate and were left to evaporate. Evaporation was continued until white fumes appeared to ensure that all the hydrofluoric acid has evaporated. After evaporation, the samples were digested in 15 ml of demineralized water and 15 ml of vycor distilled 2N HCl and were again evaporated to near dryness and left to cool overnight. The samples were then dissolved by addition of demineralized water and 2N HCl (same amounts as above). When the samples were in solution then they were ready to be filtered, otherwise more HF was added until the samples were completely dissolved. The samples were then filtered and radioactive Sr^{85} was added to each. To add the correct amount of tracer, first any one sample was taken and about ten drops of tracer was added with a dropper. The radioactivity was tested with a Geiger counter and addition of tracer was continued until a counting rate of at least three times normal background was reached. This amount of tracer was added to all the samples. Each sample was then placed

EXPLANATION OF TABLE 2

Corrected Rb/Sr values obtained by X-ray fluorescence.

TABLE 2

Correction	factor	1,4067		1.2954
EC1		0.3538	ET1	0.3293
EC2		0.2432	ET2	0.7758
EC3		0.1453	ET3	0.6197
EC5		0.1098	ET4	0.9781
EC6		0.1920	ET5	1.2104
EC7		0.09198	ET6	0.4949
EC8		0.4960	ET7	0.1155
EC9		0.3580	ET8	0.1013
EC10			ET9	0.2312
EC11		1.0757	ET10	0.6449
EC12		0.09537	ET11	0.0738
EC13		0.3118	ET12	0.1610
EC14		0.8158		
EC15		0.2669		
Correction	factor	1.303		1.308
ES1		0.0830	EW3	0,0881
ES 2		0.0744	EW4	0.0676
ES3		0.2655	EW5	0.1373
ES4		0.1416	EW6	0.1098
ES 5		0,1273	EW7	0.1691
ES 6		0.1101	EW8	0.0936
ES7		0.0500	EW9	0.1120
ES8		0.6319	EW10	0.0869
ES9		0.6262	EW11	0.0875
ES10		0.1525	EW12	0.1756
ES11		0.1288	EW13	0.6857
ES12		0.1347	EW14	0.0542
ES13		0.4613		
EW1		0.2478		
FU2		0 1000		

Corrected Rb-Sr Data on the Eskridge Shale

on an ion exchange column and allowed to sink into the resin top. Then the columns were filled with 2N HCl and the samples were moved through the resin. The level of the radioactive portions was checked with the Geiger counter. When the radioactive portion reached the bottom of the column collection of the samples was started and was continued until all the radioactivity in the resin disappeared. Collection was made in polypropylene beakers covered with a layer of parafilm to prevent contamination. The beakers were placed on the hot plate and were evaporated to dryness. After removal of the beakers from the hot plate the radioactivity of each was tested with the Geiger counter and those showing the most radioactivity were separated and the rest of them were discarded. To these separated beakers were added about 15 ml of demineralized water and 15 ml of 2N HCl and concentration of the activity was accomplished in teflon evaporating dishes by evaporation. The samples were removed from the hot plate after evaporation to dryness. To each were added a few drops of 2N HCl. The solutions were then transferred to 4 mm vycor glass beakers. These small beakers were put on the hot plate and were evaporated to complete dryness, and they were later fused. After cooling they were covered with parafilm and stored for mass spectrometer analysis.

Mass Spectrometry

The isotopic measurements of strontium were carried out in the Geochemistry laboratory at Kansas State University by Dr. D. G. Brookins. The instrument used was a Nuclide 6-inch, 60-degree direction focussing machine set up for solid source analysis. As this writer did not perform the Sr isotopic analyses, the reader is referred to Chaudhuri and Brookins (in

press) for operational details. The precision about a single $\mathrm{Sr}^{87}/\mathrm{Sr}^{86}$ analysis is ± 0.0005 as determined by replicate analyses on a standard (Eimer and Amend $\mathrm{SrC0}_3$ lot No. 492327). All $\mathrm{Sr}^{87}/\mathrm{Sr}^{86}$ ratios were normalized to a $\mathrm{Sr}^{86}/\mathrm{Sr}^{88}$ ratio of 0.1194.

