

ISOTOPIC AND CHEMICAL STUDIES OF OIL-FIELD WATERS
ASSOCIATED WITH UPPER PALEOZOIC ROCKS, MINER FIELD,
NESS COUNTY, KANSAS

by

LUCY NICASTRO

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Approved by:


Major Professor

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INTRODUCTION

The chemical composition of petroleum-associated formation waters, whose salinities can approach ten times that of seawater, is governed by their original composition, whether marine, meteoric, or a mixture of these two, and their diagenetic history. Chemical data obtained for the waters can be used to evaluate the origin, migration, and accumulation of petroleum, the reservoir properties, and the hydrologic relationships among reservoirs. A summary of the determination and applications of the geochemistry of oil-field waters is provided by Collins (1975).

Many investigators (DeSitter, 1947; Bredehoeft et al., 1963; White, 1965; Billings et al., 1969; Kharaka and Berry, 1974; Graf, 1982, among others) explained different ways by which oil-field waters attain their high salinities. Evaporation, membrane filtration, dissolution and precipitation of minerals, and mixing of different waters are among the processes commonly suggested to account for the varied chemical composition of oil-field waters. Consideration of several lines of evidence is necessary to decipher the complex developmental path of the waters' chemical character.

Early studies responded to the issue of salinity using chemical data of the waters. Later, hydrogen and oxygen isotopic investigations contributed much to the understanding of the origin of the waters, as well as some possible fluid-rock interactions that influenced the chemical composition of the waters (Graf et al., 1965; Clayton et al., 1966; Hitchon and Friedman, 1969; Kharaka et al., 1973). The isotopic composition of strontium in petroleum-associated waters has more recently been suggested by Chaudhuri (1978) and Sunwall and Pushkar (1979) to be another valuable tool in the study of the processes governing the development of petroleum reservoirs.

Strontium isotopes have not been observed to fractionate within detection

limits of modern instrumentation. Broad differences in the Sr isotopic composition exist among crustal rocks, minerals, and waters, and the high diffusion rates of the ions in a fluid medium with respect to geologic time (e.g., the mixing rate of ions in the oceans is approximately 1000 years [Faure and Powell, 1972]) insure a uniform $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for any reservoir. These criteria may warrant the use of Sr as a tracer that could serve to set limits on processes that controlled the chemical composition of the waters.

Any isotopic variations among waters of closely spaced reservoirs must be attributed to different chemical evolutionary paths of the waters. Comparison of these isotopic variations may then provide valuable information in the study of hydrologic relationships among the reservoirs.

PRESENT STUDY

Purpose of Study

This study is an investigation of the Sr isotopic composition of oil-field waters in order to provide additional information concerning possible modes of chemical evolution of the waters and the relationship between the waters and reservoir rocks. A second objective of this study is to determine whether or not the Sr isotopic composition can be used to accurately predict hydrologic continuity among several reservoirs in an oil-field. The Sr isotopic data will be integrated with geologic information and chemical and stable isotopic data of the waters. Knowledge of the evolution of the chemical and isotopic character of the waters may ultimately help in understanding oil migration and accumulation.

Selection of Study Area

Oil-bearing reservoirs have been located at depths ranging from 4,300 to 4,400 feet below the surface in Middle Pennsylvanian "Cherokee" sandstone and in Upper Mississippian "Warsaw" limestone and dolostone in the Miner field in Ness County, Kansas (Fig. 1). A portion of this field was chosen as a study area because it possesses characteristics that are desirable for the study of waters in a subsurface environment: (1) the regional geology is relatively simple, lacking complex folds and faults to complicate the hydrologic regime, (2) the field is relatively small, covering an area of approximately 7 square miles, (3) oil obtained from many wells in Townships 17 and 18 South, Range 24 West is produced from lenticular sandstone bodies whose lateral extent may be accurately determined from available well control, (4) production from the field began in 1970 and primary production has continued since then, which is sufficient time for any drilling fluids that may contaminate the waters to have been flushed out and, (5) at no time prior to collection

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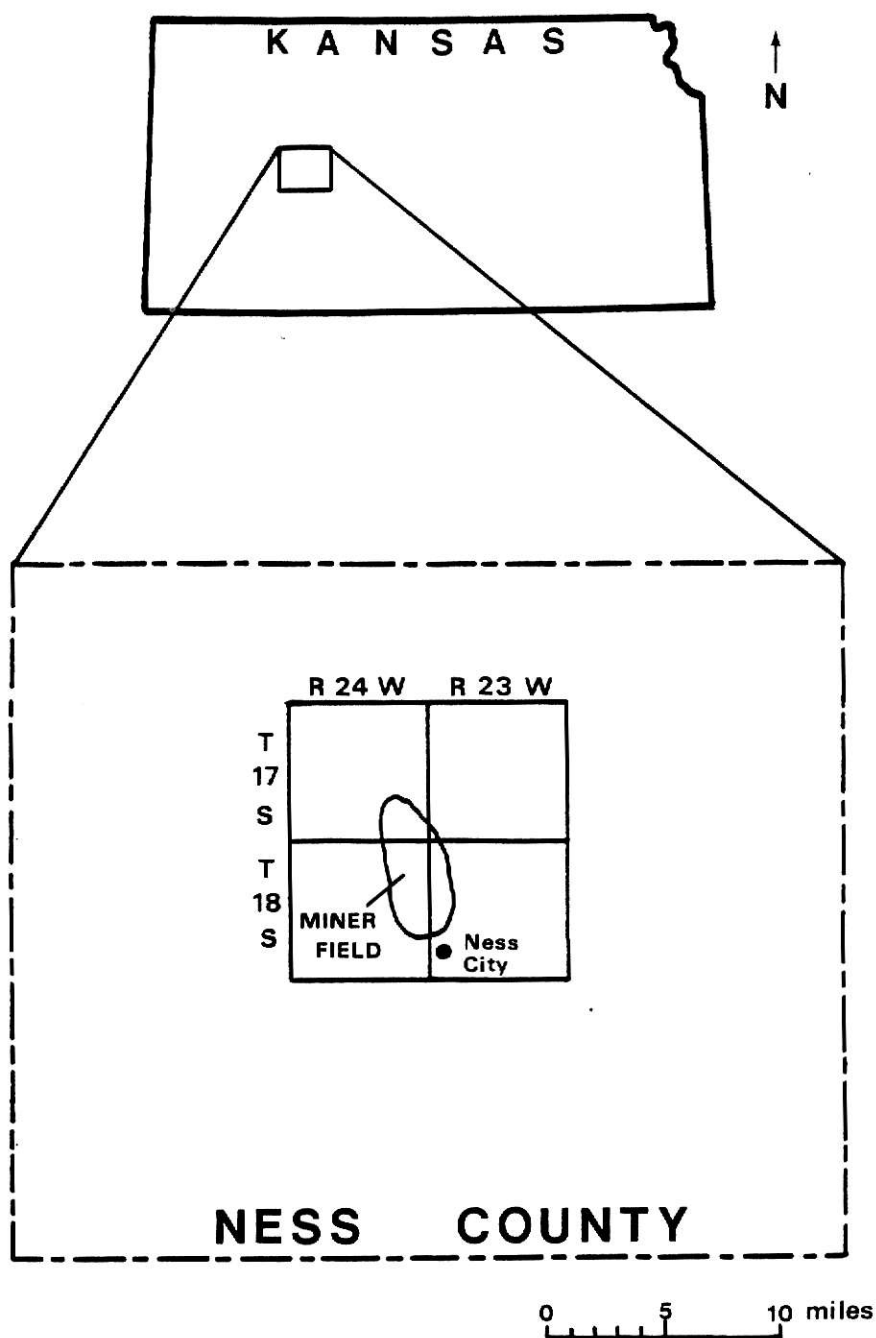


Figure 1. Location of the Miner field, Ness County, Kansas.

of these water samples for this investigation have secondary recovery methods been applied to these wells.

Excellent records on the wells, e.g. electric logs, cuttings, core fragments, and scout tickets, have been kept and are readily available through the Kansas Geological Society Well Log Library and Sample Library in Wichita, Kansas, and through Petroleum Information in Denver, Colorado. Production information was also obtained by oral communication from Thunderbird Drilling Company. Figure 2 is a plot of the wells from which formation water samples were available.

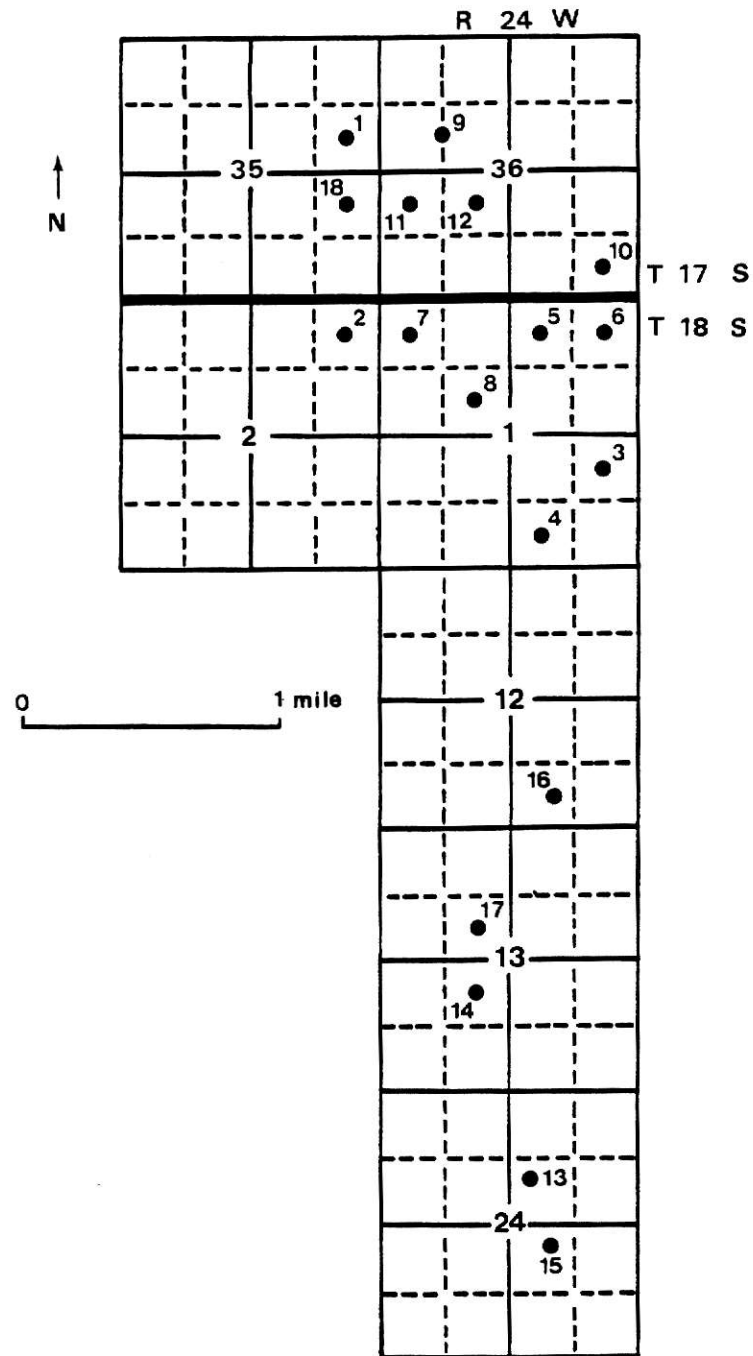


Figure 2. Plot of wells from which water samples were collected.
 (● Location of oil wells)

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Appreciation is expressed to Petroleum Information in Denver, Colorado for providing scout tickets, to the Kansas Geological Society and Library for providing well logs and cuttings, and to Thunderbird Drilling Company for their cooperation in obtaining the water samples.

This project was supported in part by a Grant-in-Aid of Research from Sigma Xi, the Scientific Research Society, and partly by National Science Foundation Grant Number EAR-7920070.

Bromide analyses were performed at Amoco Research in Tulsa, Oklahoma, and by Dr. Donald Whittemore at the Kansas Geological Survey in Lawrence, Kansas. Stable isotopic analyses were performed by Dr. S. Chaudhuri at the U. S. Geological Survey in Menlo Park, California. Appreciation is expressed to Dr. James O'Neil for cooperation in obtaining stable isotopic data and to Dr. Whittemore for the bromide analyses.

PREVIOUS INVESTIGATIONS

Two published works on the Sr isotopic composition of oil-field waters (Chaudhuri, 1978; Sunwall and Pushkar, 1979) suggested that Sr may be useful as a tracer in the formation, migration, and accumulation of these waters and petroleum. Chaudhuri (1978) investigated brines from Kansas and Colorado and found that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio did not correlate with Rb/Sr ratio, nor with the ages of the reservoir rocks. He suggested that the anomalously high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were derived from the migration of the fluids through Rb-rich clay minerals surrounding the reservoir rocks, and also speculated on the extent of hydrologic continuity among wells. Sunwall and Pushkar (1979) studied brines from petroleum fields in southeastern Ohio. They concluded that the consistency of ratios from uncontaminated fluids can identify brines under favorable conditions. The similarity of the ratios in the brines to ratios in meteoric waters from that area also convinced them that the ratios in both fluids were controlled by similar processes, or that the brines were derived from fresh water.

Bias (oral communication) analyzed brines from wells in T16S,R24W in Ness County, Kansas. He attributed low Rb/Sr ratios and high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios to a mixing of fresh and marine waters during the depositional stage of the sandstone and to migration of meteoric waters along a major unconformity into the carbonate and sandstone reservoir rocks.

GEOLOGY OF THE RESERVOIR ROCKS, MINER FIELD

In west-central Kansas, Upper Paleozoic rocks occur in the subsurface. As this study involves the investigation of oil-waters that accumulated in Middle Pennsylvanian "Cherokee" sandstone units and in Upper Mississippian "Warsaw" Limestone, an account will be given of the stratigraphy and structural setting of these units in this area during the late Paleozoic.

