# GEOCHEMICAL INVESTIGATION OF DIAGENETIC HISTORY OF PENNSYLVANIAN MORROWAN SANDSTONE, LEXINGTON FIELD, CLARK COUNTY, KANSAS

by

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# INTRODUCTION

## SCOPE OF THE STUDY

Crustal rocks differ widely in their Sr isotopic composition. These differences make possible the use of Sr isotopes as a tracer in the study of geologic systems that resulted from different fluid-rock interactions. Cementation of sedimentary rocks is a complex process which involves interactions among different minerals, rocks, and fluids of the crust. Knowledge of the history of cements in sedimentary rocks is important because it facilitates the study of the migration and accumulation of hydrocarbons in reservoir rocks. The Sr isotopic analyses of cements, in conjunction with petrographic, chemical, and other isotopic data, can be used to determine the origin of cementing materials and the relation of cementation processes to the paleohydrology of the basin.

An effective way of studying cements is by analyzing the chemical and other isotopic compositions of both cements and fluids associated with the rocks. The availability of fluids and samples of reservoir rocks from oil fields often creates an opportunity to investigate the diagenetic history of the oil-bearing strata.

This study reports on the chemical and isotopic compositions of carbonate cements in sandstones from both producing and non-producing zones and of waters associated with the reservoir rocks in the Lexington field, Clark County, Kansas. Major objectives of this investigation included determination of: 1) the chemistry of the waters, 2) the source and evolution of the cements, and 3) the extent of the influence of the present formation water on the cementation history of the rocks.

## PREVIOUS INVESTIGATIONS

Chaudhuri (1978) studied oil-field waters in Kansas and eastern Colorado and showed that brines are often enriched in radiogenic Sr, the range of $^{87}Sr/^{86}Sr$ ratios reported being from 0.7110 to 0.7331. Chaudhuri and Bias (1978) analyzed brines associated with sandstones of the Cherokee Group of the Pennsylvanian System in Ness County, Kansas. They reported that the $^{87}Sr/^{86}Sr$ ratios of the brines ranged from 0.7249 to 0.7262 and some waters were in isotopic equilibrium with potassium feldspar, but not with clay minerals or carbonate cements of the reservoir rocks.

Sunwall and Pushkar (1979) studied the isotopic composition of Sr from oil-field waters in southeastern Ohio. They suggested that the $^{87}Sr/^{86}Sr$ ratios reflected local ground and stream water and the carbonate minerals in the enclosing rocks seemed to be the dominant factor controlling the $^{87}Sr/^{86}Sr$ ratios of the fluids.

Stanley and Faure (1979) studied the isotopic composition and sources of Sr in sandstone cements in the High Plains sequence of Wyoming and Nebraska. They reported that carbonate cements from the Arikaree Group and Ogallala Group of the High Plains sequence had $^{87}Sr/^{86}Sr$ ratios of 0.7103 to 0.7112, respectively, and that potassium feldspar associated with arkosic sandstones was the principle contributor of radiogenic $^{87}Sr$ to the cements.

## HISTORY OF OIL PRODUCTION

The Lexington field was discovered in 1977 by Mesa Petroleum Company. Initial production was from the Mississippian St. Louis

Limestone. In 1978 production was established from sandstones of the Morrowan Stage (Paul and others, 1980). Presently there are 13 Morrowan oil and gas wells, 12 St. Louis oil and gas wells, and one commingled Morrowan-St. Louis oil well. Cumulative oil production as of June, 1982, was 1,780,893 barrels, and cumulative gas production as of July, 1981, was 2,626 million cubic feet.

## G E O L O G Y

### REGIONAL AND TECTONIC SETTING

The Lexington field, in the northeastern part of Clark County, Kansas, is in the Hugoton Embayment on the northern flank of the Anadarko Basin. Major pre-Desmoinesian, post-Mississippian structural features that border this study area are the Central Kansas Uplift, 50 miles to the northeast and the Pratt Anticline 25 miles to the east (Merriam, 1963)(Figure 1).

### STRATIGRAPHY

The oldest formation of primary interest to this investigation is the St. Louis Limestone. The formation is present throughout the study area and is a light gray, fossiliferous micrite that is slightly dolomitic and oolitic, and is about 200 feet thick (Figure 2).

The St. Louis Limestone of the Meramecian Stage of the Mississippian System is unconformably overlain by rocks of the Morrowan Stage. Rocks of the Morrowan Stage are generally confined to paleo-topographic lows on the underlying St. Louis Limestone. Rocks deposited during the Morrowan Stage are sandstone and interbedded shale. The sandstones are light olive-gray to brownish gray, fine- to medium-grained, ankeritic,

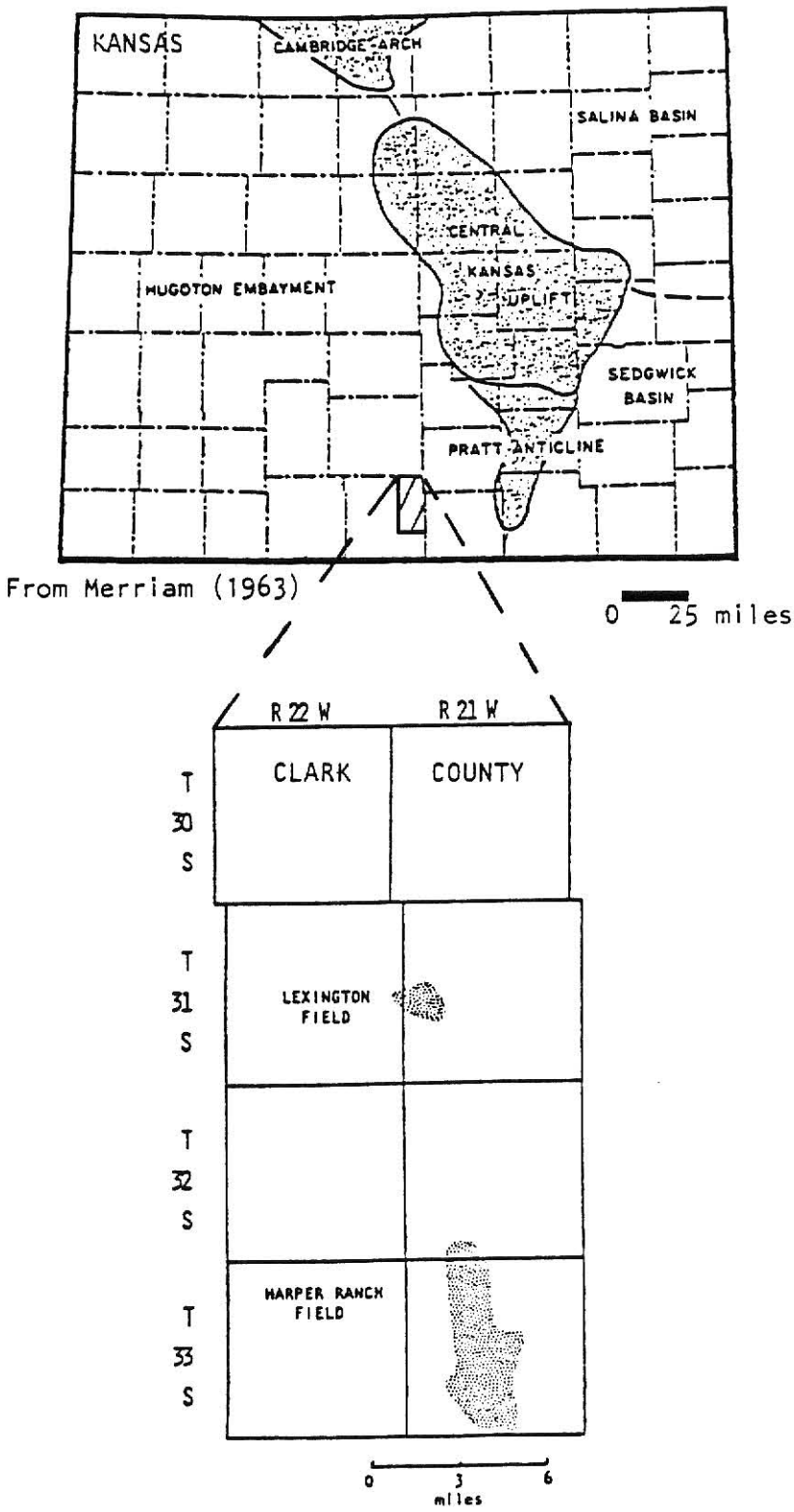



Figure 1. Location of Lexington field in relation to major pre-Desmoinesian post-Mississippian structural features of Kansas.

slightly cherty quartz arenites with thicknesses up to 40 feet. Carbonate cements locally constitute up to 50 percent of the total rock volume. Shales in this zone are dark gray, slightly carbonaceous and pyritic, and up to 25 feet thick. The overall thickness of Morrowan Stage rocks ranges from near zero to 150 feet.

Rocks of the Morrowan Stage of the Pennsylvanian System are unconformably overlain by rocks of the Atokan Stage which in the subsurface of this area have been called the "Thirteen Finger lime" (Mannhard and Busch, 1974). The "Thirteen Finger lime" constitutes the entire Atokan Stage of the Pennsylvanian System and consists of thin interbedded limestones and shales. Mannhard and Busch (1974, p. 450) stated that: "*** the "Thirteen Finger lime" is light brownish-gray to gray, mottled, fossiliferous, and finely crystalline. The interbedded shales are gray to dark gray, pyritic, micaceous, and fossiliferous." The "Thirteen Finger lime" ranges from near zero to 30 feet thick, with the thin limestone beds no more than 10 feet thick. The type locality of the "Thirteen Finger lime" is designated as Gulf Oil Company's No. 1 Stump, Section 12, Block 4T - T. & N.O. Survey, Ochiltree County, Texas (Jordan, 1957).

The "Thirteen Finger lime" is conformably overlain by the Inola Limestone Member of the Krebs Formation (Mannhard and Busch, 1974). Mannhard and Busch (1974, p. 450) stated that:

> "*** the Inola Limestone is well developed throughout the area. It is an excellent lithologic time-marker bed because of its lateral persistence and nearly constant thickness. This unit is a light brownish-gray, compact to very fine-grained, sparsely fossiliferous limestone with an average thickness of about 8 feet."

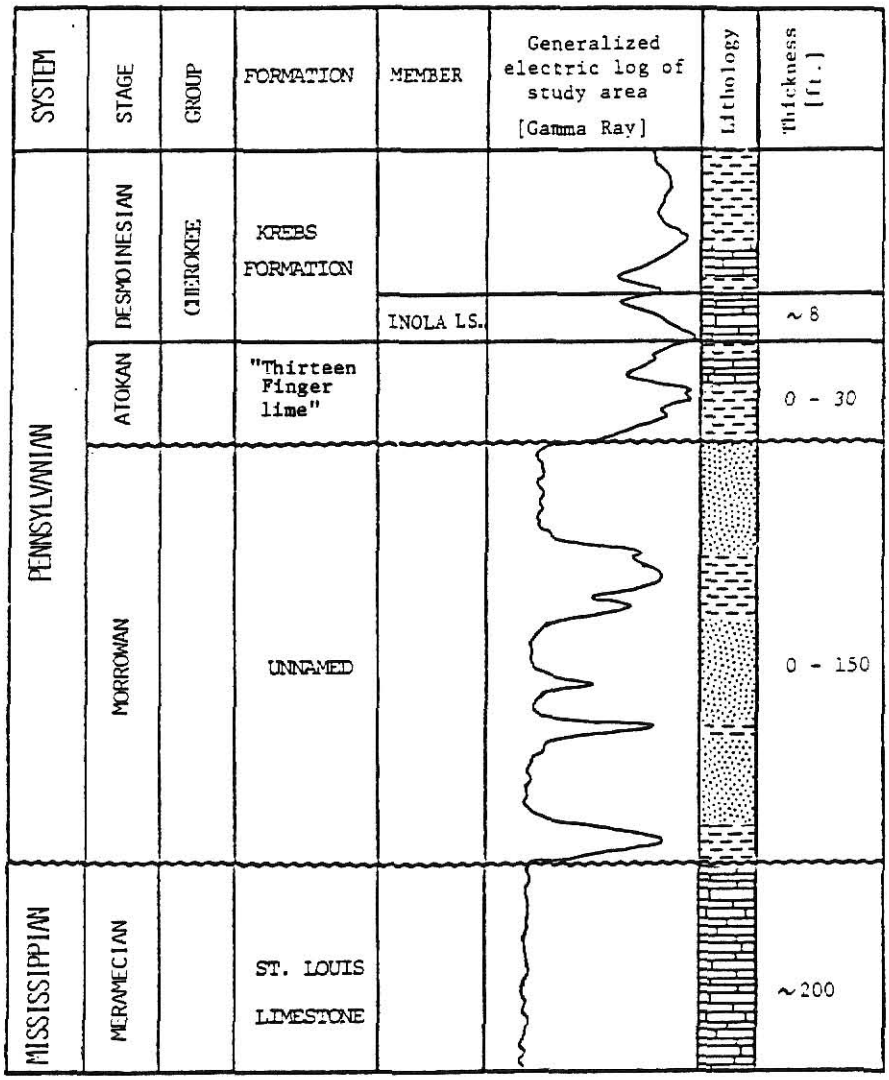



Figure 2. Stratigraphic column for the Lexington field, Clark County, Kansas (Based on correlation from Kansas Geological Society, 1966: Type log for Clark County, Kansas).

The Inola Limestone Member of the Krebs Formation belongs to the Cherokee Group of the Pennsylvanian System and was named for exposures near the town of Inola, Rogers County, Oklahoma by Lowman in 1932 (Jordan, 1957). The Inola Limestone Member of the Krebs Formation is conformably overlain by beds of limestone and shale of the Krebs Formation.

## GEOLOGIC HISTORY

Allen (1955), Barrett (1965), Khaiwka (1968), Forgotson (1970), Kasino and Davies (1979) and Swanson (1979) investigated the diagenetic and structural histories of the Morrowan Stage in northwestern Oklahoma. Mannhard and Busch (1974, p. 457) studied the beds of sandstone of the Morrowan stage in the Harper Ranch field, Clark County, Kansas, twelve miles south of the Lexington field (Figure 1) and reported that:

> "*** at the close of Mississippian time, northwestern Oklahoma and adjacent Kansas were subjected to epeirogenic upwarp. As a result, Upper Mississippian strata were elevated above sea level, homoclinally tilted toward the southwest, and exposed to subaerial erosion. A well-developed drainage system was established on the truncated Mississippian strata.* * * Tilted resistant limestone beds of the Chesterian Series stood out as subparallel cuestas with dip slopes toward the southwest. Intervening strike valleys were eroded into the nonresistant shale beds.* * *
>
> Subsidence in the Anadarko Basin in early Pennsylvanian time was accompanied by a marine transgression toward the northeast. The strike valleys were drowned progressively as the sea transgressed farther northeast. Transgression was cyclic and interrupted by several minor regressions. During these regressive phases with their associated shallow-water conditions sands were deposited. The interbedded muds were deposited when deeper water conditions returned during transgressive phases. The lowermost sandstone bodies in the section were concentrated largely within the confines of the submerged strike valleys. As the valleys were filled with sediment, the thickness and configuration of succeeding individual sandstone bodies were controlled to a progressively lesser extent by the underlying

topography.