Petrographic Study

Eight thin sections of the Eskridge Shale were studied with the petrographic microscope. The Eskridge Shale in general contains an abundance of mudrock fragments in a clayey matrix which is stained by hematite and possibly limonite. Terrigenous sediment constitutes the major portion of the Eskridge Shale (60-90%). Silt fragments of quartz, feldspar, heavy minerals such as zircon and magnetite and fossils are in the rock. Calcite cements the rock and occurs as the variety "sparry calcite." Calcite also fills dessication cracks in mudrock fragments and lines cavity walls of fossils. Dolomite is scarce. Muscovite and biotite are quite frequent (10%). The Eskridge Shale shows no signs of metamorphism. Some samples are slightly laminated. Mineralogy is described below in detail.

Quartz and chalcedony together constitute the major portion of the light minerals. Quartz is less abundant than chalcedony and composes about less than 5 per cent of the rock. Its size ranges from 0.01 mm to 0.04 mm. The grains are equant to slightly elongated and angular to subangular, clear and show no overgrowths. Chalcedony is found as cavity fillings and is colorless to pale gray or white.

Calcite constitutes about 5-10 per cent of the rock. It is identified by its high birefringence, twinkling appearance and rhombohedral cleavage. It is found randomly distributed throughout the rock and lining cavity walls of fossils and filling fractures.

Dolomite is scarce (less than 1 per cent) and found as small rhombic grains. It is distinguished from calcite by its characteristic twin structure and small size.

Some orthoclase and microcline are present but in very scarce quantities.

Muscovite occurs as tiny colorless flakes and is moderately abundant (10-15%). Biotite is less abundant and occurs as tiny brown flakes.

Hematite is found as staining the rock to a rusty reddish color and also as small flakes. It is black and opaque under plane polarized light and blood-red under reflected light when it occurs as thin flakes. It is probably an alteration product of magnetite that is found as small black opaque grains.

Limonite occurs as a reddish-brown staining material randomly scattered throughout the rock. It is identified by its reddish-brown color under plane polarized and reflected light.

Some zircon and tourmaline are found in small amounts (less than one per cent). Identification of these minerals were extremely difficult due to very small grain size (0.015-0.04 mm). Zircon and tourmaline show subrounded outlines.

Dessicated shale fragments are abundant, constituting about 15-35 per cent of the rock. They are composed of an illitic and chloritic matrix with abundant muscovite, quartz, feldspar, some zircon and tourmaline.

No attempt was made to identify the clay minerals for this is difficult due to their small grain size.

Clay Mineralogy

Clay mineral study of the Eskridge Shale consisted of the identification of minerals with particle size less than two microns. Types of clay minerals and their polymorphic mixtures of mica like minerals were determined by the X-ray diffraction method for both oriented and random powdered samples. This study was only qualitative and no attempt was made for a quantitative determination of the clay minerals and their polymorphs.

Preparation of Samples for X-ray Diffraction Analysis. 100 gram aliquots of each sample were crushed and ground to a fine size in a mortar and pestle taking care that the grinding was not excessive so as to destroy the structure of the clay minerals. Between each crushing the mortar and the pestle were cleaned and dried to prevent contamination of samples. These ground portions were then placed in a blender and distilled water was added. The blender was turned on for approximately one minute and then the samples were transferred to 500 ml bottles. The samples were left to settle (for 8 hours) and then the top 6 centimeter portions were siphoned and concentrated by centrifuging. The top 6 centimeter portions contain particles of less than 2 microns in size. Care was taken in the settling process so that there was no flocculation of the samples. When flocculation occurred the suspension was decanted without losing any material and more distilled water was added and the procedure repeated. This process was carried on until no further flocculation took place. Two slides were made of each sample. One for air-dried runs and ethylene glycol treatment, and one for heat treatment runs