Mississippian subcrops in west-central Kansas are divided into the Kinderhookian, Osagian, Meramecian, and Chesteran stages (Fig. 3). Oil production from the Mississippian in Ness County is from a post-Osage breccia, the Meramecian "Warsaw" Limestone (Walters, pers. comm.). Whether the unit is a breccia unit above the bedrock limestone, or is the "Warsaw" in place, is not clear to this author. Walters (pers. comm.) indicated that the "Warsaw" from wells to the northwest of this study area consists of a fine dolomite and greenish clay, suggesting that perhaps it may be a breccia unit that lies directly above the Osage, as in the southwestern part of the county (Nodine-Zeller, 1981). The breccia unit is 30-50 ft. thick in this study area (Walters, et al., 1979). This unit was described by Thompson and Goebel (1968, p. 9) as a "breccia with large fragments of finely crystalline limestone interspersed with green, silty, clayey shale." They designated the age of the unit as Warsaw on the basis of conodonts. Nodine-Zeller (1981) studied the same core that Thompson and Goebel described, and she pointed out that the conodonts that they found in this breccia unit actually range from Warsaw to St. Louis or Ste. Genevieve; therefore, the presence of these conodonts in the limestone fragments would not have necessarily denoted the true age of the unit. She assigned an Atokan (?) or lower Desmoinesian (?) age to the same interval because of the presence of Idiognathodus sp.

The lowermost, distinctive part of the unit consists of pebbles,

SYSTEM	SERIES	STAGE	GROUP
PENNSYLVANIAN	MIDDLE	DESMOINESIAN	MARMATON
			CHEROKEE
		ATOKAN	UNNAMED
	LOWER	* MORROWAN	UNNAMED
MISSISSIPPIAN	UPPER	CHESTERAN	UNNAMED
		MERAMECIAN	
		OSAGIAN	
	LOWER	KINDERHOOKIAN	

*Not present in area of investigation

Figure 3. Generalized stratigraphic column of Mississippian and Pennsylvanian rocks in west-central Kansas (modified from Ebanks et al., 1979).

cobbles, and boulders of Mississippian limestone of varied ages that contain chert, sponge spicules, foraminifers, and other fossils. The matrix enclosing these fragments is gray and gray-green glauconitic shale, clay, or mudstone, gray to green siltstone, and green to gray sandstone. The matrix contains pyrite, geodes, chalcopyrite, sphalerite, glauconite grains, plant and coaly debris, quartz in various crystal habits, and beekite rings. Beds above this main layer are composed mainly of sandstone that contains cobbles and pebbles of Mississippian limestone, overlain by a deeply weathered paleosol. The sandstone and paleosol may or may not be present in this study area.

Nodine-Zeller (1981) interpreted this distinctive unit as pebbles, cobbles, and boulders re-worked from an older karst terrain. Although the limestone that composes the fragments in this unit were originally deposited in a marine environment (Thompson and Goebel, 1968), the possibility exists that alternating fresh-water and marine conditions were prevalent during the deposition of this "breccia" unit.

Middle Pennsylvanian "Cherokee" beds unconformably overly the Mississippian rocks in the study area (Fig. 3). Morrowan units are not present in the Miner field, as indicated by electric logs from the wells in this study. Lenticular sandstone bodies from 4 to 16 feet thick are interbedded with shale and thin beds of limestone and coal. In general, the "Cherokee" sandstone beds are medium, calcitic, submature quartzarenites, white to light brown, moderately sorted, and contain chert pebbles and minor amounts of glauconite/celadonite, pyrite, feldspar, and clay minerals. According to Walters et al. (1979, p. 313), "Greenish clay is present in the upper fine-grained sandstones and glauconite in the lower coarse sandstones." The sandstone lenses from which oil is produced have been interpreted as channel-fill sandstone by Walters et al. (1979). This interpretation is based on the following

observations (p. 313):

- (1) their position filling sinuous valleys; (2) their cross-section shape, convex base, and flat upper surface; (3) their dimensions - to 60 ft thick, 1/4 mile wide, and over 6 mi long; (4) the coarsening downward from very fine quartz grains to coarse sand and pea gravel at the base; (5) the enhanced permeability (over one darcy) near points of change of valley direction (point bar deposits?); (6) the common presence of 10° to 20° dips and cross-bedding in cores; and (7) the lateral gradational mixing of quartz sand with clastic chert fragments from residual cherts.

The bifurcating pattern of the sandstone lenses suggests a complex upper-delta distributary environment (Walters, et al., 1979, p. 322). One sandstone bed that overlies a sequence of sandstone lenses possesses a convex top and flat bottom; Walters (1979), p. 318) suggested that this sandstone body might be a marine-bar deposit. The presence of a "marine marker bed" (Walters, et al., 1979, p.319, Fig. 4-A) above the sandstone units attests to the continuation of marine conditions after the sandstone units were deposited. Although Walters et al. (1979, p. 318) suggested that the presence of glauconite supports a marine origin for the "Cherokee" sandstone, the presence of glauconite does not, by itself, establish marine conditions. Deer, Howie, and Zussman (1962, Vol. 3, footnote on p.35) point out that "...and glauconite itself, replacing feldspar (sic) and other minerals, has been reported in alluvial and eluvial deposits ...". Therefore, the value of glauconite as an environmental indicator is reduced. Also, the mineral celadonite has properties indistinguishable from those of glauconite and occurs in a different environment (Deer, Howie, and Zussman, 1962). Considering these factors and the upper-delta distributary environment demonstrated by Walters et al. (1979), a marine origin for these sandstone units is questionable.

To the northeast, the "Cherokee" beds abut against the Central Kansas Uplift and to the southwest they thicken into the Hugoton Embayment (Fig. 4). Nearest the uplift, clastic material constitutes the "Cherokee"; farther southwestward, into the embayment, the lithology changes to limestone and

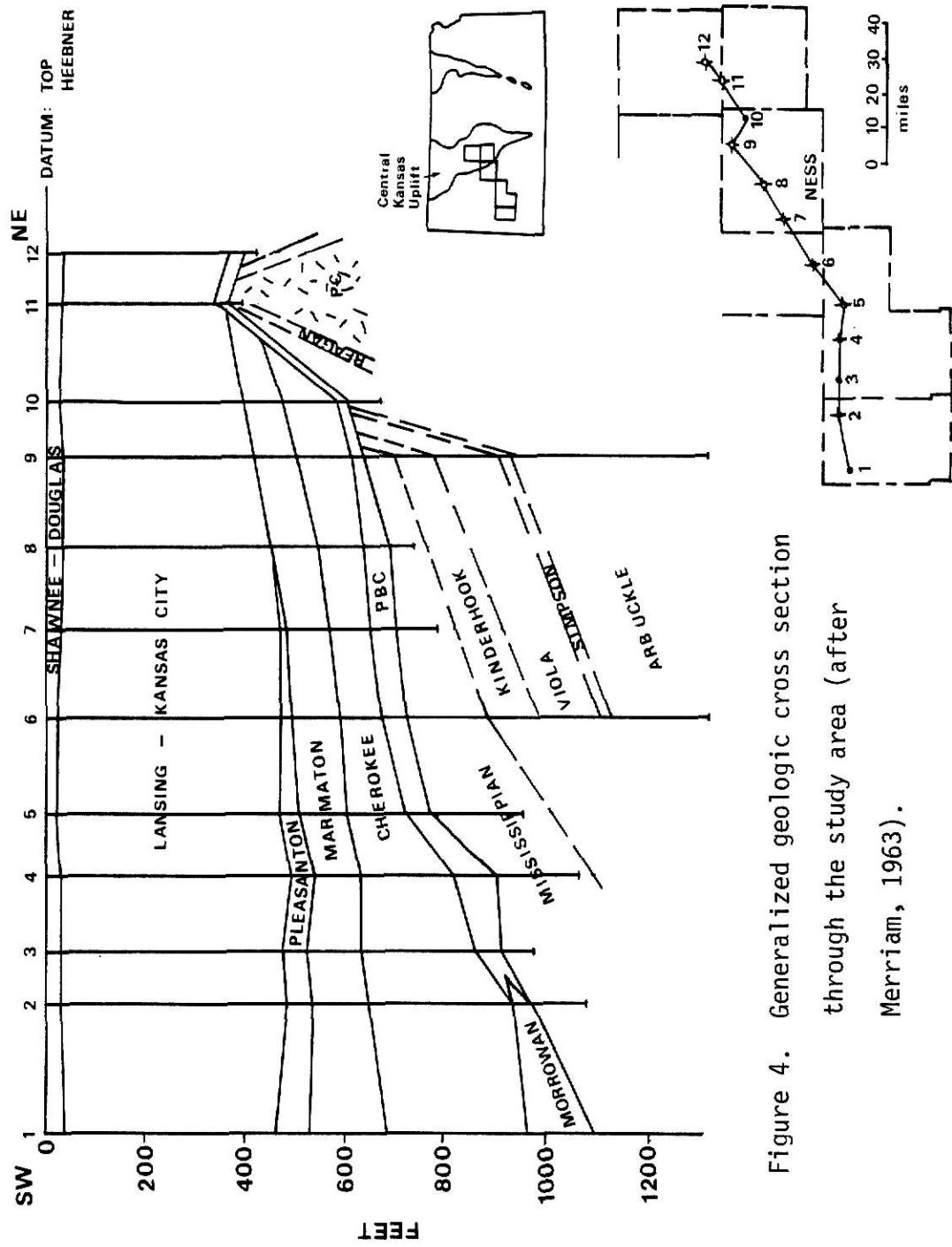


Figure 4. Generalized geologic cross section through the study area (after Merriam, 1963).

black shale. The "Cherokee" Group is 100 to 150 feet thick in the study area, as shown by Walters et al., (1979) and by electric logs from the wells that were sampled.

Descriptions of tectonic features and their relationships reported here have been taken from Merriam (1963). Many tectonic features that began to develop late in the Mississippian and early in the Pennsylvanian now constitute the present structural framework. The study area is located on the eastern shelf of the Hugoton Embayment bounded on the east and northeast by the Central Kansas Uplift and on the west by the Las Animas Arch. The embayment deepens toward the southwest into the Anadarko Basin.

The Central Kansas Uplift is a rejuvenation of the Ellis Arch, which displayed minor structural relief in pre-Mississippian time. During the Mississippian, a large inland sea spread over Kansas, as well as most of North America, resulting in extensive deposition of limestone. The crest of the Central Kansas Uplift lacks Mississippian rocks, which were stripped from the top of the structure as it was being uplifted and the Mississippian seas receded. Most of the uplift took place between mid-Mississippian (post-Meramecian) and mid-Pennsylvanian (pre-Desmoinesian) (Merriam, 1963). Drainage on the pre-Pennsylvanian surface was generally to the southwest, into the Hugoton Embayment. Vugs, sinkholes, solution valleys, and solution collapse features were produced on the exposed carbonate surface, indicated by the presence of untransported, weathered dolomite debris at the bottom of depressions (Jewett and Merriam, 1959). This period of erosion reduced the Mississippian surface to a peneplain and produced a shale- and chert- or mixed-lithoclast conglomerate. The "Cherokee" beds unconformably overlie this basal conglomerate, deposited as the Pennsylvanian sea advanced (Nodine-Zeller, 1981).

The Central Kansas Uplift continued to be active during the interval between the Mississippian and Lansing (Pennsylvanian), as shown by thinning of Pennsylvanian beds over the uplift. The Hugoton Embayment continued to subside at this time, as shown by the great thickening of both Mississippian and Pennsylvanian beds to the southwest. Movement of the Central Kansas Uplift and Hugoton Embayment continued at a slower rate during the Late Pennsylvanian and Early Permian and essentially ceased by mid-Permian.

COLLECTION OF SAMPLES

Oil and water samples were obtained at the well-head bleeder. Two water samples from each well were collected in one-liter polyethylene bottles. A few drops of Vycor-distilled 2 N HCl were added to one sample; no acid was added to the other. The bottles were pre-cleaned with concentrated HCl and rinsed several times with distilled, de-ionized water. The samples were sealed in the field and allowed to separate. In the laboratory, the samples were filtered with Whatman 42 Ashless filter paper to remove the oil and immediately analyzed for pH and HCO_3 content. The samples were then sealed and stored in similarly pre-cleaned polyethylene bottles for further analyses.

Well cuttings were available from the Kansas Geological Society Sample Library. Electric logs were used as an aid in correlation. Shale and sandstone samples were hand-picked from the cuttings. Whole cores were not available, but cuttings samples from two wells contained core fragments of the "Cherokee" sandstone, from which thin sections were made and analyses of the cements were performed.

Note: All oil-field waters and cements were analyzed for total elemental concentrations, and the chemical symbol for each element will be written without the charge sign throughout this report.

METHODS OF ANALYSIS

Major Elemental Concentrations

Cation concentrations were determined using a Perkin-Elmer model 305B atomic absorption spectrophotometer. Sodium, Ca, Mg, and Sr concentrations were measured by atomic absorption, whereas K, Rb, and Li concentrations were determined by emission spectrographic methods. Errors were obtained by analyzing a few of the samples twice for each particular element. The analytical uncertainties in the elemental values are as follows: Na-10 percent, K-10 percent, Ca-6 percent, Rb-5 percent, Mg-2 percent, Sr-1 percent, and Li-5 percent.

Three standards for each element were prepared from a certified atomic absorption reference solution (1000 mg/l) by diluting the reference solution to bracket the linear working range of each element. An excess of another alkali metal not being sought in the determination was added to the standards and samples to reduce the effects of ionization and matrix interference. Lanthanum was added to standards and samples for Ca, Mg, and Sr determinations to act as a releasing agent for these cations. The samples were diluted to bring the concentration of the element being sought to within the linear range of the instrument. A blank solution containing only the matrix was used to correct any effect of reagents on the concentrations of the elements in the sample.

For a few of the samples, Rb and Sr concentrations were determined with the mass spectrometer, using the method of isotope dilution as outlined in Faure (1977). This was done to check the values obtained by atomic absorption spectrophotometry. Estimated error in the Rb and Sr contents determined by mass spectrometry is 2 percent.

Chloride content was determined using a Buchler digital chloridometer. This method involves titration of the Cl ion by coulometric generation of Ag ion and amperometric detection of the end point. Silver ions are generated at the

anode at a constant rate by passing a constant direct current between a pair of Ag-generating electrodes. The end point is indicated by the rapid rise in the Ag-ion concentration when the Cl is consumed. The amount of Cl precipitated is proportional to the elapsed electrolysis time, because the rate of Ag-ion generation is constant. The digital readout is in units of meq/l of Cl; this value is then converted to mg/l by multiplying by the equivalent weight of Cl. The error for the Cl values is 3 percent, determined by repeated analysis.