> The marine transgression in Morrowan time continued into Atokan and Desmoinesian times. Complete submergence of the investigated area was effected with the deposition of the Inola Limestone."

The author of this study assumes the geologic history of this area is similar to that described above by Mannhard and Busch (1974), except that in this study area rocks of the Morrowan Stage unconformably overlie the St. Louis Limestone of the Meramecian Stage, whereas in the Harper Ranch field, rocks of the Chesterian Stage unconformably are overlain by rocks of the Morrowan Stage.

## SUBSURFACE STRUCTURE OF THE LEXINGTON FIELD

A structural contour map, having the base of the Inola Limestone as datum, was prepared (Figure 3). The base of the Inola Limestone was chosen due to its reliable identification and its "top" reported on completion cards. An isopachous map of the Morrowan Stage was also prepared (Figure 4).

Following Andresen's (1962) suggestion that an isopachous map can be used to show paleo-drainage patterns, the isopachous map of the Morrowan Stage indicates that in pre-Morrowan time a south flowing stream was present before the seas transgressed in Morrowan time. Figure 4 illustrates the paleo-drainage pattern in this study area.

Most of the structures indicated on the structural contour map on the base of the Inola Limestone are a result of differential compaction. In comparing the structure map on the base of the Inola Limestone to that of the isopachous map of the Morrowan Stage, the structural lows on the base of the Inola Limestone generally coincide with the axes of

maximum Morrowan thickness due to thicker shale sequences in the valley fill. This suggests that most of the structures indicated on the base of the Inola Limestone structural map are a result of differential compaction.

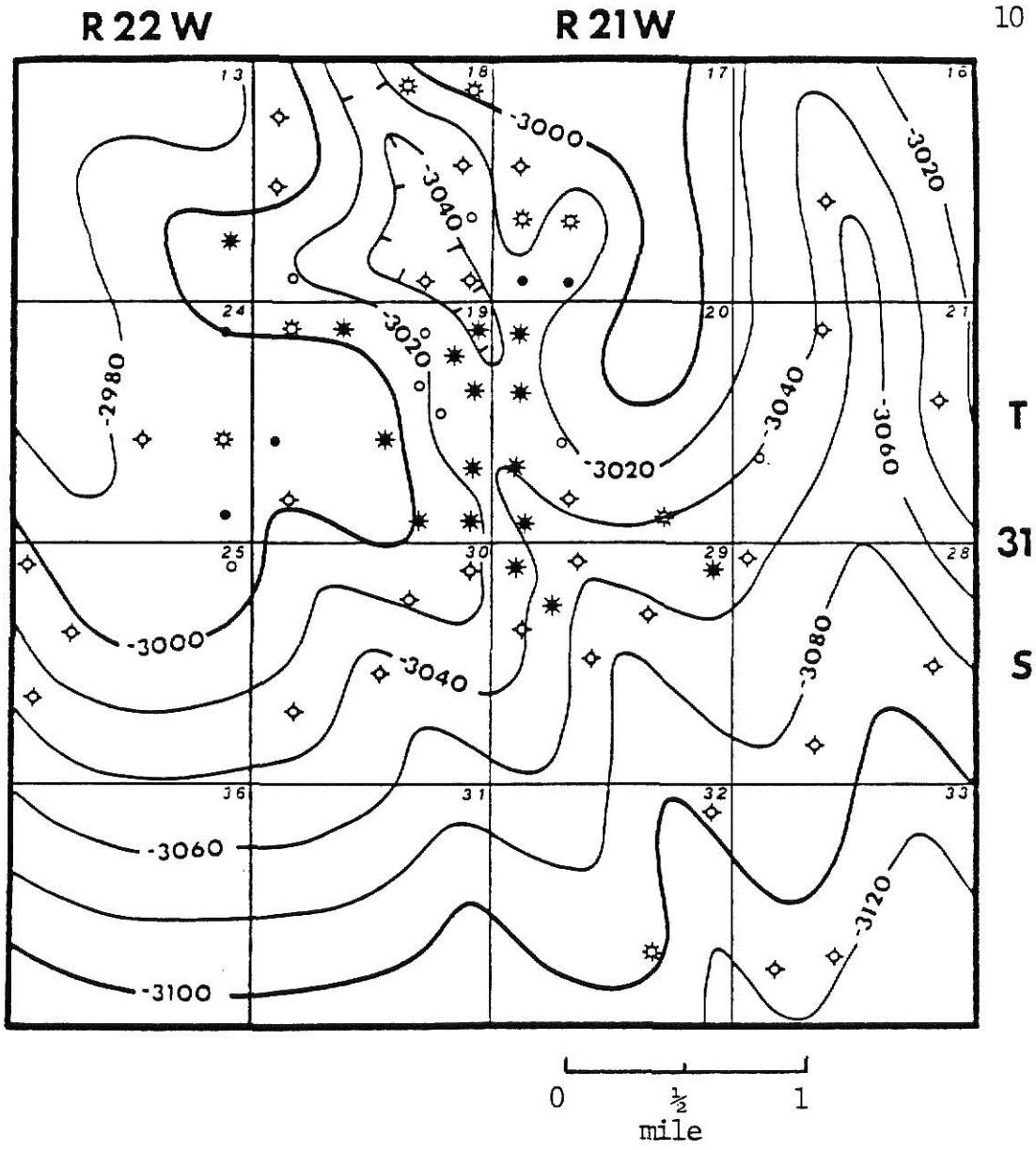



Figure 3. Structural contour map on the base of the Inola Limestone, Lexington field, Clark County, Kansas

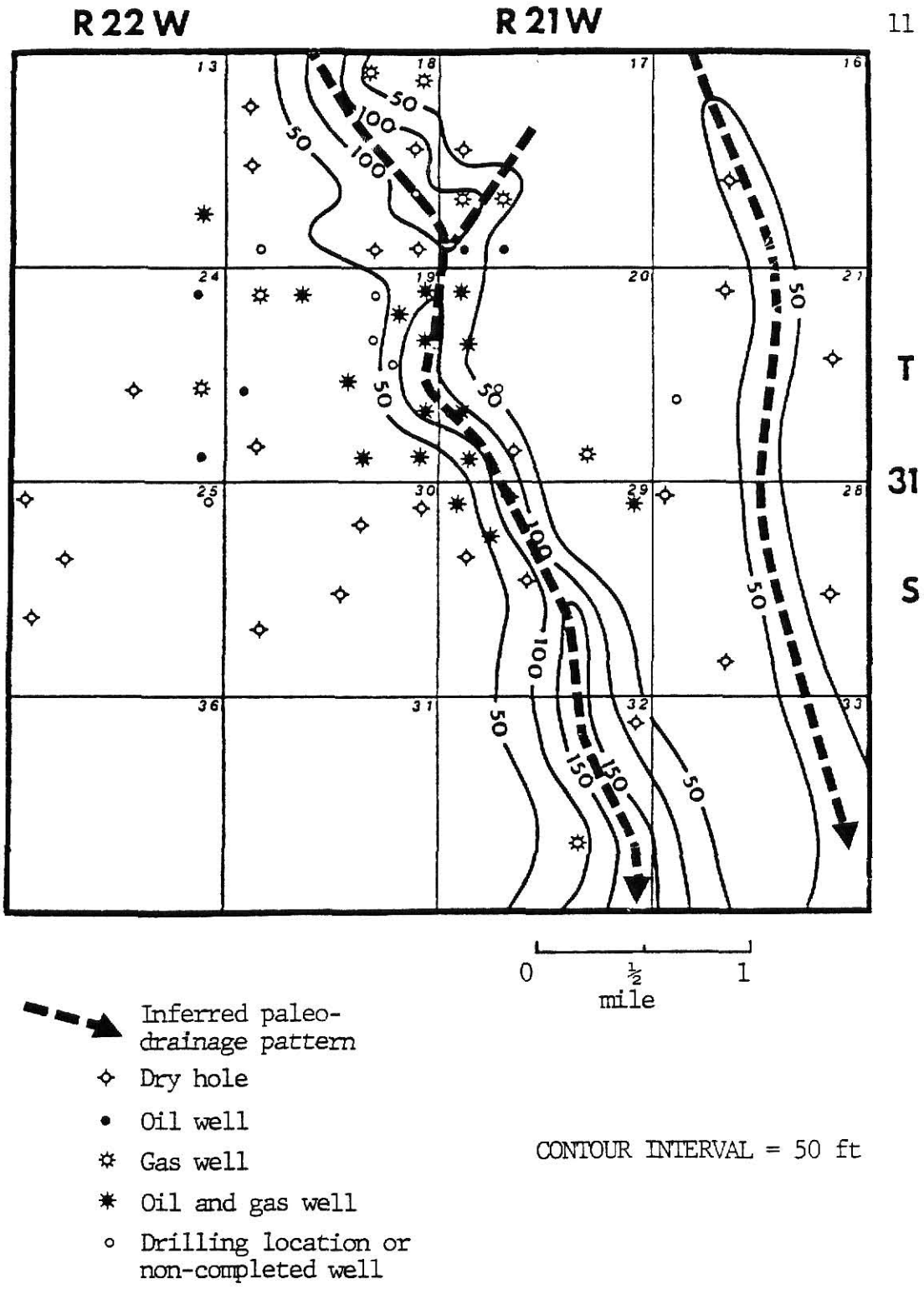



Figure 4. Isopachous map of the Morrowan Stage, Lexington field, Clark County, Kansas.

# METHODS OF INVESTIGATION

## COLLECTION OF SAMPLES

Core samples of Pennsylvanian Morrowan sandstones and Mississippian St. Louis Limestone, from five wells in the Lexington field, were investigated for this study. Samples from randomly selected intervals were provided by Mr. J. Thomas of Mesa Petroleum Company, Oklahoma City.

The Lexington field was in production for 3 years and no secondary recovery methods had been applied prior to collection of oil and water samples. The waters associated with the oil production are assumed to be formation waters. Samples were collected in pre-cleaned polyethelene bottles at the well head. After collection the samples were allowed to settle for a week before the bottles were punctured at the bottom and the water collected and stored for analysis. The location of the wells are illustrated in Appendix I.

## LABORATORY METHODS

### Petrography

Seven thin sections of core samples of sandstones of the Morrowan Stage from four different wells in the Lexington field were prepared and examined for this investigation. A Zeiss binocular petrographic microscope was used to examine the thin sections. A series of parallel traverses spaced two mm apart were made across the thin section, the mineralogy at one mm intervals were recorded on a multiple lab counter. The petrographic study included identification of constitutent minerals, cements, textures, and determination of the relative percentages of minerals present. The grain size of sandstones of the Morrowan Stage

was determined by point count using 100 points per slide. At each point the smallest projecting diameter of the grain was measured and the size of the grain was placed into class intervals of 0.25Ø. The reader is referred to McQuillan (1968) for a detailed description of the technique followed in this investigation. Roundness values of the grains were determined by comparison with roundness images proposed by Powers (1953). Sorting was determined using the Inclusive Standard Deviation as described in Folk and Ward (1957).

## Clay Mineralogy

Separation of clay minerals from sandstones was based on the technique proposed by Folk (1974). Separation of clay minerals in shales was similar to the technique used by Lee (1972). Oriented slides were prepared following the procedures of Lee (1972). General procedures for the X-ray analyses are illustrated in Figure 5.

In this study identification of clay minerals was based only upon X-ray diffraction. S. Chaudhuri provided X-ray diffraction patterns of some samples which were analyzed at the Louis Pasteur Institute, Strasbourg, France. The remaining samples were analyzed at Kansas State University using a Norelco Wide Range Diffractometer with Ni-filtered Cu K-alpha radiation. Most oriented samples were scanned from 35 to one degree two theta, at one degree per minute. Samples were glycolated for 48 hours, heat-treated at 490° C, 450° C and 600° C, and treated in hydrazine hydroxide for 48 hours and each treated sample was scanned from 16 to one degree two theta. Instrument settings for samples analyzed at Kansas State University were similar to those reported by

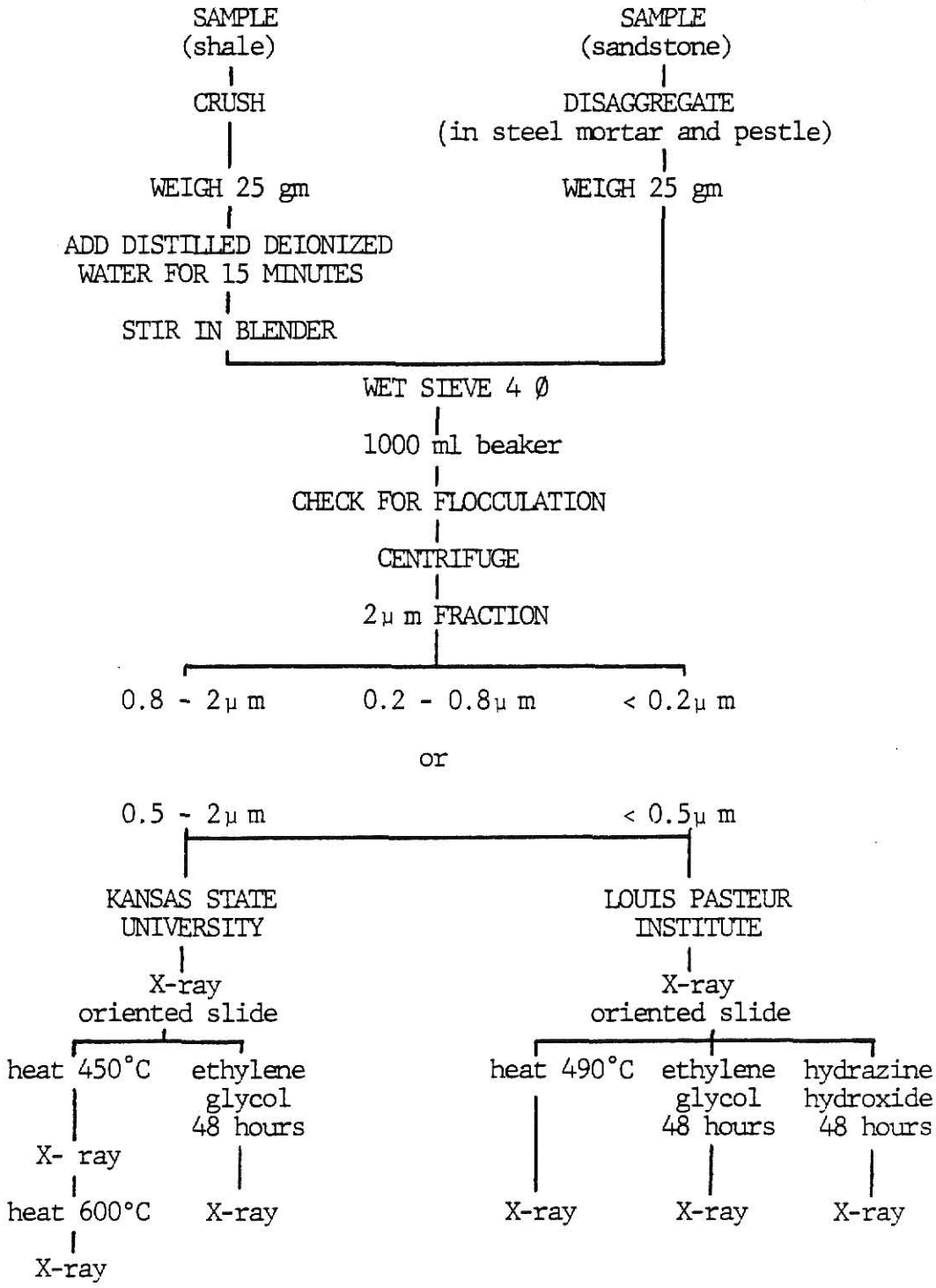



Figure 5. Flow sheet indicating procedures of clay mineral analyses.