A Norelco X-ray diffraction unit with a strip chart recorder was used for the clay mineral studies. Runs were first made of air-dried oriented

samples. The samples were then treated with ethylene glycol and were run after a period of one hour had elapsed. Finally the samples were heated to 550° C for one hour and were run again. Each sample was run from 32 degrees 20 to 2 degrees 20. A nickel-filtered copper tube with K_w radiation was used throughout the runs. Instrumental settings used are given below:

Target: nickel-filtered copper	Voltage: 35 Kv
Chart speed: 30 inches/hour	Current: 13 Ma
Scan speed: one degree/minute	Time constant: 2 seconds
Scale factor: 500	Window: 6.0 volts
Detector voltage: 1.7 Ky	Level: 7.0 volts

<u>Preparation of Samples for Powder Diffraction Analysis</u>. Polytypes of illite were identified by powder diffraction method. Finely ground samples were first treated with 2N acetic acid to dissolve the carbonates. They were washed with distilled water and centrifuged before each washing and were left to dry in 50 ml beakers. When they were completely dry they were crushed and ground to minus 200 mesh. A small portion of the samples was packed in the rectangular aluminum sample holder. Runs were made from 62 degrees 20 to 2 degrees 20 at a goniometer speed of one degree per minute.

ANALYS IS

Clay Minerals

Illite is the most abundant and the most frequently occurring clay mineral in the Eskridge Shale. It was in every sample of the Eskridge Shale studied. It was identified from the following diffraction maxima (in angstroms):

	Air-dried	ı*	Glycolated	I	Heated	I
(001)	10.04-10.15	100	10.15	100	10,04	100
(002)	4.97-5.03	13	4.97-5.03	17	4.97-5.00	29
(003)	3.33-3.34	. 28	3.34	42	3.32-3.33	53
4						

I stands for intensity.

Glycolation caused a decrease in the intensity of the illite peaks and the peaks became more symmetrical. Heating to 550° C restored the intensity of the peaks.

Expandible chlorite and chlorite-montmorillonite or chloritevermiculite appear to be the next most abundant clay minerals found in the Eskridge Shale. Identification of these minerals was made from the following reflections:

	Air-dried	I	Glycolated	I	Heated	I
(001)	14.24-14.71	100	14.71-15.49	100	13.38-14.01	100
(002)	7.07-7.18	80	7.18-7.24	100	7.13-7.18	25
(003)	4.74-4.76	40	4.74-4.79	50	4.74-4.79	50

Glycolation caused a decrease in the intensity and the sharpness of the peaks and an increase in the d-spacing. Expandable chlorite and vermiculitechlorite generally expand less than 1 % whereas chlorite can expand as much as 3 %. Because the expansion of these minerals (see above) is less than 1 % it is more likely that the minerals are either expandable chlorite, chloritemontmorillonite or chlorite-vermiculite. The expansion of the d-spacing is more apparent in the (001) reflections than that in (002) or (003) reflections.

Heating caused a further decrease in the intensity of the peaks and

the (001) reflections became broader.

It appears that there is also some illite-montmorillonite mixed-layer in the Eskridge Shale; the low angle side of the illite peaks had a less steep slope than the high angle side before glycolation, and the peaks became more symmetrical after glycolation. This is probably to the expansion of montmorillonite upon glycolation. A list of the clay minerals found in the Eskridge Shale is given in the appendix. Figure 4 is a sample X-ray diffraction pattern of the Eskridge Shale.

Polytypes

The Eskridge Shale contains an abundance of 2M and possibly some HMd and IM polytypes. Identification of the 2M was made from the following reflections:

	20	hk1	_dA
	17.7	004	5.00
	19.8	110	4.48
	21.6	022	4.10
	27.8	114	3.20
	31.2	115	2.86
20:	observed angle in	degrees: CuK ๙	= 1.5418 Å.
d:	interplanar spacin	g in A.	

Identification of the 1M and 1Md polytypes was difficult due to weak reflections. However some of the reflections that possibly characterize these polytypes are given below: EXPLANATION OF FIGURE 4

Sample X-ray diffraction pattern of the Eskridge Shale.