Sulfate concentration was determined by the Turbidimetry-Null method, using a Coleman model 14 universal spectrophotometer. In measuring SO_4 content, the SO_4 is complexed with BaCl_2 , which precipitates to form a suspended colloid in a salt-acid-glycerol solution. Fifty ml of standard SO_4 solution and the samples were mixed with 10 ml of salt-acid-glycerol solution, and stirred. Upon addition of 0.3 g of 30-40 mesh BaCl_2 crystals, BaSO_4 precipitated. This solution was poured into square matching cuvetts and percent transmittance (T) of a light source was measured. The percent T varies inversely with the SO_4 concentration in the waters. Percent T versus standard concentration was plotted on semi-log paper with percent T on the log scale and concentration of SO_4 on the arithmetic scale. Concentration of SO_4 in the unknown samples was then determined from percent T. Error was estimated to be 2 percent, determined by replication.

Bicarbonate content was determined by titrating the samples with a standardized acid to the end point of HCO_3 at pH 4.5, as outlined by Lind (1979). Bromine determinations were done at Amoco Research in Tulsa, Oklahoma, and by Dr. Don Whittemore at the Kansas Geological Survey in Lawrence, Kansas. The error in the Br analyses is 5 percent. Content of total dissolved solids (TDS) was measured by evaporating 1 ml of the water, heating to 300°C for approximately one hour, and weighing the residue.

Errors for TDS values are ± 200 mg/l. Density was determined by weighing one ml of the water sample.

Isotopic Determinations

Strontium was separated out of the waters using ion-exchange columns containing cross-linked Dowex 50W-X8 cation exchange resins. All 2 N HCl used in elution and collection was Vycor-distilled. All glassware used was Vycor-glass to avoid contamination, Teflon beakers were used for all dissolutions and separations, and all laboratory equipment was soaked in concentrated HCl acid-bath and rinsed several times with distilled, de-ionized water.

Two separations were performed on each sample, the first to remove much of the Na that would interfere with the analysis, and the second to isolate Sr. A selected amount of the oil-water was evaporated to dryness in a Teflon beaker, redissolved in 2 N HCl, and placed into the first columns. The columns were eluted with 2 N HCl to collect Na-free Sr, Ca, etc. in one beaker. This Na-free solution was evaporated to dryness, redissolved in 2 N HCl and the elution process repeated with an appropriate amount of 2 N HCl to isolate Sr. The Sr salts were converted to $\text{Sr}(\text{NO}_3)_2$ by addition of 3 N HNO_3 , heated over a Bunsen burner to oxidize any organic residue, and placed onto a Ta filament for mass spectrometric analysis.

Strontium isotopic ratios were obtained using a 15-cm, 60° solid source mass spectrometer with a Nier-type Faraday cup collector (Nuclide Corporation, model 6-60S). Isotopic ratios were normalized to the $^{86}\text{Sr}/^{88}\text{Sr}$ value of 0.1194. Errors for $^{87}\text{Sr}/^{86}\text{Sr}$ values are ± 0.0003 .

Oxygen, deuterium, and carbon isotope data were obtained at the United States Geological Survey in Menlo Park, California. The precision of $\delta^{18}\text{O}$ values, based on repeated analyses of some samples, is better than ± 0.15

per mil, whereas that of δD is better than ± 2 per mil.

Rock Sample Analysis

Shale samples were washed in distilled, de-ionized water to remove any traces of drilling mud, dried, then crushed with a mortar and pestle. The powder was suspended in distilled, de-ionized water, and centrifuged to separate the $< 0.5 \mu m$ and 0.5 to $2.0 \mu m$ clay fractions. Oriented slides were prepared for clay mineral analysis by placing the slurry on a clean glass slide, and allowing to dry. Clay mineralogy was determined using a Norelco X-ray diffractometer with a Ni filter and Cu $K\alpha$ source.

Clay minerals were prepared for $^{87}Sr/^{86}Sr$ analysis by dissolving the sample in a mixture of one to two ml $HClO_4$ and 15 ml HF by heating, then evaporating to near dryness. Two to three ml of de-ionized water were added and the solution again evaporated to near dryness. A few ml of 1 N HCl were added, heated to redissolve the solids, and then cooled overnight. The solution was then filtered and brought to 10 ml volume by addition of de-ionized water. This stock solution was then analyzed for Sr contents and $^{87}Sr/^{86}Sr$ by the procedures outlined earlier.

To analyze the sandstone cements, the core fragments were crushed, weighed, and the carbonate cement was dissolved in approximately 0.5 N HCl. The undissolved material was filtered out and the filtrate was brought to 50 ml volume. This stock solution was analyzed for $^{87}Sr/^{86}Sr$ by the procedures described earlier.

RESULTS

X-ray Diffraction Data

Diffraction patterns were obtained for the 0.5 to 2.0 μm and $< 0.5 \mu\text{m}$ fractions of "Cherokee" shale samples from four wells. The patterns are essentially identical. Figure 5 illustrates typical diffraction patterns. The clay-mineral species recognized are chlorite, illite, chlorite-smectite mixed-layer, illite-smectite mixed-layer, and kaolinite. A similar clay-mineral assemblage was found in underclays and associated lithotypes of the "Cherokee" Group (Tien, 1970).

Chlorite.--The 14.24-Å, 7.28-Å, 4.76-Å, and 3.5-Å reflections on the untreated sample correspond to the (001), (002), (003), and (004) of chlorite, respectively. These reflections persist throughout glycolation, heating to 490°C, and hydrazine treatment.

Chlorite-smectite mixed layer.--Upon glycolation, a reflection appears at 15.27 Å that was not present on the untreated sample pattern, revealing the presence of an expandable chlorite-smectite mixed-layer species. Expansion to 15.27 Å indicates that the smectite only expands partially. There are no integral higher-order reflections of this 15-Å reflection.

Illite.--The 10.13-Å, 4.98-Å, and 3.34-Å reflections correlate respectively to the (001), (002), and (003) basal spacings of untreated illite. The broad, asymmetric feathering of the low-angle side of the reflection indicates that the illite is poorly crystalline or that there may be a mixed-layer component with the illite. With hydrazine treatment, the illite reflection becomes very broad, because of the expansion of kaolinite from 7 Å to 10 Å.

Illite-smectite mixed layer.--The broad feathering of the low-angle side of the first-order illite reflection indicates the presence of an expandable mixed-layer species. Subsequent to glycolation, the expandable

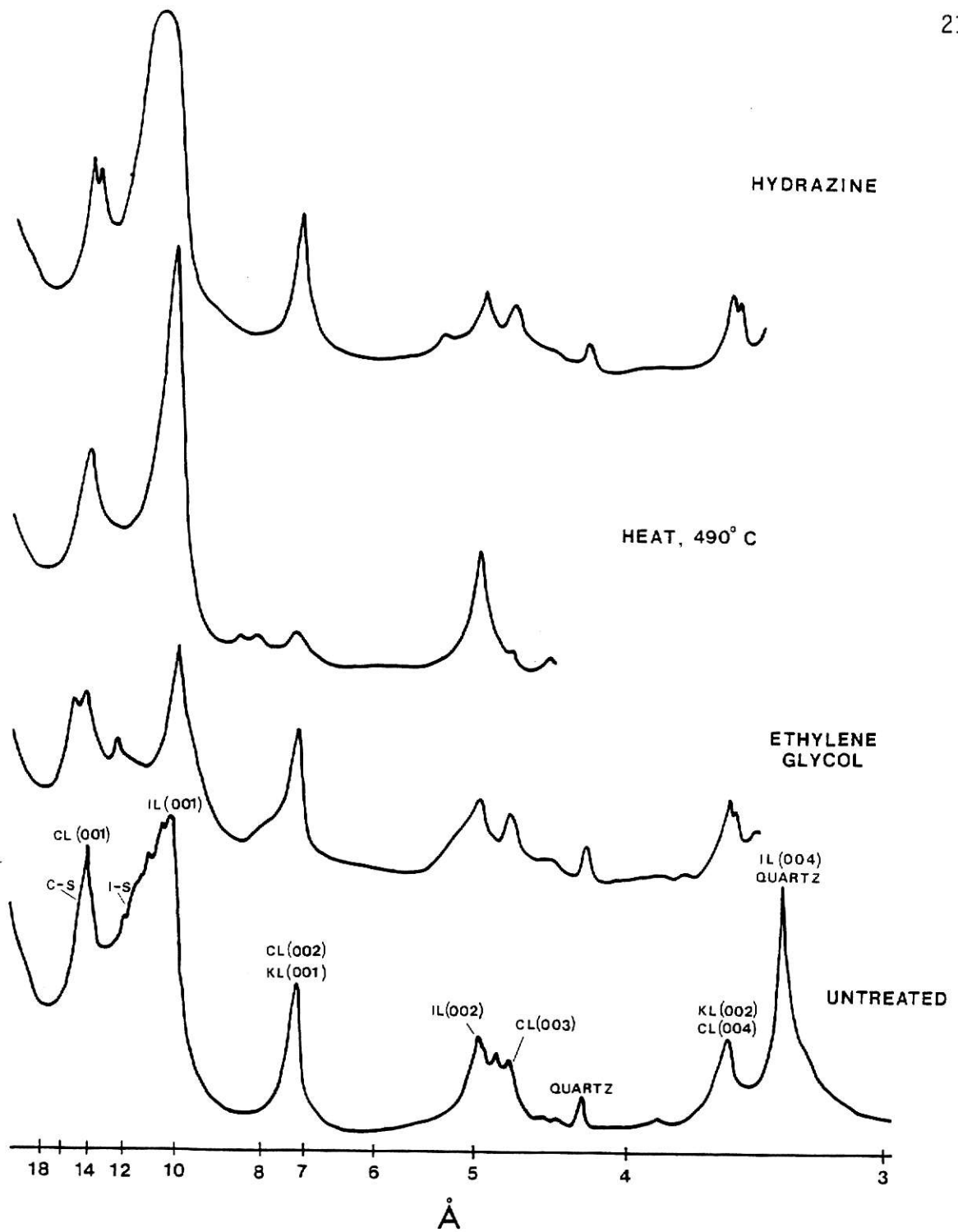


Figure 5. X-ray diffraction patterns of clay minerals in the "Cherokee" shale (CL=chlorite, C-S=chlorite-smectite, IL=illite, I-S=illite-smectite, KL=kaolinite).

portion of the mixed-layer expands to 12.54 Å. Upon heating, collapse of the layers to 10Å occurs, possibly because of expulsion of water from the inter-layer site. The smectite expands to 13.59 Å after hydrazine treatment. No integral higher-order reflections are recognized.

Kaolinite.--The 7.28-Å and 3.54-Å reflections are interpreted as the (001) and (002) of kaolinite, respectively. The (001) reflection is destroyed upon heating to 490°C, leaving a weak reflection corresponding to the (002) of chlorite. With hydrazine treatment, the kaolinite expands to about 10 Å, because the hydrazine molecule is able to break the weak bonds in kaolinite and enter the structure. This is evidenced by the broadening and intensification of the 10-Å reflection.

Chemical Data

Results of chemical analyses on oil-field waters from the Miner field, Ness County, are summarized in Table 1. The Na values range from 9090 to 11,840 mg/l, Ca values are within the range of 1150 to 1650 mg/l, Mg values lie between 405 and 497 mg/l, and K concentrations range from 209 to 265 mg/l. Strontium concentrations are within a narrow range of 44.8 to 48.8 mg/l, except for one high value of 52.3 mg/l for Sample 4. The range of Li contents is very narrow, between 11.67 and 12.8 mg/l, except for one value of 39.7 mg/l in Sample 21; Rb ranges from 0.59 to 0.92 mg/l. Chloride, ranging from 17,200 to 22,400 mg/l, is the most abundant anion. Sulfate values are between 60 and 2160 mg/l, whereas HCO₃ contents range from 73 to 542 mg/l. Bromide values are from 32 to 43 mg/l. TDS values are from 31,900 to 34,800 mg/l, except for high values in Samples 4 and 12, with TDS values of 37,600 and 36,200 mg/l, respectively. The pH values are within a narrow range of 7.3 to 8.0, and the density varies from 1.0088 to 1.0655 g/ml.

TDS content of seawater is approximately 35,000 mg/l. TDS values of all but two water samples are generally lower than the amount for seawater.

Table 1. Chemical analyses of oil-field waters, Miner field, Ness County, Kansas.

(concentrations expressed in mg/l, except density in g/ml, and pH)

Sample No.	Na	Ca	K	Mg	Sr	Li	Rb	Cl	SO ₄	HCO ₃	Br	pH	TDS	Density
LN-80-1	9300	1440	247	442	48.0	11.95	0.84	17,700	1540	531	43	8.0	32,700	1.0148
LN-80-2	10,230	1570	256	420	45.5*	12.20	0.70*	17,900	1820	102	37	7.5	31,900	1.0263
LN-80-3	9530	1260	236	440	45.6	12.80	0.72	18,800	760	322	39	7.8	32,500	1.0263
LN-80-4	11,840	1150	260	483	52.3	11.92	0.70	22,400	60	264	--	8.0	37,600	1.0358
LN-80-5	9230	1650	248	445	48.0	11.70	0.80	18,100	1800	126	--	7.7	34,700	1.0408
LN-80-6	9960	1620	265	425	44.8	11.90	0.73	17,700	1760	--	32	--	32,600	1.0257
LN-80-7	9150	1560	240	405	46.5*	11.67	0.76	18,100	1760	73	36	7.6	34,000	1.0550
LN-80-8	10,314	1490	253	432	46.0	11.90	0.70	18,100	1840	211	37	7.8	33,600	1.0323
LN-80-9	10,280	1550	239	493	48.8	11.90	0.68	19,000	1760	152	--	7.7	34,000	1.0250
LN-80-10	9090	1420	215	460	46.2	11.98	0.65	17,700	1800	123	--	7.6	32,800	1.0468
LN-80-11	9370	1380	217	497	47.2	11.86	0.64	18,400	1660	152	--	7.7	34,000	1.0446
LN-80-12	10,280	1620	248	445	47.8	12.30	0.92	18,600	1760	111	--	7.7	36,200	1.0515
LN-82-13	9470	1330	212	448	46.4	11.90	0.67	18,300	2080	318	--	7.4	32,700	1.0438
LN-82-14	9820	1530	216	458	46.4	12.04	0.59	18,100	2060	542	--	7.5	33,900	1.0349
LN-82-15	9570	1350	209	455	46.2	11.95	0.65	18,100	2100	325	--	7.5	31,900	1.0088
LN-82-16	9450	1400	210	436	46.2	12.29	0.67	17,200	2160	315	--	7.4	33,100	1.0322
LN-82-17	10,230	1390	224	444	45.3	11.70	0.61	18,400	1960	478	--	7.6	32,700	1.0383
LN-82-18	9390	1440	212	485	46.6	12.20	0.68	17,200	2120	336	--	7.3	32,200	1.0256
LN-82-20	9860	1410	--	440	45.5	12.00	0.65	17,500	1960	380	--	7.4	32,200	1.0278
LN-82-21	9500	1300	213	444	46.0	39.70	0.65	18,800	1700	542	--	7.5	34,800	1.0655

* determined by isotope dilution

According to Krieger (1963), waters containing more than 35,000 mg/1 TDS are classified as brines. Davis (1963) designated the term brine for waters that are greater than 100,000 mg/1 TDS content, and set limits of 10,000 to 100,000 mg/1 for saline waters. The waters in this study are regarded as saline waters, after Davis' classification, and will be referred to as oil-field waters.