Pecchioni (1981). Semi-quantative results were obtained by weighted peak height areas (Maiklem and Campbell, 1965).

## Analyses of Carbonate Cements

Core samples were pre-cleaned in distilled deionized water to remove contaminants prior to initial grinding. Approximately 5 grams of each sandstone were placed in a hardened steel mortar and pestle and ground until the sample was nearly disaggregated. The sample was then weighed and placed in a clean beaker with approximately 30 ml of 0.15 N hydrochloric acid to dissolve the carbonate cement from the sandstone. The solution was then filtered and stored, prior to analysis.

Cation concentrations were determined with a Perkin Elmer model 305 B spectrophotometer using the basic instrument settings as Reitz (1980) and Koch (1978). Ca, Mg, and Sr were analyzed by atomic absorption spectrophotometry and K, Rb, and Na were determined by flame emission spectrophotometry. Every sample was run in triplicate for each element. The Sr and Rb concentrations were obtained by using a limestone standard (CB-8) as a reference, whose Sr and Rb concentrations were determined by isotope dilution. The Ca and Mg concentrations were determined with the use of certified atomic absorption reference solutions obtained from Fisher Scientific Company. The standard solutions contained a similar matrix to that of the sample solutions. For each element, the carbonate cement solutions were diluted to a range of concentration, within the sensitivity limits of the spectrophotometer. Estimated maximum deviation ($1\sigma$) of the elemental concentrations are as follows: Sr, Rb $\pm$ 8 percent and Ca, Mg $\pm$ 10 percent.

## Analyses of Oil-Field Waters

Cation concentrations were determined by spectrophotometry as discussed earlier. Calcium, Mg, K, Sr, Rb, and Na concentrations were determined for the oil-field waters. Stock solutions of each cation were diluted in order to bracket the concentrations for the particular cation analyzed. One-tenth percent La was added to each sample and standard analyzed for Ca and Mg to reduce chemical interferences. Sodium was added to standards during K analyses and K was added to standards during Na analyses to supress interferences from ionization. Estimated maxium standard deviation (1 ) for K and Na were $\pm$ 5 percent, whereas those for Ca and Mg were $\pm$ 3 percent.

Standard turbidimetric methods were used in determining the $SO_4$ concentration, using a Coleman Model 14 Universal spectrophotometer. Carbonate alkalinity was determined by titration to a pH of 4.8. Sulfate and $CO_3$ procedures are outlined in the Fourteenth Edition of the Standard Methods by the American Water Works Association. Analytical precision ($1\sigma$) for the $SO_4$ and $CO_3$ were $\pm$ 5 percent. Chloride concentration was determined by coulometric titration using a Buchler digital chloridometer. The method is based on constant current electro-generation of Ag ion reagent in situ from a Ag wire anode (two electrode system). This results in the chemical precipitation of Cl as AgCl. When all the Cl is consumed, the endpoint is detected by an additional pair of electrodes designed to amperometrically signal the first excess of free Ag reagent. An electronic timer has been operating since the beginning of the titration and upon receipt of an endpoint signal from the amperometric (detector) electrodes, the instrument automatically turns off the electronic timer.

From the measured time (T) and the constant current (I), the number of coulombs (Q) passed to the endpoint are calculated ($Q = I \times T$). From this and the Faraday constant, the number of equivalents of Ag and thus Cl are automatically calculated and digitally displayed by the instrument. The analytical precision ($1\sigma$) in the Cl determination was $\pm$ 2 percent.

## Mass Spectrometry

Strontium Isotopes.--Cation exchange was used for separating Sr from sample solutions. A cross-linked resin (AG-50W-X8) was added to exchange columns and was precleaned with 100 ml of 2 N hydrochloric acid. Solutions of samples with Sr concentrations about 40 ppm, were poured into the columns and allowed to settle into the resins. Then 60 ml of 2 N hydrochloric acid was added. The position of the Sr was monitored in a separate column by a geiger counter in which a radioactive $^{85}Sr$ isotope tracer was added. The elutions containing the Sr were collected in teflon beakers, which were placed on a hot plate and evaporated to dryness. The Sr precipitate was then redissolved with a drop of nitric acid and the solution was evaporated onto either Ta or Re filaments. Sample preparations and separation procedures are also described by Chaudhuri (1966), Methot (1973), Kilbane (1978), Spaid-Reitz (1980), and Smalley (1981).

Strontium isotope ratios for samples indicated by an "*", were determined at the CONOCO Research Center, Ponca City, Oklahoma, using a Varian MAT 260 mass spectrometer with a Re filament. The Sr isotope ratios for the remaining samples were determined at Kansas State University using a Nuclide Corporation model 6-60-S with a 15 cm radius and a

60° sector, using a Ta filament.

Strontium isotope ratios were determined by comparing the abundance peaks of isotope masses 86, 87, and 88. For samples analyzed on the Varian MAT 260, the mass peaks were measured by computer and the $^{87}Sr/^{86}Sr$ ratio calculated. Samples analyzed on the Nuclide Corporation model 6-60-S required reading the mass peaks off chart paper for a minimum of 36 times. The sum of abundance intensities was used for calculating the Sr isotopic ratio.

All the Sr isotopic data were normalized to an $^{86}Sr/^{88}Sr$ ratio of 0.1194 to remove instrumental induced fractionation. Estimated errors obtained on the Varian MAT 260 are reported as $2\sigma$ standard deviations, ranging from $\pm$ 0.00002 to 0.00011. The estimated $2\sigma$ standard deviation for the data obtained on the Nuclide 6-60-S was $\pm$ 0.0005.

Carbon Isotopes.--The C isotopic data were commercially obtained from Geochron Laboratories of Krueger Enterprises Incorporated. The data are expressed as:

$$\delta^{13}C = \left[ \frac{(^{13}C/^{12}C)_{sample}}{(^{13}C/^{12}C)_{standard}} - 1 \right] X \ 1000$$

The value represents the per mil difference between the $^{13}C/^{12}C$ ratio of the sample and that of the standard PDB. The reproducibility of the data is within $\pm$ 0.1 per mil. The carbonate cements from random samples were selectively leached by phosphoric acid to measure any isotopic compositional differences that may have existed in the cement.

# R E S U L T S

## PETROGRAPHY

Morrowan Stage sandstone is generally fine- to medium-grained, submature to mature, ankeritic, slightly cherty quartz arenite. A few conglomeratic phases occur near the base of the sand body and consist of pebbles of chert and carbonate rock. The conglomeratic phases occur in two of the six available cores of the Morrowan Stage sandstone.

### Framework Grains

Morrowan Stage sandstone consists of 70 to 85 percent framework grains by volume. Quartz comprised over 90 percent of the framework minerals. Chert averaged three percent, whereas glauconite, orthoclase and plagioclase feldspar and sedimentary rock fragments (shale clasts and carbonate rock fragments) averaged one percent or less of the total volume. Tourmaline, the predominant heavy mineral, occurred in trace amounts. Conglomeratic phases contained greater amounts of rock fragments, consisting of chert, carbonate rock fragments, and shale clasts.

Petrographic details of the Morrowan age sandstone are in Tables 1 and 2. The median grain size ranged from 1.7Ø to 2.5Ø or medium- to fine-grained. Sorting, calculated by the Inclusive Standard Deviation method of Folk (1974), averaged $\pm$ 0.60Ø or moderately well sorted. Quartz grains were rounded to subangular; the decrease in roundness was partially due to the effects of etching, replacement and interpenetration that occured during diagenesis.

Table 1. Grain-size analysis of Morrowan sandstone, Lexington field, Clark County, Kansas.

| Sample | | Grain size | Sorting | Roundness |
|---|---|---|---|---|
| Moore 2-20 | 5172 ft | 1.89Ø | ± 0.65Ø | 3.3 |
| | 5185 ft | 2.33Ø | ± 0.52Ø | 3.3 |
| Moore 2-29 | 5134 ft | 2.30Ø | ± 0.63Ø | 3.1 |
| | 5151 ft | 2.71Ø | ± 0.54Ø | 3.0 |
| Seacat 5-19 | 5245 ft | 2.64Ø | ± 0.59Ø | 3.0 |
| | 5257 ft | 2.60Ø | ± 0.68Ø | 3.0 |
| McPhail 1-32 | 5172 ft | 2.14Ø | ± 0.64Ø | 3.3 |

Table 2. Point-count results of the Morrowan age sandstone, in percent by volume. (Tr = trace amounts)

| | FRAMEWORK GRAINS | | | | | | CEMENTS | | | | | PORE SPACE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | Quartz | Feldspar | Chert | Glauconite | Shale clasts | Total framework | Clay minerals | Carbonates | Quartz cement | Pyrite | Total cement | |
| Moore 2-20 | | | | | | | | | | | | |
| 5172 ft | 71 | Tr | 4 | Tr | Tr | 75 | 3 | 4 | Tr | Tr | 7 | 18 |
| 5185 ft | 61 | 1 | 2 | Tr | Tr | 63 | 1 | 32 | Tr | Tr | 33 | 4 |
| Moore 2-29 | | | | | | | | | | | | |
| 5134 ft | 65 | Tr | 2 | 1 | 3 | 71 | 2 | 9 | 2 | 2 | 15 | 14 |
| 5151 ft | 60 | Tr | 2 | Tr | Tr | 62 | Tr | 31 | 1 | Tr | 32 | 6 |
| Seacat 5-19 | | | | | | | | | | | | |
| 5245 ft | 63 | Tr | 3 | 1 | Tr | 67 | 1 | 11 | 1 | Tr | 13 | 20 |
| 5257 ft | 70 | Tr | 5 | 1 | Tr | 76 | 1 | 10 | 1 | Tr | 12 | 12 |
| McPhail 1-32 | | | | | | | | | | | | |
| 5172 ft | 73 | Tr | 6 | Tr | Tr | 79 | 2 | 4 | 3 | Tr | 9 | 12 |

## Cements

The framework minerals are bonded together by ankerite, calcite, quartz, clay minerals and pyrite, of which carbonate minerals and quartz are the most common. The proportion of quartz cements generally decreases with increasing amounts of carbonate cements.

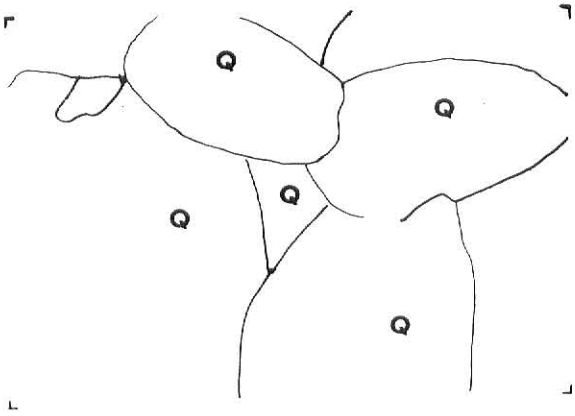
Secondary quartz.--Interpenetration of quartz grains and secondary overgrowths are two forms of quartz cement of the sandstones (Figures 6 and 7). Many quartz grains show enlargements of secondary quartz that is in optical continuity with the nucleus grain. Trace amounts of clay minerals coat the surface of the detrital quartz grains in some samples. Secondary overgrowths are an early diagenetic phenomenon (Siever, 1959). Pressure-solution effects, which led to the formation of several concavo-convex boundaries among quartz grains, destroyed features of earlier diagenetic events.

Carbonate cement.--Ankerite and less commonly calcite, are the dominant types of carbonate cements. Ankerite was identified by X-ray diffraction scanning at ¼ degree per minute, indicating the (104) reflection at 2.90 °A. The carbonate cements occur as discontinuous, irregular patches and lenses and as continuous groundmass of the quartz grains. Ankerite grains are commonly anhedral to subhedral but a few rhombohedral crystals of ankerite also occur. Carbonate minerals are the primary cement in nearly all sandstones comprising up to 32 percent of the total rock. In highly cemented rocks, the framework grains are almost completely separated from each other.