2.0	<u>hk1</u>	_d%_
19.8	020	4.48
24.3	112	3.66
29.0	112	3.07
34.7	130	2.58
36.7	131	2.45
34.9	131	2,56

Identification of the polytypes was made using the data given in Yoder and Eugster (1955). A list of the polytypes in the Eskridge Shale is given in the appendix. Figure 5 is a sample powder diffraction pattern of the Eskridge Shale.

GEOCHRONOLOGY OF THE ESKRIDGE SHALE

Isotopic measurements were made on six samples of the Eskridge Shale (ET group). This group of samples appear to be better representatives of the Eskridge Shale than the others. Table 3 gives the data on the samples analyzed in this study.

An isochron was plotted (see Figure 6) after calculating the slope and the initial intercept by the least squares method. This method gives the best fitting line through a set of data points. A discussion of this method is included in the appendix.

The least squares method gave an initial $\mathrm{Sr}^{87}/\mathrm{Sr}^{86}$ ratio of 0.710. The slope of the isochron was calculated to be 0.00499. Using this value an age of 359 ± 40 million years was calculated for the Eskridge Shale. This age applies to all six samples that were used. Individual ages were calculated for each sample using the value of the initial $\mathrm{Sr}^{87}/\mathrm{Sr}^{86}$ ratio obtained by the least squares method. Table 4 lists the ages obtained for individual

EXPLANATION OF FIGURE 5

Sample powder diffraction pattern of the Eskridge Shale.



EXPLANATION OF FIGURE 6

Isochron plot of the Eskridge Shale (ET group).



EXPLANATION OF TABLE 3

Isotopic data on the samples of the Eskridge Shale (ET group).

Sample	k [*]	Rb/Sr	Sr ⁸⁷ /Sr ⁸⁶	Rb ⁸⁷ /Sr ⁸⁶
ET2	2.898	0.73	0.7202	2.18
ET5	2.900	1.05	0.7257	3.04
ET3	2.897	0.62	0.7166	1.08
ET8	2.896	0.10	0.7114	0.29
ET11	2.895	0.06	0.7102	0.17
ET4	2.899	1.08	0.7237	3.13

TABLE 3

ISOTOPIC DATA ON THE ESKRIDGE SHALE

$${}^{*}k = \frac{(At. weight Sr) (Rb^{87}/Rb) at.}{(At. weight Rb) (Sr^{87}/Sr) at.}$$

EXPLANATION OF TABLE 4

Ages calculated from the samples of the Eskridge Shale (ET group).

TA	B	LE	4

Sample [*]	Individual Age
ET2	337 m.y.
ET5	264 m.y.
ET3	315 m.y.
ET8	371 m.y.
ET11	347 m.y.
ET4	84.6 m.y.

Overall age: 359 ± 40 m.y.

*These samples are from the roadcut on I-70 (ET group). **Based on initial $Sr^{87}/Sr^{86} = 0.710 \text{ and }\lambda = 1.39 \text{x}10^{-11} \text{ y}^{-1}$.

AGES OBTAINED FROM THE SAMPLES OF THE ESKRIDGE SHALE

samples.

Previous work on the Eskridge Shale by Chaudhuri and Brookins (1967) gave an age of 343 million years.

DISCUSSION OF RESULTS

An attempt was made to use the Rb-Sr method of geochronology to determine the age of the Eskridge Shale. A clay mineral study was also made to relate the geochronology to the clays found in the Eskridge Shale. The Eskridge Shale is Lower Permian and is believed to be 280 million years old (Smith, 1964). The age obtained from the isotopic measurements in this study of the Eskridge Shale is 359 \pm 40 m.y. The initial Sr⁸⁷/Sr⁸⁶ ratio was found to be 0.710 \pm 0.002 and the slope of the isochron 0.00499.

The least squares analysis using the data from this study combined with the data of Chaudhuri and Brookins (1967) gave an age of 372 ± 44 million years. The initial $\mathrm{Sr}^{87}/\mathrm{Sr}^{86}$ ratio was calculated to be 0.7086 \pm 0.002 and the slope 0.00518.