Table 2 summarizes the concentrations of the cations and anions in equivalents per million (EPM), and Table 3 summarizes the classification of Miner field waters.

The Schoeller diagram (Fig. 6) illustrates similarity in concentrations of major chemical constituents among the water samples. The greatest variability is apparent in the HCO_3 and SO_4 contents.

Oxygen, Hydrogen and Carbon Isotopic Data

Oxygen, hydrogen and carbon stable isotopic data are presented in Table 4. Not all samples were analyzed for these stable isotopic values because of constraints on time and funds. The $\delta^{18}\text{O}$ values, relative to Standard Mean Ocean Water (SMOW), in several saline water samples vary within a narrow range of -9.39 to -10.10 per mil (SMOW), and the δD values range from -82.07 to -84.97 per mil (SMOW). A representative sample of Kansas meteoric water, taken from Tuttle Creek Reservoir in Manhattan, Riley County, yields a $\delta^{18}\text{O}$ value of -7.38 per mil and a δD value of -52.27 per mil (SMOW). These values are similar to the values of Kansas River water near Topeka, as previously reported by Friedman et al. (1964). Because Riley County's latitudinal position is similar to that of Ness County, these isotopic values can be regarded as the composition of the meteoric waters in Ness County.

The $\delta^{13}\text{C}$, relative to PDB, of a sandstone calcite cement from Well 4 is -11.84 per mil and the $\delta^{18}\text{O}$ is +22.55 per mil (SMOW).

Table 2. Chemical analyses of oil-field waters, Miner field, Ness County, Kansas.

(concentrations expressed in EPM)

Sample No.	Na	Ca	K	Mg	Sr	Li	Rb	Cl	SO ₄	HCO ₃	Br
LN-80-1	399	71.0	6.24	35.8	1.08	1.7	0.010	493	31.6	5.7	0.54
LN-80-2	434	76.5	6.39	33.7	1.02	1.7	0.008	492	36.9	1.6	--
LN-80-3	404	61.6	5.90	35.5	1.01	1.8	0.008	516	15.4	5.1	--
LN-80-4	497	55.5	6.44	38.7	1.15	1.7	0.008	609	1.2	4.2	--
LN-80-5	386	79.4	6.11	35.2	1.05	1.6	0.009	490	36.0	2.0	--
LN-80-6	423	79.4	6.62	34.1	1.00	1.7	0.008	488	35.7	--	0.40
LN-80-7	377	74.1	5.83	31.6	1.00	1.6	0.008	483	34.8	1.1	--
LN-80-8	435	72.4	6.28	34.4	1.02	1.7	0.008	494	37.1	3.4	--
LN-80-9	436	75.4	5.98	39.6	1.09	1.7	0.008	522	35.8	2.4	--
LN-80-10	378	68.0	5.27	36.2	1.01	1.7	0.007	478	35.8	1.9	--
LN-80-11	390	66.0	5.33	39.2	1.03	1.6	0.007	498	33.1	2.4	--
LN-80-12	447	73.5	5.75	33.1	0.96	1.6	0.010	475	33.2	1.6	--
LN-82-13	394	69.0	5.19	35.3	1.01	1.7	0.008	493	41.5	5.0	--
LN-82-14	413	73.8	5.35	36.4	1.02	1.7	0.007	493	41.5	8.6	--
LN-82-15	412	67.0	5.30	37.1	1.05	1.7	0.008	506	43.4	5.3	--
LN-82-16	398	68.1	5.22	34.8	1.02	1.7	0.008	470	43.6	5.0	--
LN-82-17	433	67.4	5.50	35.5	1.01	1.6	0.007	506	39.7	7.6	--
LN-82-18	398	70.2	5.30	38.9	1.04	1.7	0.008	473	43.1	5.4	--
LN-82-20	417	68.3	--	35.2	1.01	1.7	0.007	482	39.7	6.1	--
LN-82-21	388	61.0	5.13	34.3	0.99	5.4	0.007	497	33.2	8.2	--

Table 3. Chemical Classification of oil-field waters, Miner field, Ness County, Kansas.

Sample No.	qNa	qCl	qMg	qNa/qCl	$\frac{qCl-qNa}{qMg}$	Water type
LN-80-1	77.5	93.0	7.0	0.83	2.2	Cl-Ca
LN-80-2	78.4	92.7	6.1	0.85	2.3	"
LN-80-3	79.2	96.2	6.9	0.82	2.5	"
LN-80-4	82.8	99.1	6.5	0.84	2.5	"
LN-80-5	75.8	92.8	6.9	0.82	2.5	"
LN-80-6	77.5	93.1	6.3	0.83	2.5	"
LN-80-7	76.8	93.1	6.4	0.82	2.5	"
LN-80-8	79.0	92.4	6.3	0.85	2.1	"
LN-80-9	77.9	93.2	7.1	0.84	2.2	"
LN-80-10	77.1	92.7	7.4	0.83	2.1	"
LN-80-11	77.5	93.3	7.8	0.83	2.0	"
LN-80-12	79.5	93.2	5.9	0.85	2.3	"
LN-82-13	77.8	91.4	7.0	0.85	1.9	"
LN-82-14	77.7	91.1	6.9	0.85	1.9	"
LN-82-15	78.6	91.2	7.1	0.86	1.8	"
LN-82-16	78.2	90.6	6.8	0.86	1.8	"
LN-82-17	79.6	91.5	6.5	0.87	1.8	"
LN-82-18	77.3	90.7	7.6	0.85	1.8	"
LN-82-20	79.7	91.3	6.7	0.87	1.7	"
LN-82-21	78.4	92.3	6.9	0.85	2.0	"

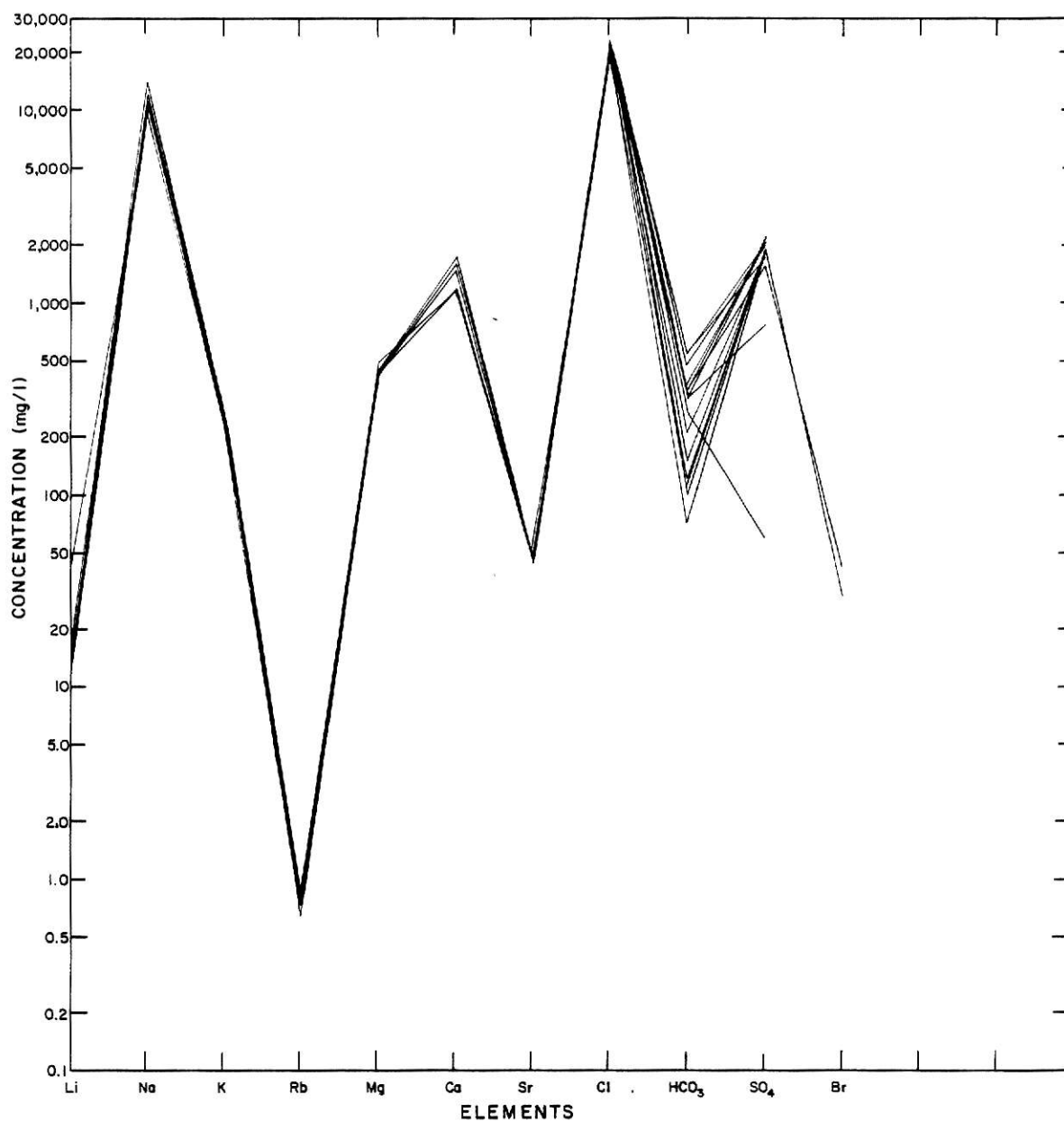


Figure 6. Schoeller diagram, comparing the concentrations of the various elements among the water samples.

Table 4. Hydrogen, oxygen, and carbon isotopic data of waters and calcite cement from Upper Paleozoic rocks, Miner field, Ness County, Kansas. The standard for oxygen and hydrogen is SMOW, and for carbon is PDB.

Sample No.	$\delta^{18}\text{O}$ (per mil)	δD (per mil)
LN-80-2*	-10.10	-84.97
LN-80-3*	-9.88	-84.46
LN-80-4*	-9.39	-82.21
LN-80-5**	-10.10	-83.20
LN-80-8*	-9.69	-84.03
LN-80-9*	-9.71	-82.07
LN-80-12*	-9.69	-83.25
LN-82-14*	-9.39	-83.69
Meteoric	-7.38	-52.27

* producing interval is "Cherokee"

** producing interval is Mississippian

LN-80-4 (calcite cement)	$\delta^{13}\text{C}$ (per mil) -11.84	$\delta^{18}\text{O}$ (per mil) +22.55
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Strontium Isotopic Data

The Rb/Sr ratios and the Sr isotopic composition of the waters, expressed as $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, are presented in Table 5. Time limits permitted analyses only of 13 of the water samples. The Sr isotopic ratios vary between 0.7254 and 0.7277. The Rb/Sr ratios range from 0.013 to 0.020. There is no apparent difference in the ratios between waters from Pennsylvanian "Cherokee" sandstone reservoir rocks, and the waters from the Mississippian carbonate rocks (samples 5, 6, and 10). The Rb/Sr ratios of the waters are too small to have much effect on the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Therefore, the waters could not have acquired their high isotopic ratios by in situ decay of ^{87}Rb to ^{87}Sr , and these ratios can be considered to be the original ratios of the fluids.

Carbonate cements from sandstone reservoir rocks from Wells 1 and 2 yield $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7216 and 0.7142, respectively (Table 6). These values are significantly lower than those in the associated waters, but higher than Pennsylvanian seawater, the value of which is 0.7080 to 0.7085, given by Peterman et al. (1970). The ratio from the 0.5-to-2.0 μm clay fraction of a "Cherokee" shale from Well 8 to 0.7191, which is also significantly lower than that of the water samples.

DISCUSSION

Chemical Classification

Ostroff (1967) and Collins (1972) reviewed different chemical classification schemes for subsurface waters that were previously suggested by Palmer (1911), Sulin (1946), Chebotarev (1955), and Schoeller (1955). According to Ostroff, Sulin's classification system is most applicable to oil-field waters, and this classification is adopted here. Sulin's classification separates waters into genetic types, groups, and sub-groups, based upon ratios of alkali metals and alkaline earth elements. The concentrations of these elements

Table 5. Rb/Sr ratio and strontium isotopic data of oil-field waters,
Miner field, Ness County, Kansas.