Two generations of carbonate cement occur, the earlier carbonate

Figure 6. Photomicrograph of Seacat 5-19 5257 ft indicating pressure-solution effects on quartz grains (Q). [Crossed nicols, bar in lower left corner is 0.05 mm]

Figure 7. Photomicrograph of Moore 2-29 5151 ft indicating quartz overgrowths (OV) on nucleus quartz grains (Q); ankerite cement (A). [Plain light, bar in upper left corner is 0.05 mm]


Q
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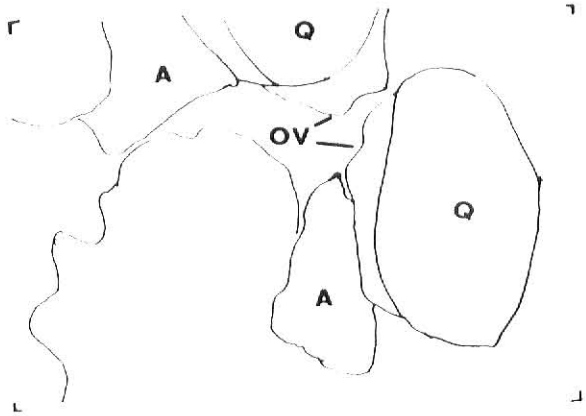
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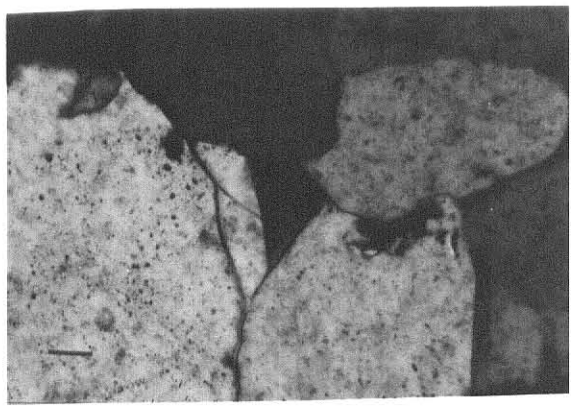
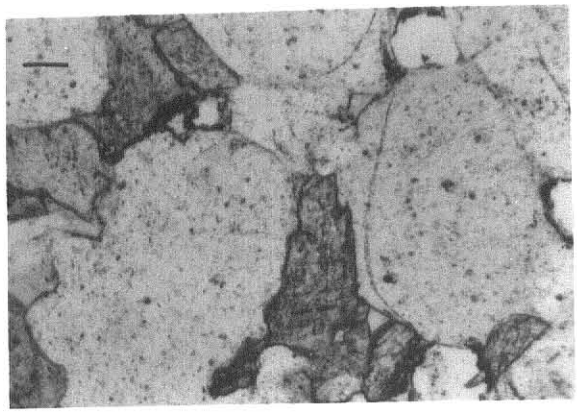
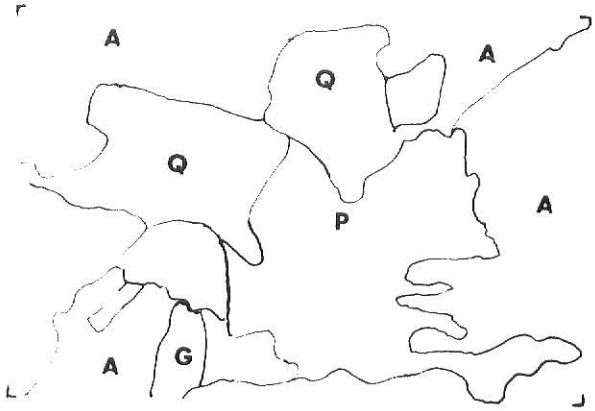







A

K

possibly calcite and the later ankerite. The earlier cement appears to have been replaced by the ankerite leaving a "ghost" outline of the original grain (Figure 8).

Clay Minerals.--Detrital clay minerals occur as coatings on quartz grains and in some cases as a coating between the detrital quartz grain and the secondary overgrowth. Detrital clay minerals also occur as pore fillings between framework grains and the total is less than one percent. The majority of clay minerals are secondary and kaolinite is dominant. Euhedral, hexagonal crystals of kaolinite often fill intergranular and secondarily-enlarged pore spaces (Figure 9). Clay minerals account for less than three percent of the total rock in all samples.

Pyrite.--Pyrite occurs as anhedral, irregular patches, and as cubic crystals. Pyrite appears to replace quartz and carbonate minerals and is in amounts of up to two percent of the total rock.

## Porosity

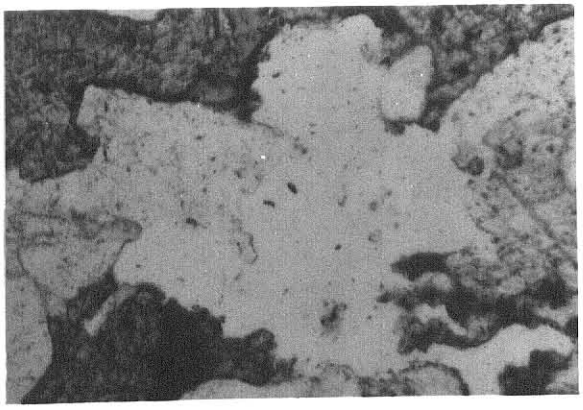
Porosity of the sandstones, estimated from thin sections, ranged from 4 to 20 percent, the low porosity sandstones had increased amounts of carbonate cement. In the sandstones with higher porosities (greater than 10 percent), porosity is predominately secondary due to dissolution and replacement of carbonate minerals and framework grains (Figure 8).

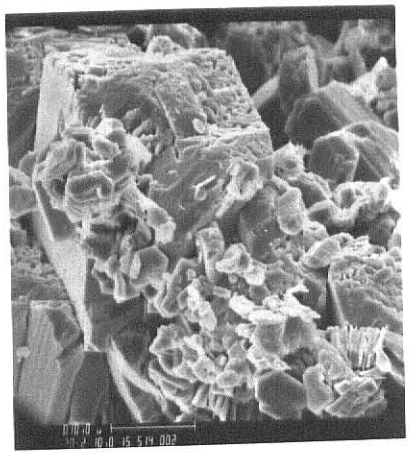
# CLAY MINERALOGY

The clay mineral compositions of both sandstones and shales from the Morrowan Stage were similar. In the 0.8 to 2.0 μm fraction of the shales, kaolinite ranged from 54 to 84 percent, illite ranged from 13 to

Figure 8. Photomicrograph of Seacat 5-19 5245 ft indicating secondary porosity (P) and "ghost" of original carbonate cement? (G) in an ankerite grain (A); and quartz (Q).
[Plain light, bar in upper left corner is 0.05 mm]

Figure 9. Scanning electron microscope photograph of Moore 2-20 5172 ft illustrating kaolinite (K) filling a cavity in a leached ankerite rhomb (A). [Bar scale is equal to 10 μ]





38 percent, mixed layer illite-smectite averaged 6 percent, and chlorite in traces. In the less than 0.2 μm fraction, illite ranged from 55 to 79 percent, kaolinite ranged from 12 to 37 percent, mixed layer illite-smectite averaged 10 percent, and chlorite in traces. In the sandstones, kaolinite was more abundant in the coarse fraction (0.8-2.0μ m) than in the fine fraction (less than 0.8μ m) in which illite was the dominant clay mineral. Relative abundances of clay minerals from beds of sandstone and shale are in Table 3.

## MAJOR AND TRACE-ELEMENT DATA

### Carbonates

Carbonate cements from 16 core samples of Morrowan Stage sandstones and two core samples of the St. Louis Limestone were analyzed for their Ca, Mg, Sr, and Rb concentrations. Calcium concentrations ranged from 94,000 to 389,000 ppm and Mg concentrations ranged from 2,000 to 105,000 ppm. Strontium concentrations ranged from 329 to 547 ppm and Rb concentrations ranged from 13 to 53 ppm. The chemical data of the carbonates are in Table 4.

### Oil-field Waters

Three oil-field waters from carbonate reservoirs of the Mississippian St. Louis Limestone and two waters from sandstone reservoirs of the Pennsylvanian Morrowan Stage were analyzed for their major and minor element contents. The chemical data of the oil-field waters are in Table 5. Using Sulin's classification (Ostroff, 1967), all waters analyzed are of the Chloride-Calcium type.

The pH of the waters ranged between 6.0 and 6.6. Except for the

Table 3. Relative percentages of clay minerals in the sandstone and shale of the Morrowan Stage, Lexington field, Clark County, Kansas. [Tr = trace amounts]

| Sample | Size fraction | Lithology | Kaolinite | Illite | Mixed layer illite-smectite | Chlorite |
|---|---|---|---|---|---|---|
| Seacat 5-19 | < 0.2 μm | shale | 21 | 66 | 13 | Tr |
| 5249 ft | 0.2 - 0.8 μm | | 49 | 46 | 5 | Tr |
| | 0.8 - 2 μm | | 73 | 27 | Tr | Tr |
| Moore 2-20 | < 0.8 μm | shale | 46 | 45 | 9 | Tr |
| 5195 ft | 0.8 - 2 μm | | 71 | 25 | 4 | Tr |
| Moore 1-29 | < 0.2 μm | shale | 12 | 79 | 9 | Tr |
| 5233 ft | 0.2 - 0.8 μm | | 40 | 53 | 5 | 2 |
| | 0.8 - 2 μm | | 62 | 32 | 6 | Tr |
| Schieb 1-18 | < 0.8 μm | shale | 75 | 25 | Tr | Tr |
| 5342 ft | 0.8 - 2 μm | | 84 | 13 | Tr | 3 |
| Schieb 1-18 | < 0.8 μm | shale | 43 | 43 | 11 | 3 |
| 5251 ft | 0.8 - 2 μm | | 54 | 38 | 5 | 3 |
| Schieb 1-18 | < 0.2 μm | shale | 38 | 56 | 6 | Tr |
| 5257 ft | 0.2 - 0.8 μm | | 52 | 39 | 7 | 2 |
| | 0.8 - 2 μm | | 65 | 30 | 3 | 2 |
| Moore 2-20 | 0.5 - 2 μm | sandstone | 35 | 59 | 6 | - |
| 5180 ft | | | | | | |
| Moore 2-29 | 0.5 - 2 μm | sandstone | 22 | 71 | 7 | Tr |
| 5127 ft | | | | | | |
| Moore 2-29 | < 0.8 μm | sandstone | 43 | 51 | 6 | Tr |
| 5135 ft | 0.8 - 2 μm | | 54 | 43 | 3 | Tr |

Table 4. Chemical analyses of carbonate cements of Morrowan sandstone and carbonate rock of St. Louis Limestone. [in ppm.]

| Sample | Sr | Rb | Ca $\times 10^{-3}$ | Mg $\times 10^{-3}$ | Ca/Mg |
|---|---|---|---|---|---|
| | Carbonate cements | | | | |
| Moore 2-20 | | | | | |
| 5161 ft | 253 | 23 | 119 | 40 | 3 |
| 5172 ft | 518 | 38 | 316 | 105 | 3 |
| 5180 ft | 281 | 24 | 94 | 32 | 3 |
| 5185 ft | 312 | 23 | 196 | 76 | 3 |
| 5195 ft | 320 | 25 | 237 | 87 | 3 |
| Moore 2-29 | | | | | |
| 5127 ft | 369 | 26 | 152 | 52 | 3 |
| 5134 ft | 320 | 24 | 172 | 58 | 3 |
| 5135 ft | 269 | 20 | 136 | 34 | 4 |
| 5141 ft | 371 | 30 | 151 | 53 | 3 |
| Seacat 5-19 | | | | | |
| 5232 ft | 287 | 25 | 389 | 102 | 4 |
| 5239 ft | 321 | 28 | 182 | 62 | 3 |
| 5245 ft | 352 | 28 | 201 | 69 | 3 |
| 5251 ft | 281 | 27 | 160 | 56 | 3 |
| 5257 ft | 239 | 18 | 208 | 66 | 3 |
| Mc Phail 1-32 | | | | | |
| 5166 ft | 547 | 48 | 294 | 2 | 147 |

Table 4. Chemical analyses of carbonate cements of Morrowan sandstone and carbonate rock of St. Louis Limestone. -Continued.

| Sample | Sr | Rb | Ca $\times 10^{-3}$ | Mg $\times 10^{-3}$ | Ca/Mg |
|---|---|---|---|---|---|
| Carbonate rocks of the St. Louis Limestone | | | | | |
| Moore 2-29 | | | | | |
| 5155 ft | 356 | 32 | 211 | 77 | 3 |
| 5157 ft | 538 | 53 | 366 | 4 | 92 |

Sr/Ca ratios, the waters from the Mississippian and the Pennsylvanian reservoirs are indistinguishable based on the chemical data. The Sr/Ca ratios of the Mississippian waters range between 0.056 and 0.062, whereas those of the Pennsylvanian waters range between 0.083 and 0.108.

The relationship of Ca, Mg, Na, K, Sr and Li contents versus Cl contents for the waters are compared to that of evaporated seawater (Collins, 1975)(Figures 10, 11, 12, 13, 14, 15). The waters are enriched in Ca, Sr and Li and depleated in Mg and K relative to evaporated seawater. Only Na versus Cl reflects a stage of evaporated seawater.

## ISOTOPIC ANALYSES

### Strontium Isotopes

Measured $^{87}Sr/^{86}Sr$ ratios for carbonate cements and oil-field waters are in Table 6. The Rb/Sr ratios of the cements and waters are extremely small and range between 0.070 and 0.099, indicating that their isotopic ratios have remained essentially unchanged from the decay of $^{87}Rb$ to $^{87}Sr$.

In samples of the Moore 2-20 core of the Morrowan age sandstone, the Sr isotopic ratios ranged from 0.70865 to 0.70940. In the Moore 2-29 core, the Sr isotopic ratios of the carbonate cements had values between-0.70874 and 0.70890, whereas in the the Seacat 5-19 core, the cements had $^{87}Sr/^{86}Sr$ ratios ranging from 0.70841 to 0.70871. In contrast, two samples from the Mississippian St. Louis Limestone had $^{87}Sr/^{86}Sr$ ratios of 0.70822 and 0.70856. The $^{87}Sr/^{86}Sr$ ratios of the carbonate cements from sandstones of Morrowan age are plotted against depth in Figure 16. This plot suggests that no predictable Sr isotopic trends occur

vertically within the core of the sandstone or laterally between the wells.

Five oil-field waters from the Lexington field were analyzed for their Sr isotopic composition. The waters associated with Mississippian St. Louis Limestone production had $^{87}Sr/^{86}Sr$ ratios ranging from 0.70950 to 0.71050, whereas the waters associated with Pennsylvanian Morrowan age sandstone production had $^{87}Sr/^{86}Sr$ ratios of 0.70990 and 0.71010.

## Carbon Isotopes

The $\delta^{13}C$ of carbonate cements from sandstones of the Morrowan Stage ranged from -1.73 to +2.82 per mil. The most depleted $\delta^{13}C$ cement of a Morrowan sandstone was associated with the highest Ca/Mg ratio noted in this study; the sample (McPhail 1-32 5166 ft ) was from a non-productive well. The $\delta^{13}C$ data of the carbonate cements are reported in Table 7.