Calculations of the ages were done following the method described by Bottino and Fullagar (1966); first the initial Sr^{87}/Sr^{86} ratio and the slope were calculated using the least squares analysis and then the age was obtained using the slope. Individual ages were calculated for each sample except for the ones with a Rb^{87}/Sr^{86} ratio less than one. Finally the standard deviation of the ages was calculated from the individual ages (see Table 5).

The discrepancy between these ages and the 280 m.y. age is too large to be attributed to the analytical and systematic errors alone and must come from a different source or sources.

EXPLANATION OF TABLE 5

Ages obtained from the samples of the Eskridge Shale and Stearns Shale.

- T	Δ.		E.	5
	n	Dr	مذد	2

Overall age: 372 ± 44 * m.y.

Sample ^{**}	*** Individual ages
М-З	673 m.y.
M-4	418 m.y.
L-1	361 m.y.
L-2	333 m.y.
L-3	354 m.y.
U-1	417 m.y.
1072	386 m.y.
1073	359 m.y.
1074	363 m.y.
1075	394 m.y.
1078	363 m.y.
ST4	446 m.y.

*44 m.y. is the standard deviation of the ages.
**Chaudhuri and Brookins (1967):

M,L,U = Eskridge Shale

1072-1078 = Stearns Shale

ST4 = Insoluble residue from Cottonwood Limestone **** Based on initial $\mathrm{Sr}^{87}/\mathrm{Sr}^{86}$ = 0.7086 and λ = 1.39x10⁻¹¹ y⁻¹ The isochron method of dating sedimentary rocks gives good results only for rocks that have uniform initial $\mathrm{Sr}^{87}/\mathrm{Sr}^{86}$, different $\mathrm{Rb}^{87}/\mathrm{Sr}^{86}$ ratios, and which have remained as a closed system to Rb and Sr. If a suite of rocks satisfies these requirements the plot of the points representing the rocks will define a straight line with each point falling on the line. The initial $\mathrm{Sr}^{87}/\mathrm{Sr}^{86}$ ratio represents the isotopic composition of the Sr at the time of the formation of the rocks. The isochron plot of the Eskridge Shale (see Figure 4) did not show good alignment of the data points on the isochron. This might be to one or more of the following alternatives:

- (1) Complete homogenization of the Sr isotopes did not take place.
- The rock contains detrital material that was derived from older source areas.
- (3) Lack of data.

Petrographic study of the Eskridge Shale showed that it contains an abundance of mudrock fragments (15-35 per cent) and other terrigenous sediment. On the other hand no evidence for metamorphism was observed in the Eskridge Shale. Study of the polytypes showed that the Eskridge Shale contains abundant 2M and possibly some minor amounts of 1M and 1Md polytypes. Because the 2M is a high temperature phase and would not be found with 1M and 1Md in a low temperature environment, the author thinks that at least the 2M is detrital and must have come from older source areas. The abundance of mudrock fragments and other terrigenous sediment also suggest that the detrital material in the Eskridge Shale is probably one of the causes for the high age.

The initial $\mathrm{Sr}^{87}/\mathrm{Sr}^{86}$ ratio for both sets of data is $\rightleftharpoons 0.710$. This figure is somewhat higher than the probable 0.708 Permian sea water value

but still suggests that large scale re-homogenization of Sr isotopes did not take place during diagenesis or epigenesis, otherwise higher initial Sr^{87}/Sr^{80} ratios and a lower age would have resulted.

The loss or gain of Rb and/or Sr during transportation, deposition and/or diagenesis might have also contributed to the high age obtained, but no concrete conclusions can be made due to lack of analytical data.