Sample No.	$^{87}\text{Sr}/^{86}\text{Sr}^a$	Rb/Sr	$^{87}\text{Sr}/^{86}\text{Sr}^b$
LN-80-1*	0.7264	0.018	
LN-80-2*	0.7268	0.015	
LN-80-3*	0.7259	0.016	
LN-80-4*	0.7254	0.013	0.7247
LN-80-5**	0.7254	0.017	
LN-80-6**	0.7262	0.016	
LN-80-7*	0.7267	0.106	
LN-80-8*	0.7262	0.015	
LN-80-9*	0.7271	0.014	
LN-80-10**	0.7277	0.014	0.7270
LN-80-11*	0.7254	0.014	
LN-80-12*	0.7261	0.020	
LN-82-13*	0.7274	0.014	

a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio \pm 0.0003

b resampled after a two-year interval

* produced from the Pennsylvanian "Cherokee" sandstone

** produced from Mississippian carbonate rocks

Table 6. Rb/Sr ratio and strontium isotopic composition of clay minerals and sandstone cements of the "Cherokee" Group, Miner field, Ness County, Kansas.

Sample No.	Material	$^{87}\text{Sr}/^{86}\text{Sr}$	Rb/Sr
LN-80-4	0.5 to 2.0 μm fraction	--	2.44*
LN-80-8	0.5 to 2.0 μm fraction	0.7191	1.01*
LN-80-8	<0.5 μm fraction	--	1.73*
LN-80-1	Calcite cement	0.7216	--
LN-80-2	Calcite cement	0.7142	--

* determined by X-ray fluorescence

must be expressed in equivalents to classify waters by this method.

Equivalents per 100 g of water are calculated for each anion and cation concentration. The sum of the equivalents for each ion is obtained and the percentage (q) of a particular ion is calculated by dividing the number of equivalents of each ion by the total. If qNa/qCl ratio is greater than 1, more equivalents of Na ion are present and the excess Na can combine with SO_4 or HCO_3 . If $qNa - qCl/SO_4$ is less than 1, the water is of the sulfate-sodium type; if this ratio is greater than 1, the water is a bicarbonate-sodium type. If qNa/qCl is less than 1, excess chloride can combine with Ca and Mg. If $qCl - qNa/qMg$ is greater than 1, the water is chloride-calcium type, and if it is less than 1, the water is chloride-magnesium type.

Each of these water types is found in a certain geologic environment. Sulfate-sodium and bicarbonate-sodium waters are characteristic of land surface (fresh water) conditions; marine environments produce chloride-magnesium type waters, and chloride-calcium waters are typical of deep, stagnant, subsurface conditions.

All the waters in this study are the chloride-calcium type, indicating deep, hydrostatic conditions. Sulin (1946) and Collins (1972) found that chloride-calcium type waters are most often associated with petroleum-producing formations.

Major Chemical Composition

In any investigation involved in the interpretation of the chemical composition of formation waters, the investigator must be cognizant of a lack of knowledge regarding the chemical composition of the water originally present at the time of sediment deposition and the composition of the water presently in the rocks.

The bulk of the evidence supports the idea that most of the "Cherokee"

sandstone was the result of deposition in the upper delta plain of a delta system by freshwater. As this sandstone was buried during marine transgression, marine waters may have mixed with or flushed any original interstitial fresh water out of the sediments. Mixing may have been hampered by muds that would cover sand deposits during flood stages of the stream, or as a result of abandonment of the channel (Swanson, 1979). Mixing between marine and freshwater is difficult, as demonstrated by a) the freshwater 'lid' effect, b) the sharp contact between marine water and freshwater in coastal aquifers, and c) the rise in the freshwater table as marine conditions encroach on the land, pushing fresh water up and landward.

Evidence of a karst terrain on the Mississippian units (Nodine-Zeller, 1981) also supports the possibility of mixing of fresh and marine waters during transgression of the seas. Although some fresh water admittedly may have been a part of the original waters in the sandstone and carbonate reservoirs, association of these rocks with marine conditions allows the assumption that the original water in the sediments had a composition very similar to that of seawater, and that a component in the present oil-field waters is of seawater origin. At the very least, the original waters would have been brackish and would still contain dissolved ions in the same proportions as those of seawater. Any differences between the present formation waters, which undoubtedly have a complex chemical history, and seawater have then arisen as a result of a major redistribution of the elements. This redistribution can be effected by one or more of the following mechanisms that operate in the subsurface: (1) mixing of water close to seawater in composition with low salinity water, (2) shale membrane filtration, (3) reaction with silicates, (4) ion exchange on clay minerals, (5) dissolution of evaporites, (6) formation of new minerals, and (7) interaction with organic matter.

A useful way of investigating the chemical character of the waters is by comparing the chemical constituents of the oil-waters with those of evaporating seawater. Any chemical difference between the two waters can be evaluated by comparing the element/Cl ratio. A water is enriched in an element if its element/Cl ratio is greater than that of seawater, and depleted in an element if this same ratio is less than that of seawater. Modern-day seawater composition may be taken as representative of seawater in the past, at least during the Phanerozoic. According to Garrels and McKenzie (1971), there is no compelling evidence to indicate that the chemical composition of seawater had changed in the last two billion years. Hence, a comparison of the formation waters with modern seawater may provide a useful basis for an understanding of the origin and diagenetic history of the oil-field waters from the Miner field in Ness County, Kansas (Table 7).

Comparison of the element/Cl ratio of the petroleum-associated water to this ratio in seawater shows that the former are depleted in Na, K, Mg, SO_4 , and Br and enriched in Ca, Sr, Rb, and Li. Except for a few samples, the HCO_3 content relative to Cl is higher than that of seawater. As the HCO_3 concentrations were not determined at the well-site but were determined later in the laboratory, possible contamination with atmospheric CO_2 may have produced questionable data. Therefore, no interpretation of HCO_3 content is attempted.

Strontium and calcium enrichment and magnesium depletion.--The Ness County oil-field waters are depleted in Mg and enriched in both Sr and Ca, relative to seawater (Figs. 7, 8, and 9, Table 7). Other oil-field waters are also depleted in Mg and enriched in Ca and Sr, relative to seawater (Collins, 1975). These depletions and enrichments have been suggested to be caused

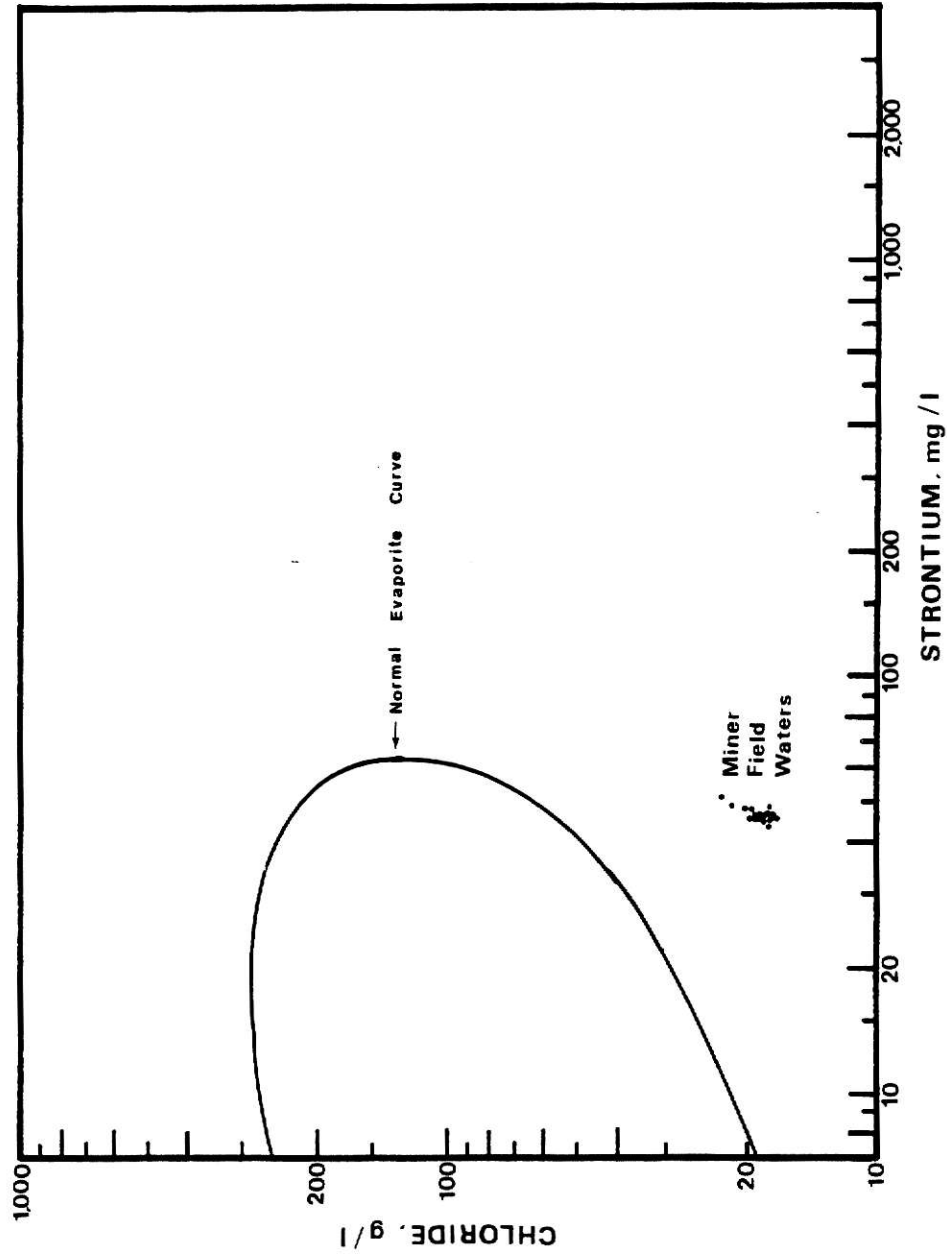


Figure 7. Comparison of chloride versus strontium concentration in oil-field waters, Miner field, Ness County, Kansas in relation to that of evaporating seawater (modified from Collins, 1974).

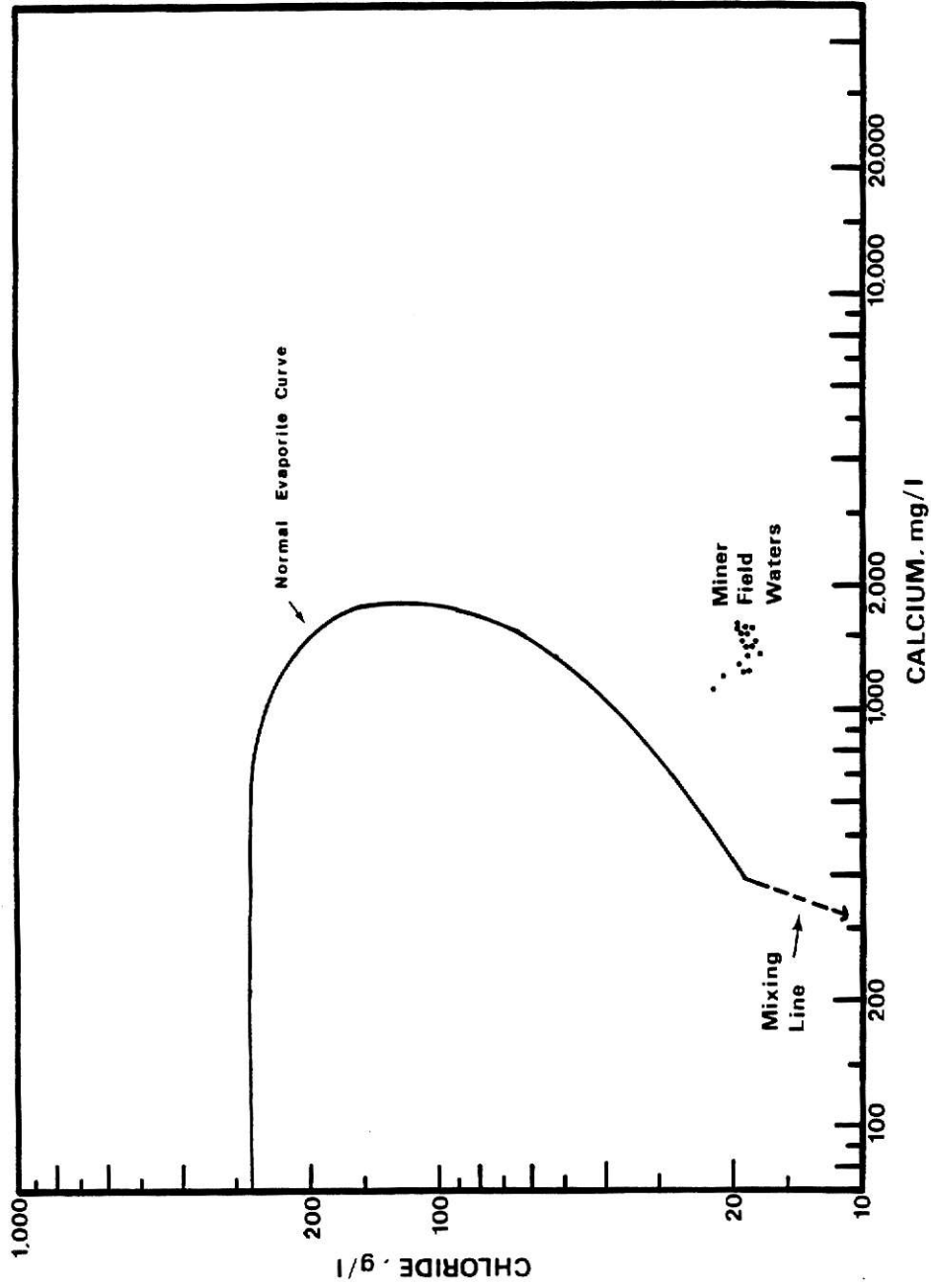


Figure 8. Comparison of chloride versus calcium concentration in oil-field waters, Miner field, Ness County, Kansas in relation to that of evaporating seawater (modified from Collins, 1974). Mixing line is between seawater and average meteoric water.