Table 5. Geochemical data of oil-field waters of the Lexington field.
[Results in mg/l, except for pH]

| Sample | pH | $HCO_3$ | $SO_4$ | Cl | Na | K | Ca | Mg | Sr |
|---|---|---|---|---|---|---|---|---|---|
| St. Louis Limestone oil-field waters | | | | | | | | | |
| Moore 3-20 | - | - | 320 | 131,165 | 63,350 | 570 | 16,425 | 2,272 | 915 |
| Giles 1-24 | 6.4 | 59 | 550 | 127,088 | 66,500 | 600 | 9,900 | 2,200 | 610 |
| Seacat 8-19 | 6.6 | - | 620 | 121,771 | 65,800 | 726 | 9,750 | 2,562 | 560 |
| Morrowan Stage oil-field waters | | | | | | | | | |
| Moore 4-29 | 6.0 | 7 | 280 | 127,974 | 69,600 | 464 | 9,300 | 2,490 | 1,000 |
| Frances 2-20 | 6.4 | 29 | 270 | 125,316 | 65,800 | 630 | 8,550 | 2,520 | 710 |

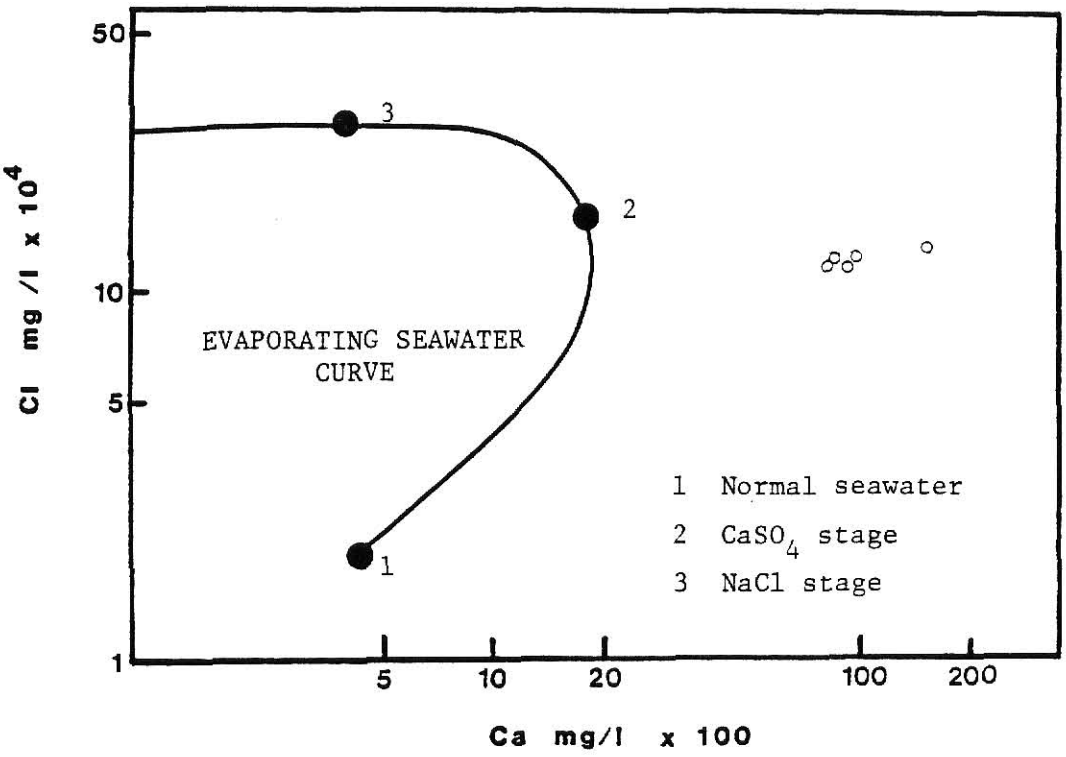
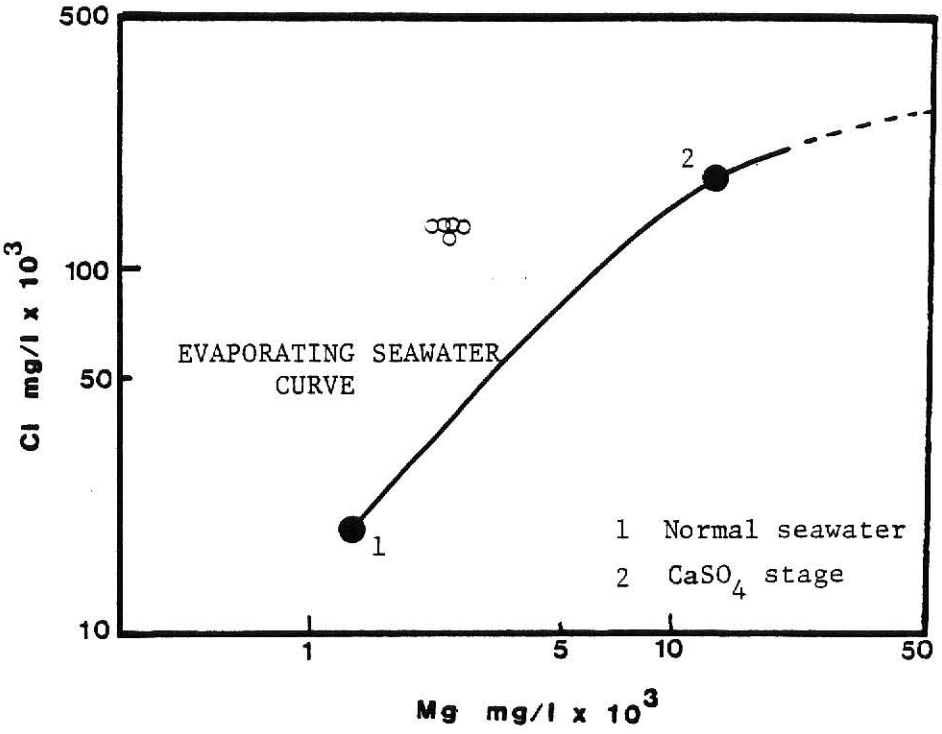



Figure 10. Ca versus Cl contents for water samples of the Lexington field compared to that of evaporating seawater (Collins, 1975).




○ Oil-field water samples of the Lexington field

● Stage of evaporation of seawater

Figure 11. Mg versus Cl contents for water samples of the Lexington field compared to that of evaporating seawater (Collins, 1975).

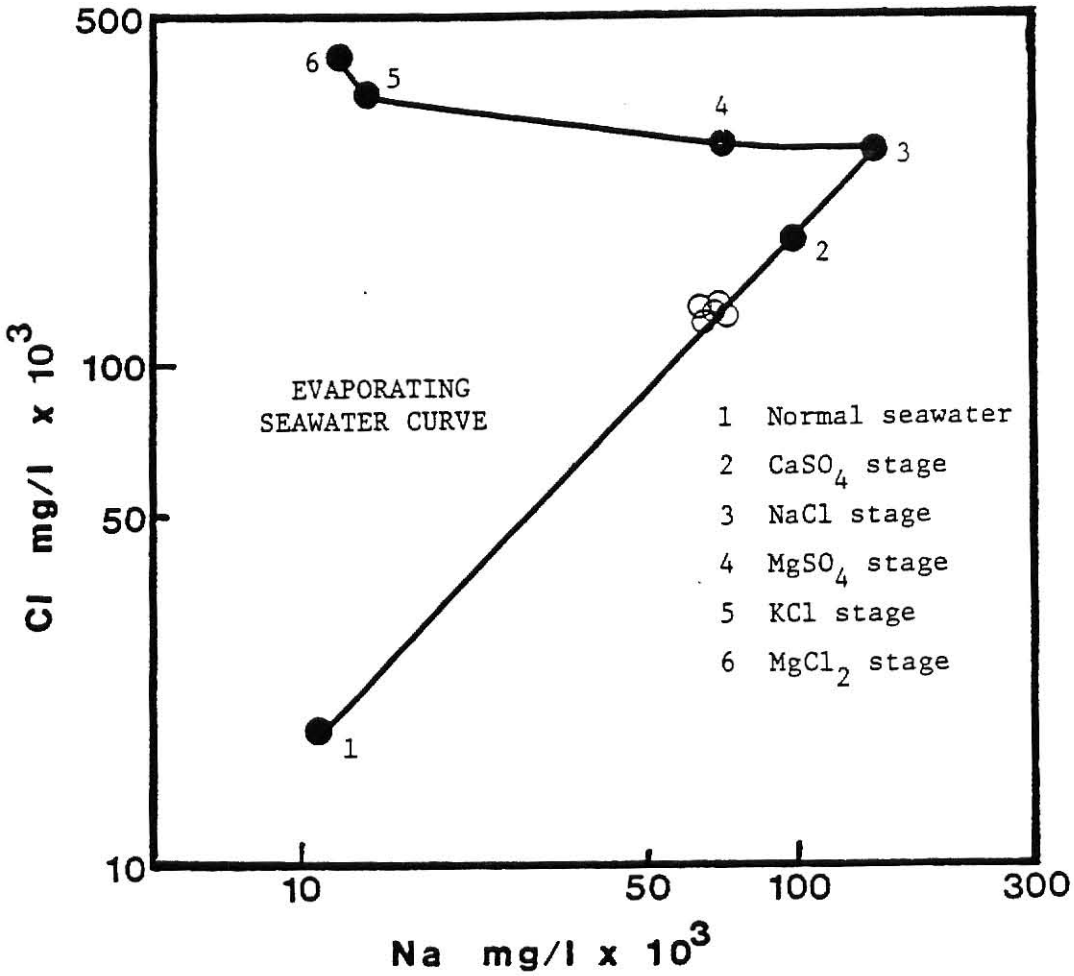
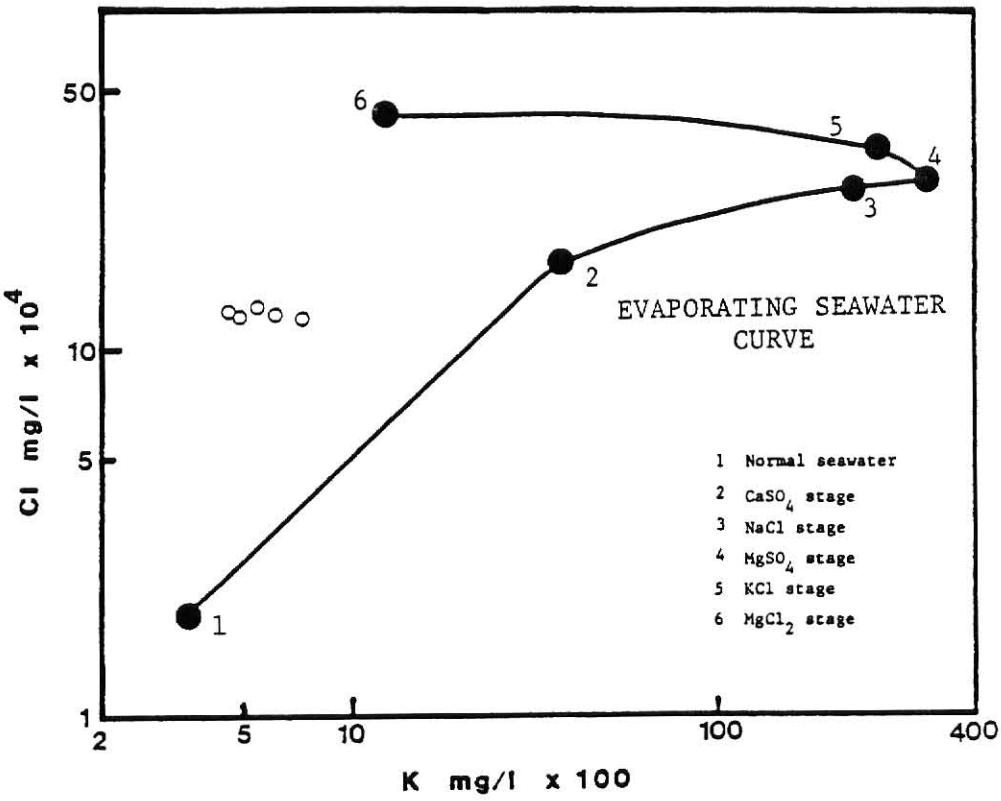


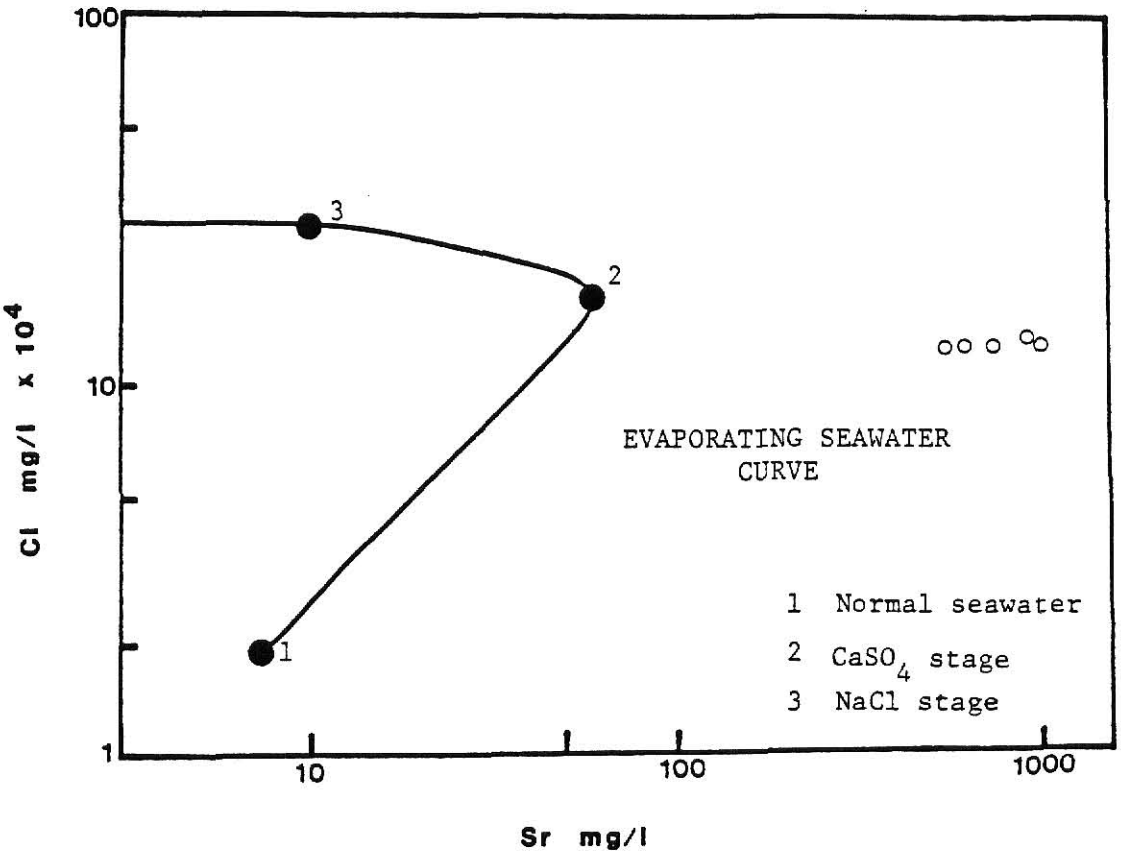

Figure 12. Na versus Cl contents for water samples of the Lexington field compared to that of evaporating seawater (Collins, 1975).