CONCLUSIONS

- The 2M illite is the most abundant clay mineral in the Eskridge Shale.
- (2) The Rb-Sr geochronological study along with no petrographic evidence for metamorphism and abundant terrigenous sediment leads to the conclusion that the detrital material probably accounts for the high age obtained.
- (3) The initial Sr⁸⁷/Sr⁸⁶ ratio for both sets of data is ≤ 0.710. This suggests that severe re-homogenization of Sr isotopes did not occur during diagenesis or epigenesis, otherwise a higher initial Sr⁸⁷/Sr⁸⁶ ratio and a lower age would have resulted.
- (4) This writer suggests that, in order to more accurately determine the age of deposition of sedimentary rocks, future approaches should be aimed at methods for non-destructive separation of different polytypes of illite.

ACKNOWLEDGMENTS

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The Least Squares Method

In using the Rb-Sr rock dating method one faces the problem of obtaining the best isochron. An isochron is a straight line, the slope of which is used to calculate the age of a rock or mineral. The better the fit of this line into a set of points the more accurate the age will be. This is where the least squares method comes into application. In general, the equation of a straight line is given as y = bx + a where a is the intercept on the y-axis and b is the slope. The least squares method is used to calculate these two parameters that will define the line fitting best into a set of points. The slope and the y-intercept are calculated from the following equations (Youden, 1964):

$$b = \frac{N \Sigma x y - \Sigma x \Sigma y}{N \Sigma x^{2} - (\Sigma x)^{2}}, \qquad a = \frac{\Sigma y \Sigma x^{2} - \Sigma x \Sigma x y}{N \Sigma x^{2} - (\Sigma x)^{2}}$$

Here N is the number of points plotted. In the Rb-Sr method the $\text{Rb}^{87}/\text{sr}^{86}$ is plotted on the x-axis and the $\text{Sr}^{87}/\text{sr}^{86}$ on the y-axis. Therefore in order to calculate the slope and the y-intercept of the isochron one substitutes in the equation above $\text{Rb}^{87}/\text{sr}^{86}$ for x and $\text{sr}^{87}/\text{sr}^{86}$ for y. The slope calculated is equal to At where A is the decay constant of Rb^{87} and t is the age. The age obtained from the slope is one that applies to all the data points. Once the y-intercept has been obtained separate ages can be calculated for each individual point (Bottino and Fullagar, 1966). These authors used the initial $\text{Sr}^{87}/\text{sr}^{86}$ (y-intercept) which they determined by drawing the best fitted line and then calculated the ages of the individual samples and determined the standard deviation of the mean of the ages of all samples.

	illite	mont.	chlor.	illite- mont.	chlor mont.	chlor vermic.	calcite	dolomite
301	+	+	°* +	ı	°.+ +	**	ı	i
303	+	ı	÷	+	÷+	I	+	ı
508	+	+	2+	+	¢. +	¢* +	+	ı
SC11	+	44	+	+	°+	:+	+	ı
SC1 4	÷	+:+	+	÷	÷+	2+	+	I
IW2	+	:+	î	+	÷-	¢;-	+	+
W2	+	÷+	° I	+	+	÷	+	ı
EW3	+	÷+	I	+	+3	¢.+	ı	ı
6M3	+	÷+	+	÷	°+	°.+	+	+
W13	+	:+	+	+	÷+	°. +	ı	ı
W14	+	÷+	+	+	:+	°. +	+	ı

CLAY MINERALS OF THE ESKRIDGE SHALE

dolomíte	ı	ı		ı	ı	ı	ı	ı	+	+
calcite	+	÷	ı	+	+	ı	ı	ı	+	+
chlor vermic.	¢+	÷+	÷+	¢÷ +	°* +	+	ċ+	+	÷+	÷+
chlor mont.	÷+	÷+	÷+	¢+	÷+	÷	:+	÷		÷+
illite- mont.	1	+	÷	1	+	ı	+	I	ı	1
chlor.	÷	1	č+	ł	+	+	+	+	:+	ı
mont.	č+	÷+	÷+	÷	÷+	+	2+	÷	÷+	÷+
illite	+	÷	+	+	÷	+	+	+	+	+
	ES 2	ES3	ES8	ES13	ET2	ET3	ET4	ET5	ET9	ET12