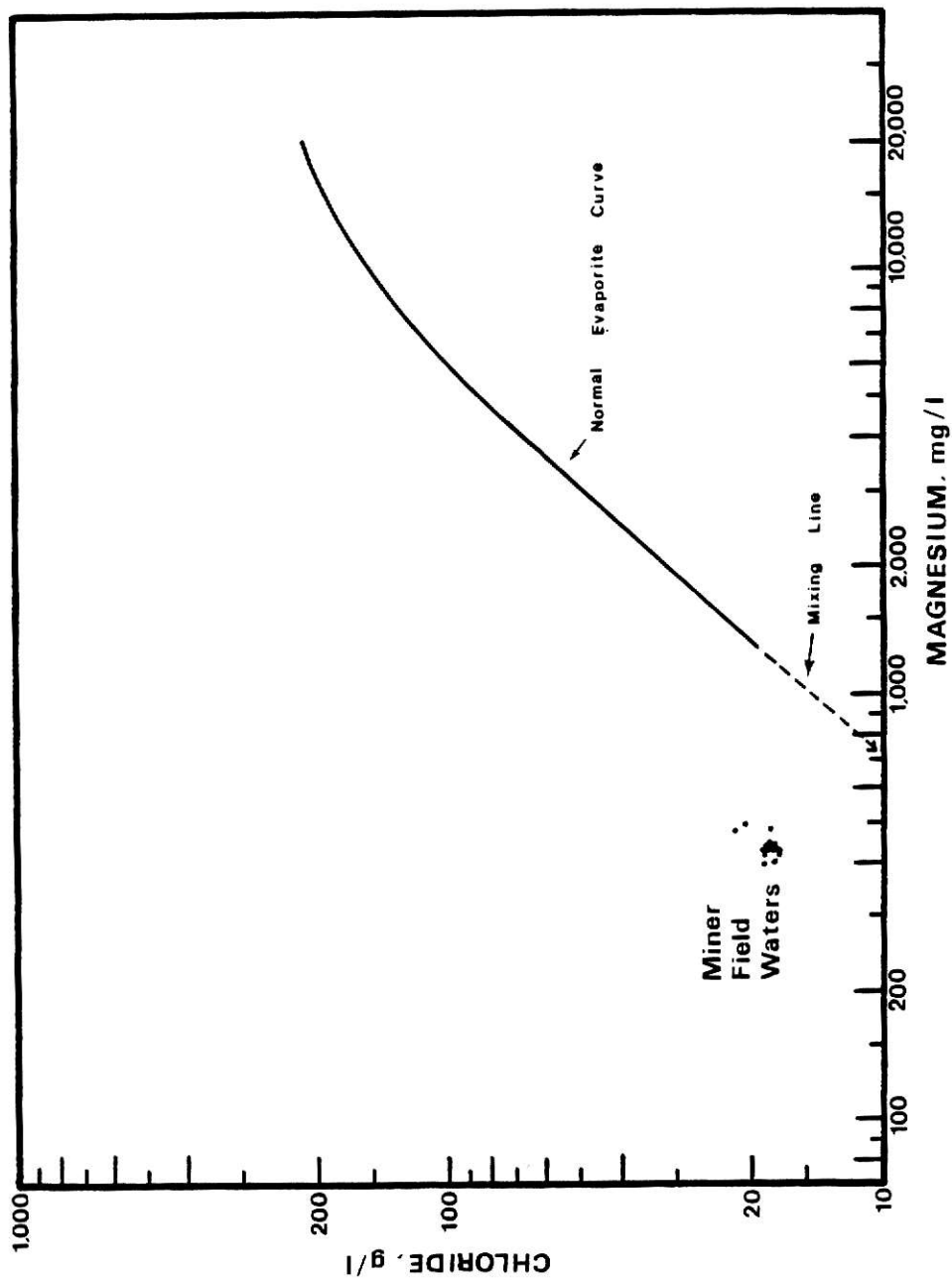


Figure 9. Comparison of chloride versus magnesium concentration in oil-field waters, Miner field, Ness County, Kansas in relation to that of evaporating seawater (modified from Collins, 1974). Mixing line is between seawater and average meteoric water.

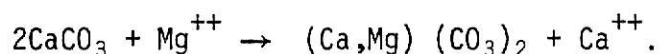
Table 7. Enrichment factors* for major elements in oil field waters,
Miner field, Ness County, Kansas.

Element	Average concentration in water (mg/l)	Average concentration in seawater	Enrichment Factor
Na	9770	11,000	0.89
K	234	350	0.70
Mg	450	1300	0.35
Ca	1450	400	3.60
Sr	46.6	8	6
Rb	0.7	0.1	7
Li	12	0.2	60
Cl	18,300	19,000	0.96
Br	37.5	65	0.58
SO ₄	1880	2670	0.70
HCO ₃	272	400	0.70

* $\frac{\text{Concentration of element of oil-water}}{\text{Concentration of element in seawater}} = \text{Enrichment factor}$

by (1) dolomitization of limestone, (2) chloritization of clay minerals and other layer silicates, (3) mixing of different water types, and (4) membrane filtration by clay minerals in shale (DeSitter, 1947; Hitchon et al., 1971; Collins, 1975).

Dolomitization of limestone occurs by uptake of Mg and release of Ca. The following reaction describes the dolomitization process;



Strontium would also be released into the water, because of a large difference in the sizes of the Sr and Mg ions.

Dolomitic rocks are present in the vicinity of the "Cherokee" sandstone. The underlying Mississippian carbonate rocks are dolomitic. The "Cherokee" sandstone units, however, are lithified by calcite cement; therefore, these cements cannot account for Mg depletion and concomitant Ca and Sr enrichment in their associated waters. However, dolomitization of the Mississippian and other dolomitic rocks in the vicinity of the producing zones in the Miner field could account for enrichment of Ca and Sr and depletion of Mg in the oil-waters.

If the oil-field waters are assumed to have been in equilibrium with the dolomitic rocks in the vicinity of the reservoirs, then the Sr/Ca ratio of the fluid should be approximately 14 times that of the rock, based on the knowledge of the partition coefficient values of Sr in equilibrium with dolomite at about 25°C. The average Sr/Ca ratio in the oil-field waters is 0.03. The Sr/Ca of the solid in equilibrium with this fluid must then be 0.0021, using a partition coefficient of 0.07 (Land, 1980). This value (0.0021) is reasonable, provided the original rock had a high Sr content (as much as 500 ppm).

If dolomitization is the single factor that controlled the distribution

of Sr, Ca, and Mg in the waters, then Ca and Mg contents of the waters may be expected to exhibit an inverse relationship. No trend ($r = -0.35$) between Ca and Mg is evident from the plot of Ca versus Mg (Fig. 10). Therefore, the scatter must be attributed to some other processes.

Fixation of Mg by smectite or degraded illite can cause depletion of Mg in the waters. This process of fixation of Mg by clay minerals can be accompanied by release of Ca and Sr into the waters, and may account, at least in part, for the relative enrichment of Ca and Sr in the waters. Shale beds that enclose the reservoir rocks contain small amounts of chlorite and chlorite-smectite mixed layer clay. The chlorite-smectite mixed layer clay is an intermediate stage in the formation of chlorite from smectite, and its presence indicates that chlorite in the "Cherokee" shale could have been formed by fixation of Mg by smectite. Therefore, chloritization may account, at least partly, for the depletion of Mg.

Simple mixing of normal or evaporated seawater with a low-salinity average meteoric water, can account for lower TDS values in the waters; however, this will not affect the abundances of Ca, Mg, and Sr, relative to Cl. In any instance of mixing, at least an additional process is needed to account for the observed Sr and Ca enrichment and Mg depletion in the oil-field waters.

Membrane filtration is another factor to be considered here. As water passes through shale membranes, the concentration of the ions in the water increases on the influent side, while the ionic concentration decreases on the effluent side. This selective filtration not only affects the concentration of the ions, it also produces changes in the ionic composition (element/Cl) of the water (DeSitter, 1947; McKelvey and Milne, 1962; Billings et al., 1969; Kharaka and Smalley, 1976). Kharaka and Smalley (1976) reported the retardation sequence of various ions, when water flows through

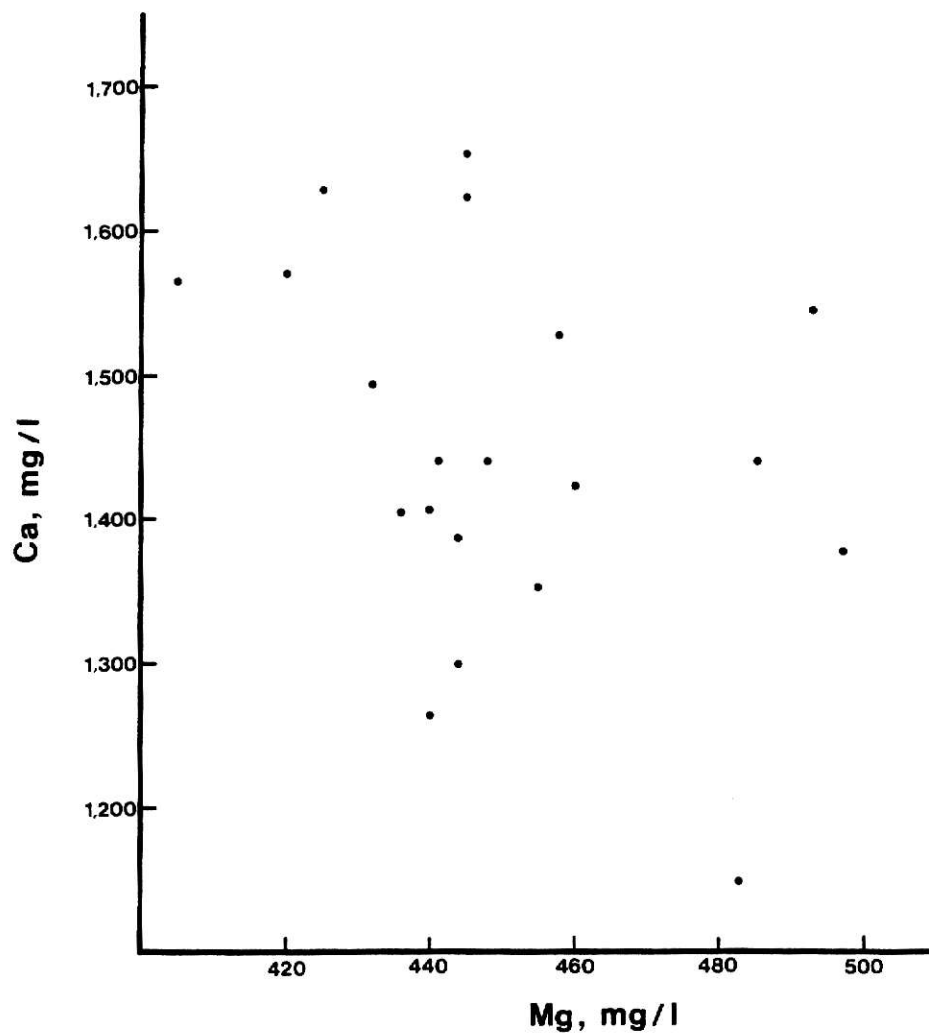


Figure 10. Scatter-plot of calcium versus magnesium concentrations in oil-field waters, Miner field, Ness County, Kansas.

($r = -0.35$, not significant at 95% confidence level)

a clay membrane, as follows: $Mg < Ca < Sr$. The enrichment factors of 0.35 for Mg, 3.6 for Ca, and 6.0 for Sr in the Miner field waters seem to be in the same order as this sequence. These enrichment factors indicate that the oil-field waters appear to have been membrane-concentrated.

Membrane filtration may be accompanied by mixing of fresher water, such as meteoric water, with seawater. If a seawater is concentrated by membrane filtration, the result will be a water with higher TDS than seawater, and the relative abundances of Ca, Sr, and Mg will be such that the water is depleted in Mg and enriched in Ca and Sr relative to the seawater. This would explain two of the Miner field water samples, but not the majority of them. The majority of the Miner field water samples have lower TDS than seawater. Therefore, waters that have been concentrated by membrane filtration must be diluted with fresher water to lower the TDS without disturbing the relative abundances of Ca, Sr, and Mg.

The dominant causes of Ca and Sr enrichment and Mg depletion in the Ness County oil-field waters are the combined effects of:

- (1) Mixing of a low-salinity water with seawater that has been membrane-concentrated.
- (2) Fixation of Mg by chloritization of smectite.

Dolomitization does not seem to be a likely factor involved in production of the Ca, Sr, and Mg relationships in these oil-waters.

Potassium and sodium depletion and rubidium and lithium enrichment.--

Formation waters from the Miner field are depleted in K and Na and enriched in both Rb and Li (Figs. 11, 12, and 13, and Table 7).