○ Oil-field water samples of the Lexington field

● Stage of evaporation of seawater

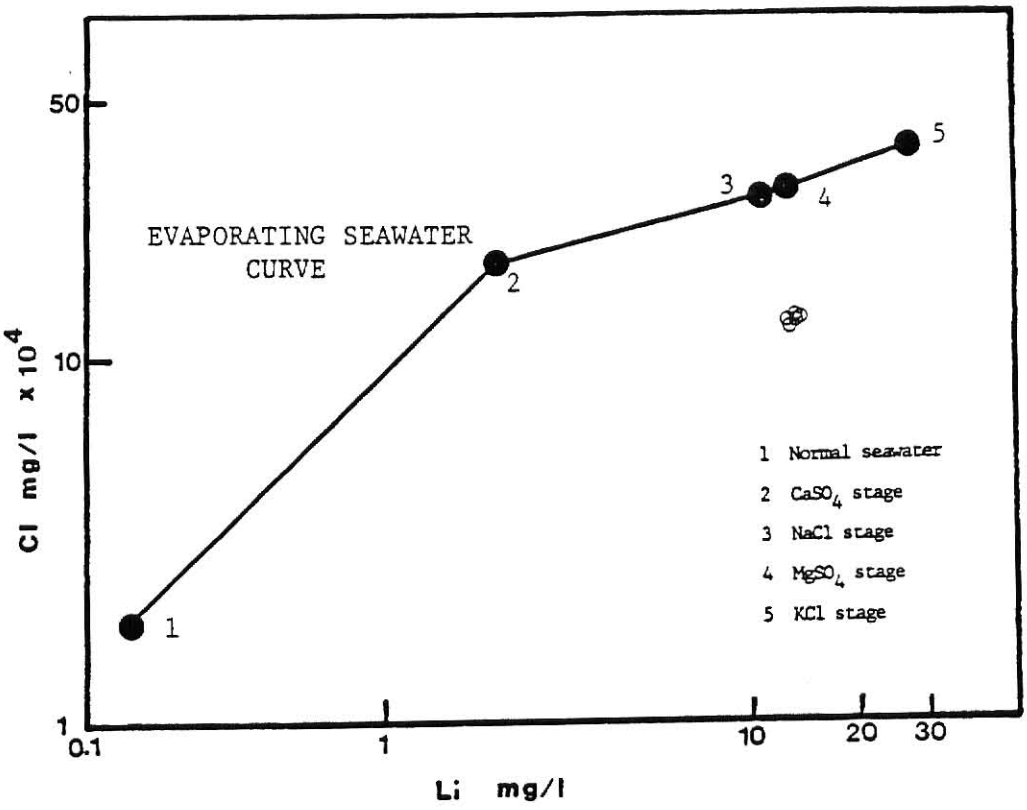
Figure 13. K versus Cl contents for water samples of the Lexington field compared to that of evaporating seawater (Collins, 1975).




○ Oil-field water samples of the Lexington field

● Stage of evaporation of seawater

Figure 14. Sr versus Cl contents for water samples of the Lexington field compared to that of evaporating seawater (Collins, 1975).




○ Oil-field water samples of the Lexington field

● Stage of evaporation of seawater

Figure 15. Li versus Cl contents for water samples of the Lexington field compared to that of evaporating seawater (Collins, 1975).

Table 6. Strontium isotopic data of carbonate cements from Morrowan age sandstone, St. Louis Limestone carbonate rocks and oil-field waters, from the Lexington field, Clark County, Kansas.

| Sample | | Rb/Sr | 1/Sr | $^{87}Sr/^{86}Sr$ |
|---|---|---|---|---|
| Carbonate cements of the Morrowan age sandstone | | | | |
| Moore 2-20 | 5161 ft | 0.009 | 0.004 | $0.70871 \pm 0.00010^{*}$ |
| | 5172 ft | 0.007 | 0.002 | $0.70940 \pm 0.0005$ |
| | 5180 ft | 0.009 | 0.004 | $0.70916 \pm 0.00009^{*}$ |
| | 5191 ft | 0.009 | 0.003 | $0.70865 \pm 0.00005^{*}$ |
| Moore 2-29 | 5127 ft | 0.007 | 0.003 | $0.70874 \pm 0.00003^{*}$ |
| | 5135 ft | 0.007 | 0.003 | $0.70877 \pm 0.00002^{*}$ |
| | 5141 ft | 0.008 | 0.003 | $0.70883 \pm 0.00006^{*}$ |
| | 5151 ft | 0.007 | 0.003 | $0.70890 \pm 0.0005$ |
| Seacat 5-19 | 5232 ft | 0.009 | 0.004 | $0.70871 \pm 0.00004^{*}$ |
| | 5239 ft | 0.009 | 0.003 | $0.70860 \pm 0.00002^{*}$ |
| | 5245 ft | 0.008 | 0.003 | $0.70870 \pm 0.0005$ |
| | 5251 ft | 0.010 | 0.004 | $0.70841 \pm 0.00003^{*}$ |
| McPhail 1-32 | 5166 ft | 0.009 | 0.002 | $0.70923 \pm 0.00015^{*}$ |

Table 6. Strontium isotopic data of carbonate cements from Morrowan age sandstone, St. Louis Limestone carbonate rocks and oil-field waters from the Lexington field, Clark County, Kansas - Continued.

| Sample | | Rb/Sr | 1/Sr | $^{87}Sr/^{86}Sr$ |
|---|---|---|---|---|
| St. Louis Limestone carbonate rocks | | | | |
| Moore 2-29 | 5155 ft | 0.009 | 0.003 | $0.70856 \pm 0.00004$* |
| | 5158 ft | 0.010 | 0.002 | $0.70822 \pm 0.00011$* |
| St. Louis Limestone oil-field waters | | | | |
| Moore 3-20 | | - | 0.001 | $0.71050 \pm 0.0005$ |
| Giles 1-24 | | - | 0.002 | $0.70950 \pm 0.0005$ |
| Seacat 8-19 | | - | 0.002 | $0.71035 \pm 0.00002$* |
| Morrowan Stage oil-field waters | | | | |
| Moore 4-29 | | - | 0.001 | $0.70990 \pm 0.0005$ |
| Frances 2-20 | | - | 0.001 | $0.71010 \pm 0.0005$ |

Samples indicated with (*) were analyzed by the author at CONOCO Research Center, Ponca City, Oklahoma. The remainder of the samples were analyzed at Kansas State University.

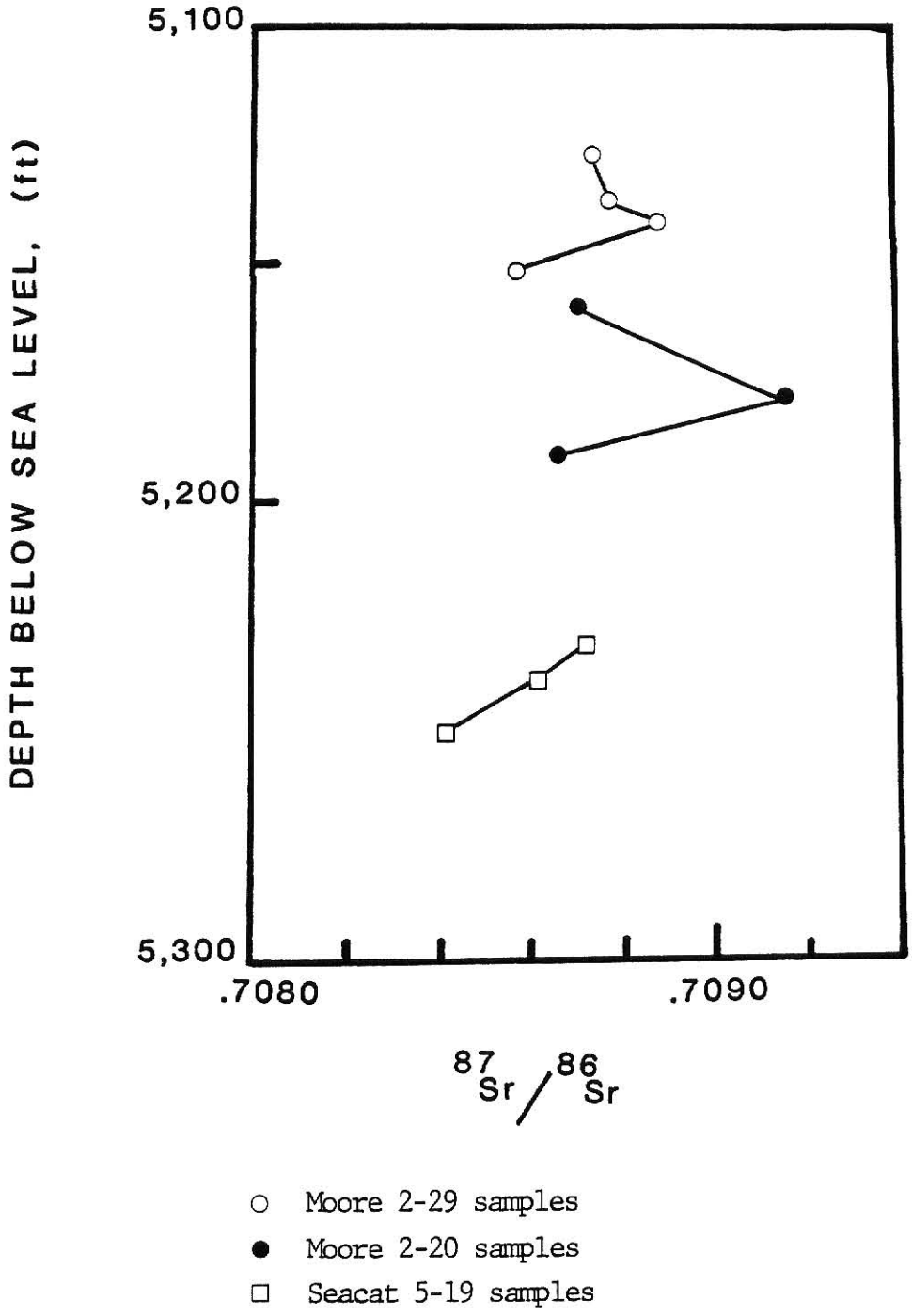



Figure 16. Relationship between the depth of the Morrowan sandstone sample and the Sr isotopic ratio of the carbonate cement of the Morrowan sandstone, Lexington field, Clark County, Kansas.

Table 7. $\delta^{13}C$ data of carbonate cements from Morrowan age sandstone from the Lexington field, Clark County, Kansas.

| Sample | | | $\delta^{13}C$ per mil |
|---|---|---|---|
| Moore 2-20 | 5161 ft | cement 1* | -0.15 |
| | | cement 2 | -0.05 |
| | | total cement | -0.08 |
| | 5191 ft | cement 1 | +2.82 |
| | | cement 2 | +2.73 |
| | | total cement | +2.69 |
| Moore 2-29 | 5141 ft | total cement | +0.92 |
| Seacat 5-19 | 5239 ft | total cement | +1.00 |
| | 5257 ft | total cement | +0.67 |
| McPhail 1-32 | 5166 ft | total cement | -1.73 |
| | 5177 ft | total cement | -0.16 |

* Samples 1 and 2 are from selected leachates.

# D I S C U S S I O N

The diagenetic history of the sandstone is determined by integrating information from the petrographic, chemical, and isotopic data of the rocks. The sequence of deposition of different cements, the mechanism of their deposition, and the source of some chemical components of the cements are among the major questions which need to be considered in an attempt to reconstruct the diagenetic history.

## DEPOSITIONAL HISTORY OF CEMENTS

The earliest diagenetic event, in the cementation history of the sandstones of the Morrowan Stage, was the formation of quartz overgrowths on quartz grains. This initial overgrowth was probably due to a lowering of the pH of the pore waters, arising from oxidation of organic material at shallow depth. Compaction of sediments led to further reduction of porosity as is evident from the pressure-solution effects on quartz grains which resulted in the formation of several concavo-convex boundaries among neighboring quartz grains. With continued burial, the quartz became unstable and was partly replaced by calcite. Upon deeper burial the increase in temperature causes the solubility of silica to increase. The temperature increase can also bring about precipitation of calcium carbonate while the solubility of silica increases, provided that the partial pressure of $CO_2$ for the pore water remained constant and that the water composition is near that of calcium carbonate saturation (Siever, 1959). Following the deep burial and replacement by carbonate, a change in the hydrodynamic system occurred which led to the ankeritization of the previously formed calcite and created secondary porosity

in the rock. The process of ankeritization can be described as:

$$2\ CaCO_3 + 0.4\ Mg^{2+} + 0.1\ Fe^{2+} \longrightarrow (Ca,Mg_{0.4},Fe_{0.1})(CO_3)_2 + Ca^{2+}$$

Partial leaching of these carbonate minerals created additional secondary porosity. Formation of patches of kaolinite, post-dates the partial dissolution of the carbonates and reduced the porosity. The formation of kaolinite in the Morrowan age sandstones can be described as:

$$2\ Al^{3+} + 2\ H_4SiO_4 + H_2O = Al_2Si_2O_5(OH)_4 + 6\ H^+$$

Pyrite was the last diagenetic mineral formed, replacing silicate and carbonate minerals. Sulfate in the waters possibly was reduced to sulfide by anaerobic bacteria, creating hydrogen sulfide. Dissolved Fe then combined with hydrogen sulfide to precipitate pyrite. The overall reaction can be expressed as:

$$2\ CH_2O + SO_4^{2-} = H_2S + 2\ HCO_3^-$$

$$Fe^{2+} + 2\ H_2S = FeS_2 + 4\ H^+ + 2\ e^-$$

## SOURCE OF CHEMICAL COMPONENTS OF CARBONATE CEMENTS

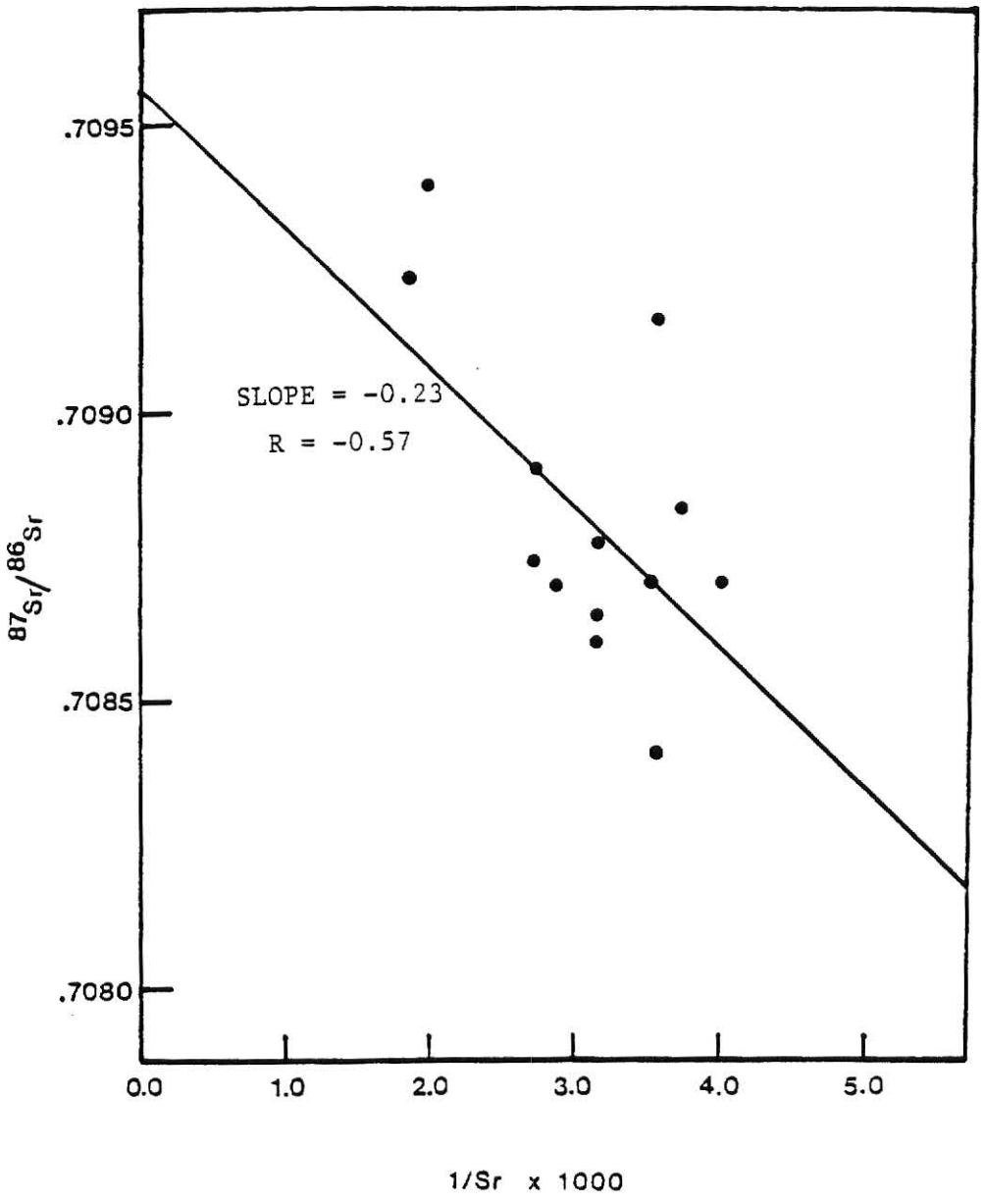
Isotopic data are useful in tracing the source of the chemical components of cements and in defining the geochemical environments in which the cements formed. A broad understanding of the depositional environments can emerge from these geochemical data.

The $^{87}Sr/^{86}Sr$ ratios of the carbonate cements ranged between 0.70841 and 0.70940. The spread in the $^{87}Sr/^{86}Sr$ ratio is indicative of the different Sr isotopic compositions of the carbonate cements.

Petrographic and X-ray analyses indicated that there are two distinct cements, calcite and ankerite. These two carbonate phases, each having different Sr isotopic compositions contributing in different proportions, may explain the observed isotopic variations.

The calcite cement seems to be the earliest among the carbonate cements. The $^{87}Sr/^{86}Sr$ ratio (0.70923) of the cement with the highest Ca/Mg ratio (McPhail 1-32 5166 ft ) is within the range of values for contemporaneous Morrowan seawater, as reported by Peterman and others (1970). The source of the Sr for this early carbonate phase, therefore, could have come from the contemporary seawater. The ankeritic cement, the later of the carbonate cements, had $^{87}Sr/^{86}Sr$ ratios as low as 0.70841. The low $^{87}Sr/^{86}Sr$ ratio of the ankeritic cements is similar to the Sr isotopic ratios reported in this study for the carbonate rocks of the St. Louis Limestone. This indicates that a possible source of the Sr in the ankerite cements could be the underlying St. Louis Limestone. Because of the different Sr isotopic composition of carbonate cements, involvement of different sources of Sr during precipitation of cement is strongly suggested. A two-component mixing model, however, can be tested by plotting $^{87}Sr/^{86}Sr$ ratios against their corresponding 1/Sr values, wherein a linear trend indicates mixing in different amounts between two components. In this study the Sr isotopic composition versus 1/Sr values are roughly linear (R= -0.57)(Figure 17). The rough linearity indicates the existence of a more complex than a two component system.

The observed relationship between the $^{87}Sr/^{86}Sr$ ratios and the Sr contents of the cements cannot be explained solely in terms of different




● Carbonate cement samples

Figure 17. $^{87}Sr/^{86}Sr$ ratio versus 1/Sr for the carbonate cements of the Morrowan age sandstone of the Lexington field.

amounts of ankerite replacing calcite. Petrographic evidence suggests that carbonates replace silicate minerals (glauconite, detrital clay minerals and quartz). These silicate minerals, especially clay minerals and glauconite, are known to contain radiogenic Sr. Chaudhuri (personal communication) observed that the quartz grains from the Morrowan age sandstones of the Lexington field had an $^{87}Sr/^{86}Sr$ ratio of 0.720. Replacement of the silicate minerals, in different degrees, therefore, yields different amounts of radiogenic Sr. The isotopic inhomogenity of carbonate cements can result, provided the precipitation of carbonate and the replacement of silica are simultaneous events. The isotopic differences among cements separated vertically by a couple of feet attest to the possibility that the isotopic homogeneity could have been limited to a small area (Figure 17). Fluids that later entered the pore spaces to bring about ankeritization encountered calcium carbonate cements of different Sr isotopic composition. The newly-formed ankerite cement thus assumed different isotopic compositions, possibly on a microscopic scale.

The $\delta^{13}C$ values between -1.73 and +2.82 of the carbonate cements indicate that the $CO_3$ ions were primarily derived from the dissolution of either marine carbonate rocks or from contemporary seawater. The differences of C isotopic values is outside the range of experimental error. Isotopic fractionations resulting from temperature differences or change in the chemical composition of the fluid could account for isotopic differences. Because, in this study area, all sandstones of the Morrowan Stage had a nearly identical burial history, temperatures of precipitation for all these carbonate cements are considered to be

nearly identical. Therefore, compositional differences of the fluid, from which the cements precipitated, appear to be the controlling factor governing the C isotopic distribution of the cements. This concept of different sources of C related to different generations of carbonate cements also recieve support from Sr isotopic data, that were discussed earlier.

## OIL-FIELD WATERS

The salinity of the oil-field waters are greater than 203,000 mg/l. High salinity and chemical compositions of formation waters have been attributed to: 1) evaporation of low salinity waters, 2) filtration of low salinity waters through shale membrane, 3) mixing of waters of different salinities, 4) reactions of waters and silicate minerals, 5) dissolution of halite and gypsum, and 6) dolomitization of limestone (Collins, 1975).

If the oil-field waters had a seawater composition, then the Na/Cl ratio of the waters would represent a stage of evaporation before $CaSO_4$ precipitation. The enrichment of Ca, Sr, and Li and the depletion of Mg and K in the waters imply that the composition of the original water had changed. Dolomitization of limestone has been suggested to account for the Ca and Sr enrichment and concomitant depletion of Mg. The reaction can be described as:

$$2\ Ca_{1-x}Sr_xCO_3 + Mg^{2+} \longrightarrow (Ca_ySr_yMg_{1-y-y'})(CO_3)_2 + Ca^{2+}2(1-x)-y + Sr^{2+}2x-y'$$

The amounts of ankerite cement in the Morrowan sandstone is as much as 40 percent of the total rock. The underlying St. Louis Limestone carbonate rocks are partly dolomitic. Thus it may be assumed that these

reservoir rocks could account for the Mg depletion and the Ca and Sr enrichment of the waters. But an examination of the chemical characters of the rocks and waters reveals that the reservoir rocks had little influence in the evolution of the Mg, Ca and Sr relationship of the waters. Assuming that the waters reached chemical equilibrium with the rocks, the Sr/Ca ratio of the waters would be nearly equal to or seven times that of the dolomite or limestone (Wedepohl, 1978). As the Sr/Ca ratio of the waters range between 0.06 and 0.10, compared to less than 0.002 for the ankerite cements of the Morrowan sandstones and St. Louis Limestone carbonate rocks (Table 4), the reservoir rocks cannot account for the Mg, Ca and Sr relationship of the waters. The same conclusion of minimal influence of host reservoir rocks on the Sr contents of the waters has been reached from Sr isotopic data. Dolomitization outside the boundaries of the reservoir rocks of the Lexington field is a possible explaination for the observed Mg, Ca and Sr relationship of the waters. Even if dolomitization influenced the chemical composition of the waters, an additional process is needed to account for the high Sr/Ca ratios of the waters.

The depletion of Mg and the enrichment of Ca and Sr of the waters have also been attributed to chloritization of smectite or other layer silicate minerals. The reaction may be described as:

$$\text{Ca-Montmorillonite} + Mg^{2+} + H_2O \longrightarrow \text{Mg-Chlorite} + H_4SiO_4 + Ca^{2+}$$

which may account for depletion of Mg in oil-field waters, but only trace amounts of chlorite are in reservoir rocks of Morrowan sandstone. Thus, chloritization within the reservoir rocks seems to have had

little influence on the chemical character of the water.

The oil-field waters are depleted in K relative to evaporated seawater. The depletion of K in the oil-field waters may be attributed to formation of clay minerals or ion exchange with clay minerals, because clay minerals preferentially absorb K in the interlayer sites. The K depletion could also be related to the formation of potassium feldspar (Collins, 1975). Silicate-water interactions could account for the K depletion and could explain the Li enrichment of the waters. During ion exchange by clay minerals, Li could be released into the water in exchange for K. The possibility of interactions of silicate and water exists and is discussed with the Sr isotopic ratios of the waters.

Unlike the relationships between other cations and chloride, the Na versus Cl compositions are close to the seawater evaporating curve. This indicates that Na and Cl contents of the oil-field waters were derived from a common source like that of seawater. If there were any significant amounts of Na introduced or absorbed by clay minerals, then the formation waters would have been enriched or depleted in Na relative to seawater. A close similarity with that of seawater in the Na/Cl ratio suggests that reaction with clay minerals had little influence in controlling the Na-Cl characteristics of the waters. As the Na/Cl ratios of the waters averaged 0.53, the dissolution alone of halite, having a Na/Cl ratio of 0.65, by a marine or meteoric water is insufficient to explain the Na/Cl relationship of the waters.

Shale-membrane filtration alone cannot account for the chemical composition of the waters. The membrane filtration of seawater, or of a

mixture of seawater and meteoric water, will increase the salinity, and the Ca/Cl, Sr/Cl, and K/Cl ratios and will decrease the Mg/Cl and Li/Cl ratios of the waters on the input side, relative to the original composition of the water. Although membrane filtration can account for the Ca, Sr and Mg relationship of the waters, the process cannot explain the observed K depletion and Li enrichment. Thus, at least an additional process, such as ion exchange by clay minerals, would be needed to explain the K and Li relationships.

The $SO_4$ concentrations of the oil-field waters are depleted relative to seawater which could have resulted from precipitation of $SO_4$ minerals or reduction of $SO_4$ by bacteria. Barite, celestite, gypsum or anhydrite have not been found in the reservoir rocks of the Lexington field; therefore, the $SO_4$ reduction is not a result of these chemical processes within the reservoir rocks. Because the barium contents were not determined and the activity coefficients of Ca and $SO_4$ for these highly saline waters cannot be accurately determined, the knowledge of the degree of saturation of the waters with respect to gypsum or anhydrite remains unknown. Sulfate reduction can also be explained by bacterial action as described by the following reaction:

$$2\ CH_2O + SO_4^{2-} \longrightarrow H_2S + 2\ HCO_3^-$$

The $H_2S$ produced could then react with Fe to form pyrite. The Morrowan sandstones contain pyrite; therefore, this process of pyrite formation may account for the $SO_4$ depletion of the oil-field waters.

Information on the chemical composition of formation waters is

often used in the reconstruction of the diagenetic history of reservoir rocks. An important question in the diagenetic history is what role the present formation waters had on the porosity of the associated reservoir rocks. In this study of the Morrowan age sandstones, the ankerite cement was a major diagenetic phase, the formation of which led to the development of secondary porosity. If the present waters were responsible for ankeritization of the rocks, then the Sr isotopic composition of the waters and the ankerite cements would be identical. The $^{87}Sr/^{86}Sr$ ratios of the waters range between 0.70950 and 0.71050, whereas the $^{87}Sr/^{86}Sr$ ratios of the ankerite cements range from 0.70841 to 0.70940. The isotopic differences between the two indicate that the ankeritization was not related to the present water. Similar isotopic differences also exist between the waters and the St. Louis Limestone carbonate rocks, two samples of which had $^{87}Sr/^{86}Sr$ ratios of 0.70822 and 0.70856. The Sr isotopic data indicate that the isotopic character of the oil-field waters did not evolve locally from either the carbonate cements of the Morrowan age sandstones or the St. Louis Limestone carbonate rocks. The isotopic characteristics of the waters must have been inherited prior to accumulation into the present reservoir rocks of Morrowan and Meramecian age.

The Sr isotopic ratios of the waters are slightly, but significantly, higher than that of any known marine Sr during the Phanerozic. Peterman and others (1970) reported that the $^{87}Sr/^{86}Sr$ ratios of Phanerozic marine carbonate rocks range between 0.7068 and 0.7091. An enrichment of $^{87}Sr$ indicates that the oil-field waters, if originated

primarily as seawater and then evolved chemically through different physical and chemical processes in the crustal environment, must have interacted with some minerals that are known to be enriched in $^{87}Sr$, such as clay minerals and feldspar.

Although the waters from the Lexington field were produced from two different reservoirs (Mississippian age carbonate rocks and Pennsylvanian age sandstones), the Sr isotopic composition of waters from both reservoirs are identical, within experimental error. Because the isotopic characters of the waters were inherited prior to their migration into the present reservoirs, the similarity in the isotopic composition of the waters from these two reservoir systems indicates that the waters had a common migrational history.

# SUMMARY

Morrowan age sandstone of the Lexington field was assumed to be deposited in strike valleys, similar to those described by Mannhard and Busch (1974) in the Harper Ranch field. Diagenesis had significant effect on the destruction and creation of porosity in the Morrowan age sandstone. Original porosity at the time of deposition was reduced by quartz cement and later by calcite cement. The process of ankeritization helped create secondary porosity. The formation of kaolinite later reduced porosity in some sandstone units.

The source of the chemical components of the carbonate cements is complex. Two possible sources are the carbonate rocks of the St. Louis Limestone and seawater of Morrowan age. Strontium isotopes indicate that more than two components of Sr are needed to explain the observed roughly linear (R= -0.57) plot of the 1/Sr versus $^{87}Sr/^{86}Sr$ ratio of the carbonate cements. A possible model is that the initial carbonate cements had different Sr isotopic composition that resulted from the carbonate cements partially replacing minerals that contain radiogenic strontium (glauconite, detrital clay minerals and quartz). Fluids that brought about ankeritization encountered calcite cements of different Sr isotopic composition. The ankerite cement thus evolved a different $^{87}Sr/^{86}Sr$ ratio, possibly on a microscopic scale. Carbon isotopic data indicate that the $CO_3$ ions were primarily derived from the dissolution of either marine carbonate rocks or from contemporary seawater. Compositional differences of the fluid, from which the cements precipitated, seem to be the controlling factor governing the C isotopic distribution

of the cements.