POLYTYPES OF ILLITE IN THE ESKRIDGE SHALE

ET1:	2M,	1M	EC1:	2M, 1M
ET8:	2M,	1Md or 1M(?)	EC2:	2M, 1Md(?)
ET10:	2M,	1Md or 1M(?)	EC5:	2M, 1Md or 1M(?)
ET13:	2M,	1M	EC6:	2M, 1Md
			EC8:	2M, 1M
EW5:	2M,	1Md or 1M(?)	ES3:	1Md, 2M(?)
EW7:	2M,	1Md or 1M(?)	ES6:	1 Md
EW9:	2M,	1Md or 1M(?)	ES10:	1Md, 2M(?)
EW12:	2M,	1M	ES12:	2M, 1Md
EW13:	2M,	1M	ES13:	2M, 1Md

DESCRIPTION OF SAMPLES

Location: Sec.12, T.105, R.7E, roadcut on Highway 412, 1.4 mi from junction of 412 and 113, northwest of Manhattan

Sample	ũ	Thickness (cm)	Distance from the base of Cottonwood Limeston
EC1:	grayish yellow (5Y 7.5/4) [*] limy shale	35	20
EC2:	pale greenish yellow (10Y 7.5/2) limy shale	60	55
EC3:	yellowish gray (5Y 6/2) limy shale	4.5	115
EC4:	yellowish gray (5Y 8/1) limestone	40	150
EC5:	very light gray (N 8.5) limy shale	30	190
EC6:	pinkish gray (5YR 7/1) limy shale	60	220
EC7:	yellowish gray (5Y 7/1) limy shale	30	280
EC8:	light brownish gray (5YR 7/1) limy shale	65	310
EC9:	grayish orange pink (5YR 6/2) limy shale	35	375
EC10:	light brownish gray (5YR 7/1) limestone	45	410
EC11:	greenish gray (5GY 6.5/1 limy shale	45	455
EC12:	yellowish gray (5Y 7.5/1) limy shale	40	500
EC13:	greenish gray (5GY 6.5/1) limy shale	70	540
EC14:	greenish gray (5GY 6/1) limy shale	60	610
EC15:	light brownish gray (5YR 5.5/1) limy shale	50	670
*			

Colors are described according to Rock-Color Chart, National Research Council, Washington D.C., 1948.

Manhattan
of
west
Park,
Warner
from
across
18,
Highway
uo
roadcut
R.7E,
T.10S,
Sec.12,
Location:

e e

Sampl	Ũ	Thickness (cm)	Distance from the bas of Cottonwood Limesto
EW1:	yellowish gray (5Y 7/2) limy shale	35	15
EW2:	pale greenish yellow (10Y 7/2) limy shale	60	50
EW3:	grayish yellow (5Y 7/4) limestone	10	110
EW4:	yellowish gray (5Y 7.5/1) limy shale	15	120
EW5:	light greenish gray (5GY 7.5/1) limy shale	10	135
EW6:	pale brown (5YR 6/2) shale	20	155
EW7:	pale olive (10Y 5.5/2) shale	20	175
EW8:	yellowish gray (5Y 7/2) limy shale	65	240
EW9:	greenish gray (5GY 7/1) limy shale	15	255
EW1 0:	pale brown (5YR 6/2) limy shale	25	280
EW11:	light olive gray (5Y 6/2) limy shale	50	330
EW12:	light olive gray (5Y 7/1) limy shale	20	350
EW13:	medium gray (N 5.5) limy shale	15	345
EW14:	light gray (N 7.5) limestone	25	370

10 CAL	1011: Sec.20, 1.113, K.85, TOAGCUT ON 1-/U COWATGS TOP	eka, 2.9 mi from junctio	on of I-70 and K-177
Sample	e 1	nickness (cm) Dif of	stance from the base Cottonwood Limestone
ET1:	yellowish gray (5Y 7/2) limy shale	20	10
ET2:	yellowish gray (5Y 7/2) limy shale	50	30
ET3:	yellowish gray (5Y 7/2) limy shale	40	80
ET4:	pale brown (5YR 5/2) limy shale	75	120
ET5:	pale brown (5YR 5/2) shale	40	195
ET6:	light olive gray (5Y 6/1) limestone	60	235
ET7:	light olive gray (5% 6/2) limy shale	25	260
ET8:	grayish orange pink (5Y 6/2) limy shale	25	285
ET9:	light olive gray (5Y 7/1) limy shale	20	305
ET1 0:	yellowish gray (5Y 7.5/1) limy shale	55	360
ET11:	grayish red (R 5/2) shale	45	405
ET12:	light brownish gray (5YR 7/1) limestone	35	440
ET13:	light olive gray (5% 7/1) limestone	25	4:65