The process of membrane filtration can be invoked to account for the distribution of alkali elements in oil-field waters. Concentration by membrane filtration would produce an enrichment trend in the order $Li < Na < K < Rb$ in the water (Kharaka and Smalley, 1976). Miner field waters

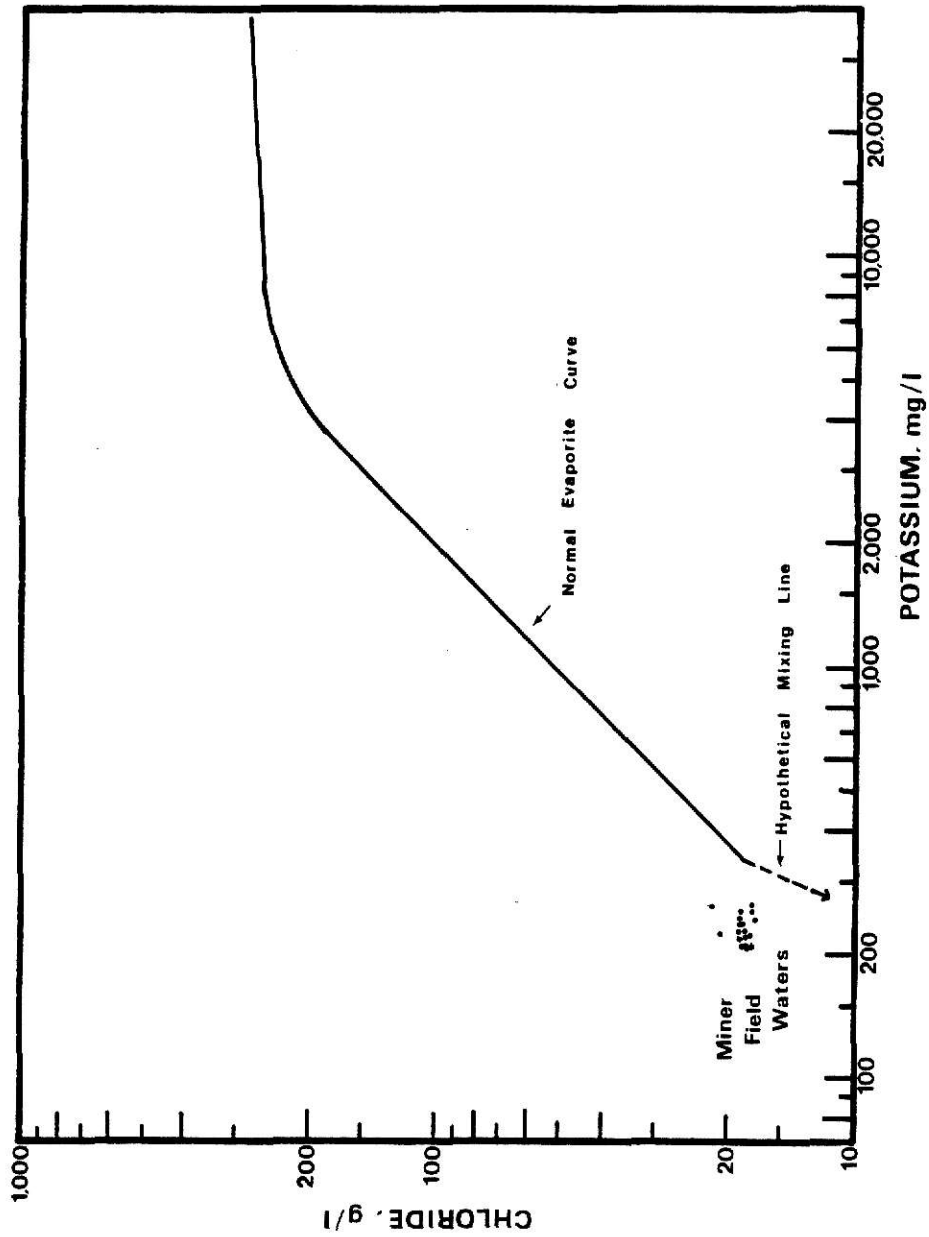


Figure 11. Comparison of chloride versus potassium concentration in oil-field waters, Miner field, Ness County, Kansas in relation to that of evaporating seawater (modified from Collins, 1974). Mixing line is between seawater and average meteoric water.

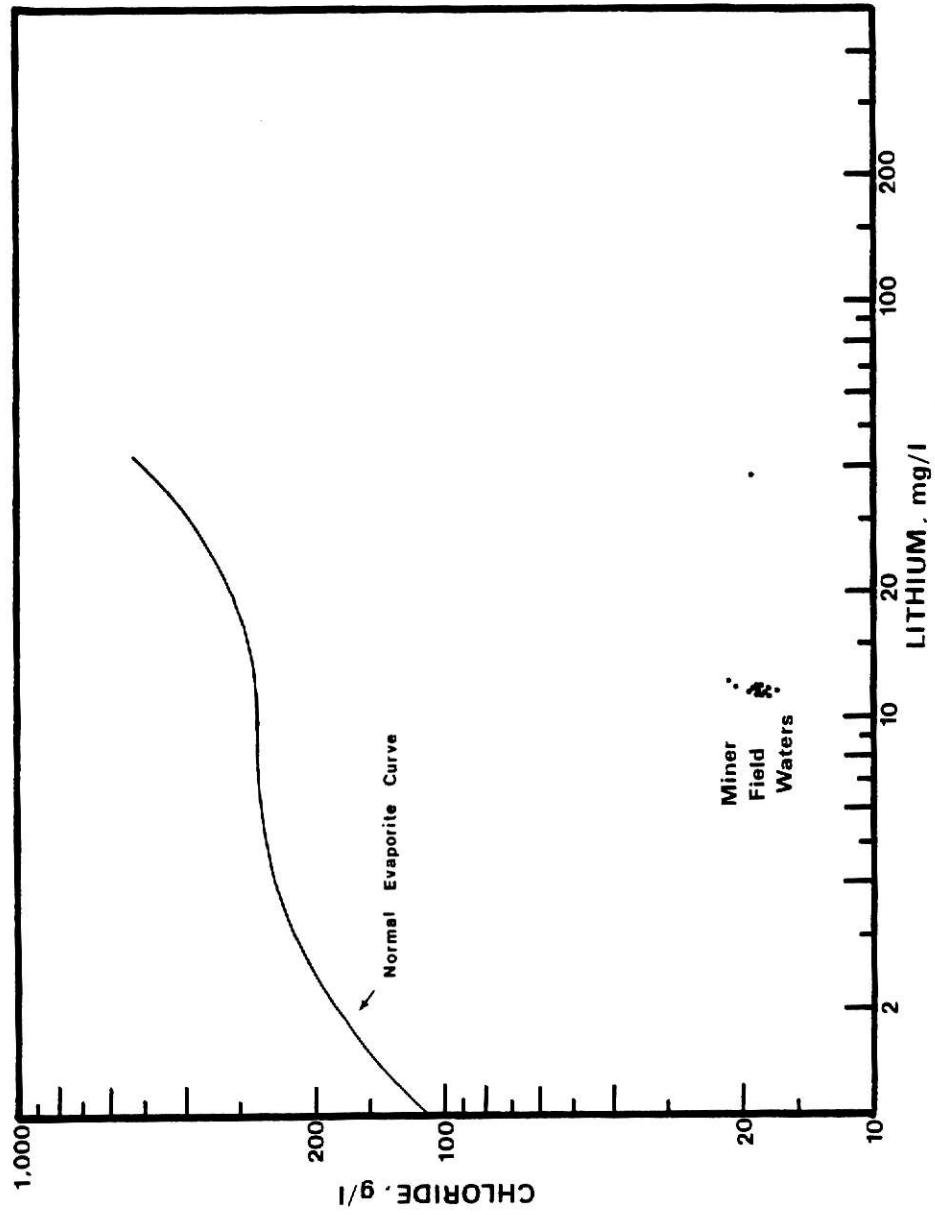


Figure 12. Comparison of chloride versus lithium concentration in oil-field waters, Miner field, Ness County, Kansas in relation to that of evaporating seawater (modified from Collins, 1974).

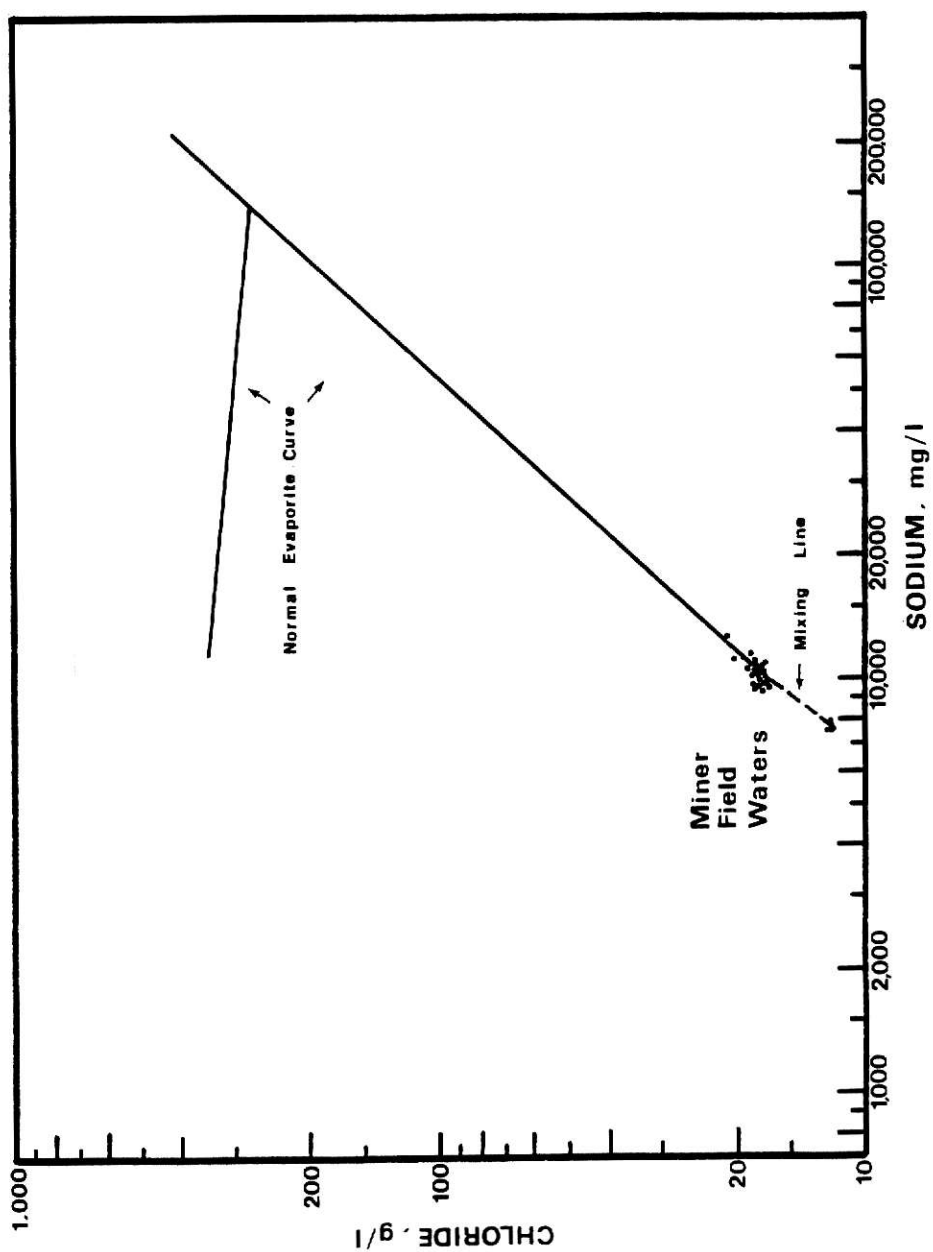


Figure 13. Comparison of chloride versus sodium concentration in oil-field waters, Miner field, Ness County, Kansas in relation to that of evaporating seawater (modified from Collins, 1974). Mixing line is between seawater and average meteoric water.

exhibit enrichment factors (Table 7) for these elements ($K = 0.7$, $Na = 0.89$, $Rb = 7$, and $Li = 60$) such that the order does not conform to Kharaka and Smalley's sequence, i.e. $K < Na < Rb < Li$. The enrichment factors for Na and K are very similar, and errors in determination of the concentrations of these elements could easily reverse their order, in which case they could conform to the sequence. The position of Li in this sequence is anomalous and, inasmuch as it is enriched by a factor of 60, cannot be accounted for by experimental error. Lithium enrichment can result partly from exchange reactions on clay minerals. The replacing power of Li in relation to other ions is, according to Grim (1968):

- (1) In NH_4 , kaolinite: $Cs > Rb > K > Ba > Sr > Ca > Mg > H > Na > Li$.
- (2) In NH_4 , montmorillonite: $Cs > Rb > K > H > Sr > Ba > Mg > Ca > Na > Li$.

Kaolinite, illite, smectite and mixed-layer clays, are present in the shale enclosing the reservoir rocks; therefore, exchange reactions with these clay minerals can account for the Li enrichment in the oil-waters. Thus, if membrane filtration has occurred in the development of the chemistry of the Miner field waters, it can explain the K, Rb, and Na relationships, but additional processes are necessary to explain the Li enrichment.

Collins (1975), among many others, has frequently attributed K depletion to fixation of K by clay minerals. The phenomenon of clay fixation will be viewed here in terms of the K/Rb ratio. The relative absorptive affinity for alkali elements by clay minerals is $Rb > K > Na > Li$ (Kharaka and Smalley, 1976); therefore, the K/Rb ratio in any water coming into contact with clay minerals would be raised. The K/Rb ratio for seawater ranges from 3500 to 3800. If the Miner field waters had originated as seawater,

migrated into the sandstone reservoirs and had come into contact with the clay minerals there, the K/Rb ratio would be greater than 3500, as Rb is fixed more readily by clay minerals than K. The K/Rb ratios in the Miner field waters range from 270 to 371, which is much lower than that of seawater. Therefore, simple clay fixation in the reservoirs cannot account for low K/Rb ratios in the oil-waters.

The relationships of the alkali elements have been previously discussed without regard to the TDS contents of the waters. All but two of the water samples contain lower TDS contents than seawater. If the Miner field waters originated as seawater, dilution of this seawater by a low-salinity water would generate low TDS values in the mixture. However, this will not account for the Na and K depletion and Rb and Li enrichment observed in the Miner field waters, nor the K/Rb ratio, because the average K/Rb ratios of both components (fresh water and seawater) are far in excess of the observed K/Rb ratios of the oil-field waters. If mixing of the two waters is a viable process, then a source for low K/Rb is necessary. This source could be a diagenetically-modified water low in K/Rb.

The role of membrane filtration in producing the Na, K, and Rb relationships in the Miner field waters has already been discussed. Concentration of seawater by this process also raises the TDS in the water. As the TDS contents of the Miner field waters are for the most part lower than seawater, dilution of seawater that has been membrane-concentrated by fresher water, such as meteoric water, can generate low TDS values, without affecting the K, Rb, and Na relationships in the waters.

Halite dissolution by infiltrating water is often suggested to account for the high Na and Cl contents found in petroleum-associated waters. If halite dissolution had occurred, the process would explain the high Na and Cl contents in the Miner field waters, but not the other constituents. Furthermore, water that had dissolved halite would contain Na/Cl in the same

proportion as, or greater than halite. The Na/Cl ratio is 0.65 in halite, 0.86 in average fresh water, and 0.58 in average seawater. Dissolution of halite in varying amounts by either water type would produce values between 0.58 and 0.86. The Na/Cl ratio in the Ness County waters averages 0.55. As this ratio is below the Na/Cl ratio to be expected from dissolution of halite by either fresh or seawater, another process, such as formation of Na-bearing silicates, could have occurred to lower the Na/Cl ratio of the formation waters. However, dissolution of halite would effect low Ca/Cl, Sr/Cl, Rb/Cl, and Li/Cl ratios in the waters, which have already been shown to be enriched in the waters relative to seawater. The dissolution of halite can thus be disregarded in this study as a major factor in causing the salinity of the oil-field waters.