The oil-field waters of the Lexington field have a high salinity. The waters are enriched in Ca, Sr, and Li and depleted in Mg and K relative to evaporated seawater. The major processes controlling the chemical characteristics of the waters are mixing of waters, membrane filtration and reaction of the waters with silicate minerals.

Strontium isotopic data indicate that the present water had no noticeable effect on changing the porosity of the present reservoir rocks. The reservoir rocks above and below the oil-water contact are similar, indicating that no detectable new mineralization from the present water has occurred. The Sr isotopic character of the oil-field waters did not evolve locally from either the carbonate cement of the Morrowan age sandstones or from the carbonate rocks of the St. Louis Limestone. Strontium isotopic data indicate that if the present oil-field waters were originally derived from seawater, then the waters must have interacted with some minerals that are known to be enriched in $^{87}Sr$, such as clay minerals and feldspar. The isotopic character must have been inherited prior to the migration of the waters into the present reservoir. Reconstruction of diagenetic events and the geochemistry of the waters indicate that the oil migration into the reservoirs occurred sometime after the ankeritization stage.

# A C K N O W L E D G E M E N T S

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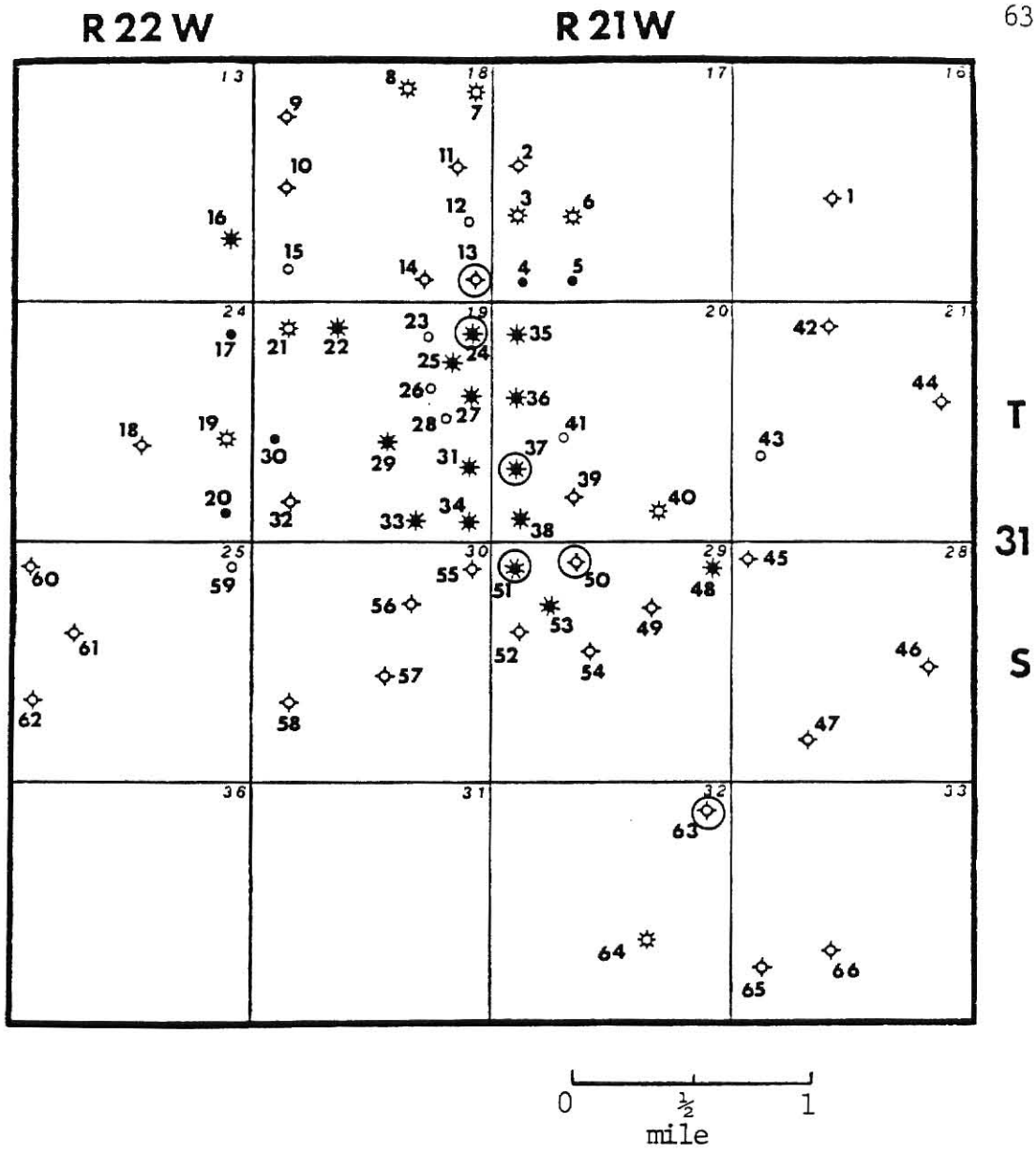
# A P P E N D I X I.

## Location of wells in the Lexington field area

Appendix I contains an index map of well locations and a list of the wells, operators, farm names and the status of each well in the Lexington field area.




- Oil well
- Gas well
- Oil and gas well
- Dry hole
- Drilling location or non-completed well
- Cored well used in this study

Appendix I. Location of wells in the Lexington field area.

| Well number | Operator | Farm name | Producing interval or Dry and abandoned (D&A) |
|---|---|---|---|
| 1 | Imperial Oil Co. | Shattuck 1-16 | D&A |
| 2 | Mesa Petroleum Co. | Schieb 1-17 | D&A |
| 3 | Imperial Oil Co. | Daily 2-17 | Morrowan age sandstone |
| 4 | Imperial Oil Co. | Daily 1-17 | Morrowan age sandstone |
| 5 | Imperial Oil Co. | Daily 3-17 | St. Louis Limestone |
| 6 | Imperial Oil Co. | Daily 4-17 | Morrowan age sandstone |
| 7 | Imperial Oil Co. | Schieb 1-18 | St. Louis Limestone |
| 8 | Imperial Oil Co. | Schieb 2-18 | Morrowan age sandstone |
| 9 | Mesa Petroleum Co. | Giles 1-18 | D&A |
| 10 | Imperial Oil Co. | Schieb 4-18 | D&A |
| 11 | Imperial Oil Co. | Schieb 3-18 | D&A |
| 12 | Robert A. Clark | Schieb #1 | No information released |
| 13 | Mesa Petroleum Co. | Schieb 1-18 | D&A |
| 14 | Mesa Petroleum Co. | Schieb 2-18 | D&A |
| 15 | Mesa Petroleum Co. | Giles 2-18 | No information released |
| 16 | Mesa Petroleum Co. | Giles 1-13 | Morrowan age sandstone and St. Louis Limestone |
| 17 | Mesa Petroleum Co. | Giles 1-24 | St. Louis Limestone |
| 18 | Mesa Petroleum Co. | Giles 4-24 | D&A |
| 19 | GS Oil and Gas Co. | Giles 2-24 | St. Louis Limestone |
| 20 | Mesa Petroleum Co. | Giles 3-24 | St. Louis Limestone |
| 21 | Mesa Petroleum Co. | Seacat 3-19 | St. Louis Limestone |
| 22 | Mesa Petroleum Co. | Seacat 8-19 | St. Louis Limestone |
| 23 | Mesa Petroleum Co | Seacat 14-19 | Drilling location |
| 24 | Mesa Petroleum Co. | Seacat 5-19 | Morrowan age sandstone |

| Well number | Operator | Farm name | Producing interval or Dry and abandoned (D&A) |
|---|---|---|---|
| 25 | Mesa Petroleum Co. | Seacat 11-19 | Morrowan age sandstone |
| 26 | Mesa Petroleum Co. | Seacat 13-19 | Drilling location |
| 27 | Mesa Petroleum Co. | Seacat 4-19 | Morrowan age sandstone |
| 28 | Mesa Petroleum Co. | Seacat 12-19 | Testing |
| 29 | Mesa Petroleum Co. | Seacat 2-19 | St. Louis Limestone |
| 30 | Mesa Petroleum Co. | Seacat 9-19 | St. Louis Limestone |
| 31 | Mesa Petroleum Co. | Seacat 7-19 | Morrowan age sandstone |
| 32 | GS Oil and Gas Co, | Seacat 10-19 | D&A |
| 33 | Mesa Petroleum Co. | Seacat 1-19 | St. Louis Limestone |
| 34 | Mesa Petroleum Co. | Seacat 6-19 | Morrowan age sandstone |
| 35 | Mesa Petroleum Co. | Francis 2-20 | Morrowan age sandstone |
| 36 | Mesa Petroleum Co. | Francis 1-20 | Morrowan age sandstone |
| 37 | Mesa Petroleum Co. | Moore 2-20 | Morrowan age sandstone |
| 38 | Mesa Petroleum Co. | Moore 1-20 | Morrowan age sandstone |
| 39 | Mesa Petroleum Co. | Moore 5-20 | D&A |
| 40 | Mesa Petroleum Co. | Moore 3-20 | St. Louis Limestone |
| 41 | Mesa Petroleum Co. | Moore 4-20 | Drilling location |
| 42 | Beren Corporation | Strodtman #1 | D&A |
| 43 | Beren Corporation | Strodtman #2 | Drilling location |
| 44 | Imperial Oil Co. | Strodtman 1-21 | D&A |
| 45 | Imperial Oil Co. | Pentz 1-28 | D&A |
| 46 | Imperial Oil Co. | Hughes 2-28 | D&A |
| 47 | Imperial Oil Co. | Hughes #1 | D&A |
| 48 | Mesa Petroleum Co. | McPhail 1-29 | St. Louis Limestone |

| Well number | Operator | Farm name | Producing interval or Dry and abandoned (D&A) |
|---|---|---|---|
| 49 | Energy Resources Co. | McPhail #1 | D&A |
| 50 | Mesa Petroleum Co. | Moore 1-29 | D&A |
| 51 | Mesa Petroleum Co. | Moore 2-29 | Morrowan age sandstone |
| 52 | Mesa Petroleum Co. | Moore 3-29 | D&A |
| 53 | Mesa Petroleum Co. | Moore 4-29 | Morrowan age sandstone |
| 54 | Mesa Petroleum Co. | Moore 5-29 | D&A |
| 55 | Mesa Petroleum Co. | R.J. Seacat 1-30 | D&A |
| 56 | GS Oil and Gas Col | R.J. Seacat 1-30 | D&A |
| 57 | Molz Oil Co. | Carrol #1 | D&A |
| 58 | Mesa Petroleum Co. | John 1-30 | D&A |
| 59 | GS Oil and Gas Co. | R.J, Seacat 1-25 | No information released |
| 60 | GS Oil and Gas Co. | Fox #1 | D&A |
| 61 | Michigan Wisconsin Pipeline Co. | Fox #1 | D&A |
| 62 | The Texas Co. | F.J. Moore #1 | D&A |
| 63 | Mesa Petroleum Co. | McPhail 1-32 | D&A |
| 64 | Banks Oil Co. | Vallentine #1 | Morrowan age sandstone |
| 65 | Reading and Bates Oil and Gas Co. | Vallentine #1 | D&A |
| 66 | Mohawk Energy Co. | Vallentine #1A | D&A |

# GEOCHEMICAL INVESTIGATION OF DIAGENETIC HISTORY OF PENNSYLVANIAN MORROWAN SANDSTONE, LEXINGTON FIELD, CLARK COUNTY, KANSAS

by

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# A B S T R A C T

Chemical and isotopic compositions of carbonate cements from sandstone of the Pennsylvanian Morrowan Stage and oil-field waters from the Lexington field, Clark County, Kansas, were analyzed to determine the diagenetic history of the reservoir rocks. The Lexington field produces from both Pennsylvanian Morrowan sandstone and Mississippian St. Louis Limestone carbonate rocks.

The earliest diagenetic event in the Morrowan sandstone was formation of quartz overgrowths, probably resulting from a lowering of the pH of the pore waters. Compaction of sediments led to pressure solution of quartz grains. With continued burial the temperature increased causing a reduction in silica solubility and precipitation of calcite. Following the replacement of silica by carbonate, a change in the hydrodynamic system led to ankeritization of the previously formed calcite, creating secondary porosity. Kaolinite, partially filling pore spaces, post-dates creation of secondary porosity. Pyrite was the last diagenetic mineral formed.

The source of chemical components of carbonate cements is complex. The $^{87}Sr/^{86}Sr$ ratios of carbonate cements of the Morrowan sandstone ranged between 0.70841 and 0.70940. Two carbonate rocks of the St. Louis Limestone had $^{87}Sr/^{86}Sr$ ratios of 0.70822 and 0.70856. The $^{87}Sr/^{86}Sr$ ratios of the cements are higher than that of contemporaneous seawater. The isotopic data of the cements cannot be explained by a simple, two-component model that requires two different sources of Sr, because the data of 1/Sr versus $^{87}Sr/^{86}Sr$ ratio of the carbonate cements are greatly scattered. Possibly the different Sr isotopic

compositions of the cements were caused by carbonate cements partially replacing minerals of different radiogenic Sr contents such as glauconite, clay minerals and quartz. Fluids that brought about ankeritization encountered calcite cements of different Sr isotopic composition, so that the replacement of calcite by ankerite resulted in a different Sr isotopic ratio, possibly on a microscopic scale.

The $\delta^{13}C$ values of the carbonate cements of Morrowan sandstone are between -1.73 and +2.82. Carbon isotopic data indicate that $CO_3$ ions were derived primarily from either marine carbonate rocks or contemporary seawater. Compositional differences of fluids from which the cements precipitated, appear to be the controlling factor governing the C isotopic distribution of the cements.

Salinities of Lexington oil-field waters are greater than 203,000 mg/l. Oil-field waters are of the Chloride-Calcium type. The waters are enriched in Ca, Sr, and Li and depleted in Mg and K, relative to evaporated seawater. Major processes controlling chemical composition of oil-field waters are: mixing of waters, membrane filtration and reaction of waters with silicate minerals.

Strontium isotopic compositions of oil-field waters from the Lexington field range from 0.70950 to 0.71050. Strontium isotopic data indicate that the isotopic character of the waters was not altogether inherited from the present Morrowan sandstone or the St. Louis Limestone carbonate rocks and that at least the present formation waters were not involved in diagenetic processes at the time of, and prior to, ankeritization of Morrowan sandstone.