locat	ion: Sec.13, T.10S, R.7E, Sunset Zoo, Manhattan		
Sample	Q	Thickness (cm)	Distance from the base of Cottonwood Limestone
ES1:	yellowish gray (5Y 8/1) limy shale	35	10
ES2:	yellowish gray (5Y 8/1) limy shale	60	50
ES3:	yellowish gray (5Y 6.5/2) limy shale	4.0	110
ES4:	pale greenish yellow (10Y 8/2) limy shale	30	150
ES5:	yellowish gray (5Y 8/1) limy shale	30	180
ES6:	yellowish gray (5Y 8/1) limy shale	15	210
ES7:	light greenish gray (5GY 8/1) limestone	25	225
ES8:	pale yellowish brown (10YR 6.5/2) shale	40	250
ES9:	light olive gray (5% ó.5/l) limy shale	30	280
ES10:	very light gray (N 8.5) limy shale	15	295
ES11:	light brownish gray (5YR 7/1) limy shale	50	345
ES12:	light gray (N 7.5) limy shale	55	400
ES13:	greenish gray (5GY 7/1) limy shale	50	450
ES14:	pale brown (5YR 6/2) limestone	25	475
ES15:	medium light gray (N 6) limy shale	40	515
ES16:	light olive gray (57 7.5/1) limy shale	20	535

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GEOCHRONOLOGY AND CLAY MINERALOGY OF THE ESKRIDGE SHALE NEAR MANHATTAN, KANSAS

by

ERHAN DULEKOZ

B. S., University of Illinois, 1966

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Geology and Geography

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In this investigation an attempt was made to apply the Rb-Sr whole-rock geochronological dating method to the Eskridge Shale. A clay mineral study was also made to relate the geochronological results to the clays found in the Eskridge Shale. Samples were collected from locations near Manhattan, Kansas. Identification of clay minerals and their polytypes was made by X-ray diffraction analysis.

The Eskridge Shale contains abundant illite, randomly interstratified chlorite and montmorillonite, chlorite and vermiculite, and illite and montmorillonite. The dominant illite polytype is 2M with possibly some 1Md and 1M.

Preliminary determination of Rb-Sr ratios was made by the X-ray fluorescence method and the samples with suitable Rb-Sr ratios were chosen for isotopic analysis. Isotopic measurements were made by the use of a mass spectrometer.

Calculation of the ages was made from the isochron plot of the analyzed samples. Least squares analysis was employed to calculate the most accurate slope and the initial $\mathrm{Sr}^{87}/\mathrm{Sr}^{86}$ ratio. Previous geochronological data on the Eskridge Shale were used for comparison with this study.

The age calculated in this study is 359 ± 40 m.y. with an initial $\mathrm{Sr}^{87}/\mathrm{Sr}^{86} = 0.7100 \pm 0.002$. This age along with the 372 ± 44 m.y. age with initial $\mathrm{Sr}^{87}/\mathrm{Sr}^{86} = 0.7086 \pm 0.002$ from the combined data of this study and previous work on the Eskridge Shale are considerably higher than the presumed 280 m.y. Lower Permian age to which the Eskridge Shale is assigned.

No petrographic evidence for metamorphism in the Eskridge Shale exists. This fact, coupled with the abundance of 2M illite and mudrock fragments. suggests that the Eskridge Shale is in part composed of detrital material that probably accounts for the high age. Loss or gain of the Sr isotopes during the sedimentary cycle probably account for the scatter in the analytical data.