The Na, K, Rb, and Li contents of the Miner field waters can thus be best explained by:

- (1) Mixing of membrane-concentrated water and a meteoric water,
- (2) Lithium enrichment can be a result of ion exchange with clay minerals .
- (3) Clay fixation of K and Rb that would result in high K/Rb ratios of waters.

The Miner field waters' K/Rb ratios are lower than those to be expected from clay fixation. Therefore, clay fixation of K and Rb, cannot be the ultimate process that has produced the present K/Rb ratios in the waters.

Bromide depletion.--The Miner field fluids are depleted in Br relative to seawater (Fig. 14). Rittenhouse (1967) divided oil-field waters into five groups, based on their Br and TDS contents, that reflect their chemical history (Fig. 15). Group I waters contain Br and TDS in amounts that can be modeled by ordinary concentration of seawater, or by its dilution with other water containing small amounts of Br and TDS. Group II waters are those that possess Br concentrations in amounts varying from slightly above, to twice that which would be expected from simple dilution or concentration of seawater.

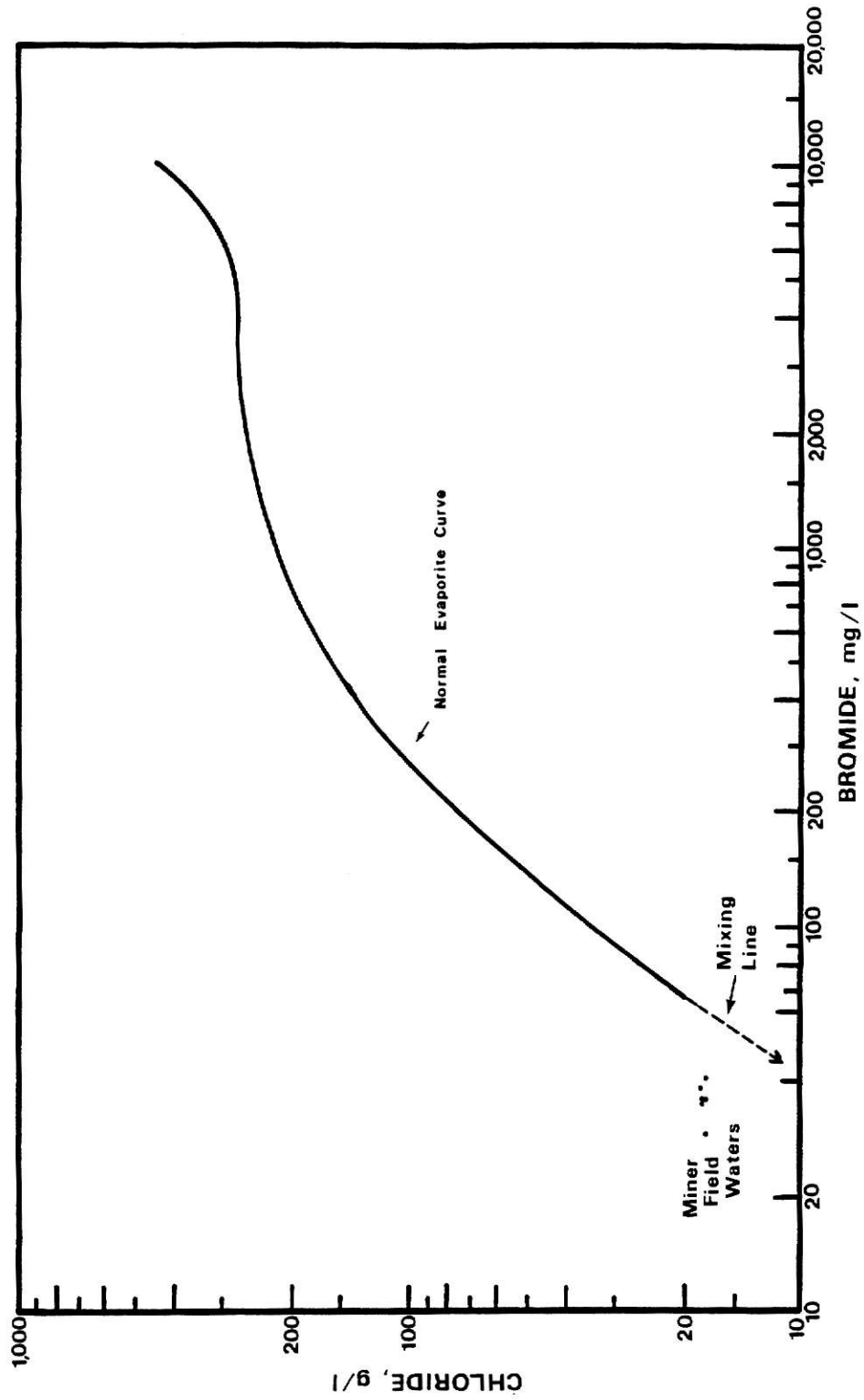


Figure 14. Comparison of chloride versus bromide concentration in oil-field waters, Miner field, Ness County, Kansas in relation to that of evaporating seawater (modified from Collins, 1974). Mixing line is between seawater and average meteoric water.

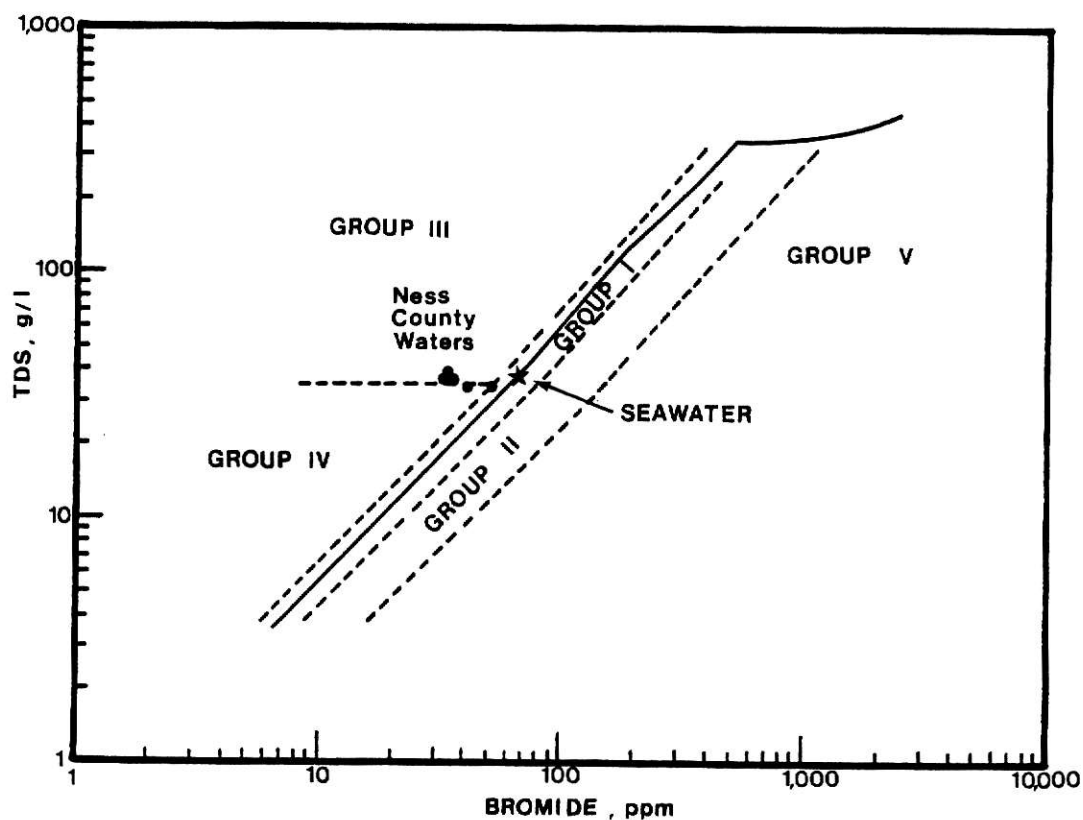


Figure 15. Total dissolved solids versus bromide concentration in oil-field waters, Miner field, Ness County, Kansas. Solid line represents bromide and TDS contents to be expected from either concentration of seawater by evaporation or its dilution with distilled water (modified from Rittenhouse, 1967).

Rittenhouse (1967) suggested that high Br and TDS contents are a result of concentration by semipermeable shale-membrane filtration, evaporation of seawater, addition of Br during early diagenesis, or a result of a combination of Group V and Group III waters. Waters in Group III have a higher TDS content than seawater, but a lower Br content that cannot be explained by simple evaporation of seawater. These waters are explained by various combinations of the processes of halite dissolution, concentration and dilution of seawater, and addition of Br during early diagenesis. Group IV waters possess lower TDS and Br concentrations than seawater and may have part of their development as Group III waters that have mixed with waters having low TDS and Br contents. Waters that are classified as Group V are characterized by high TDS and high Br contents. They are suspected to be altered bitterns, but the origin of many of these waters is unknown.

Sample 1, containing Br and TDS values of 43 and 32,700 mg/l, respectively, is included in Group I. Samples 2, 3, 7, and 8, which have Br values of 36 to 39 mg/l and TDS values of 17,900 to 18,100 mg/l are Group III waters, and Sample 6, containing Br and TDS concentrations of 32 and 32,600 mg/l, respectively, is designated as a Group IV water.

The Group I water evidently has a low-Br, low-TDS meteoric component that has mixed with water of presumably seawater origin. This postulate of mixing is also supported by Sr and O isotopic data (see pages 53-80).

The Br content in the Group III and IV waters is too low to merit explanation by simple dilution of seawater. Group III waters, and Group IV waters, which may form by dilution of Group III waters, have a history of halite dissolution, according to Rittenhouse (1967). Halite dissolution has already been shown to be an unlikely factor in the development of the alkali/Cl relationships in the Miner field waters. It is therefore unlikely that the Miner field waters classified as Groups III and IV waters involved halite

dissolution as part of their chemical development. These waters could have resulted from a dilution of Group I or II waters by waters containing considerable TDS but low Br concentrations.

The causes of Br depletion in the Ness County waters are:

- (1) Mixing of seawater with meteoric water.
- (2) Dilution of a Group I or Group II water by a low-Br, high-TDS water.

Sulfate depletion.--The SO_4 contents of the waters are lower than that of seawater. Depletion of SO_4 , relative to seawater, could result from several processes, such as precipitation of sulfate minerals (gypsum, celestite, barite), bacterial reduction of SO_4 , and shale-membrane filtration.

Barite and celestite could precipitate easily from solution, as they have low solubility products, but these minerals are not known from the rocks encountered in the Miner field. Therefore, formation of these minerals, at least in the immediate surroundings of the reservoir rocks, is not a factor in lowering the SO_4 content in the waters. Anhydrite is known to be present in the Permian units above the "Cherokee" shale. Precipitation of gypsum, whose dehydration forms anhydrite, could be part of the cause of SO_4 depletion in the Miner field waters. This can be true only for waters which have been involved in gypsum precipitation, as the oxygen and hydrogen isotopic data, to be discussed later, do not indicate that the saline oil-field waters have been involved in the dehydration of gypsum to form anhydrite.

The depletion of SO_4 in the Miner field waters could also result from bacterial reduction, given by the reaction:



Hydrogen sulfide produced from this reaction may combine with Fe in the waters to form pyrite. Pyrite crystals were noted in the "Cherokee" sandstone. This points to bacterial reduction of SO_4 as a likely cause for

depletion of SO_4 .

Hydrogen and Oxygen Isotopic Composition

Stable isotopes of oxygen and hydrogen can also be used to trace the history of the development of the chemical character of oil-field waters. A meteoric component mixing with, or flushing out, ancient seawater (Degens et al., 1964), and mixing of diagenetically-altered seawater with meteoric water (Billings et al., 1969; Hitchon and Friedman, 1969) have been reported as the origin of oil-field waters. The history of oil-waters can be linked to the waters at the time of deposition provided their subsequent chemical changes are known. Changes in the original composition of the depositional waters have been attributed to (1) reaction with carbonate minerals (Clayton et al., 1966), (2) fractionation by membrane filtration (Graf et al., 1965; Clayton et al., 1966; Coplen and Hanshaw, 1973; Kharaka and Berry, 1974), (3) neo-formation of hydrated minerals (Sofer, 1978), and (4) isotopic exchange with organic constituents (Clayton et al., 1966; Hitchon and Friedman, 1969).

Any reference to past ocean water for explaining chemical evolution of oil-field waters requires an assumption that ocean water composition in the past was very similar to that of present-day ocean water, which is quite uniform and very close to $\delta D = 0$ and $\delta^{18}O = 0$. Studies of Lowenstam (1961) and others have shown that the isotopic composition of ocean water has remained essentially constant throughout the Phanerozoic. Because the isotopic composition of ocean water apparently has not been any different from the present value, the isotopic composition of water from the Miner field may be compared to the isotopic composition of present-day seawater. The standard for comparison is SMOW, Standard Mean Ocean Water, as defined by Craig (1961b). As the seawater isotopic composition is assumed to be constant throughout the Phanerozoic, and the isotopic composition of meteoric waters is largely

controlled by the isotopic composition of the ocean, a similar case concerning the constancy of isotopic values exists for meteoric water. Craig (1961a) found that the H and O isotopic composition of all meteoric waters plot along a line whose relationship is defined by the equation (Fig. 16):

$$\delta D = 8\delta^{18}O + 10.$$

The equation of this line reflects, primarily, latitudinal effects, as fractionation during evaporation is significantly affected by temperature. The H and O isotopic composition of meteoric waters is closest to zero at the equator and gradually decreases away from the equator, becoming highly negative at the poles (Friedman, et al. 1964; Dansgaard, 1961). The deviation in this meteoric water line from its present position is thought to have been ± 1 per mil in $^{18}O/^{16}O$ and ± 10 per mil in D/H (Barnes, 1979). Therefore, comparison of the H and O isotopic composition of Miner field waters to present meteoric values can apply to past meteoric values.

The Miner field waters have $\delta^{18}O$ values ranging between -9.39 and -10.10 per mil (SMOW), and δD values from -82.07 and -84.97 per mil (SMOW). The depletion of D and ^{18}O in these waters relative to seawater may be attributed to 1) mixing the seawater with a component depleted in D and ^{18}O such as meteoric water, 2) isotopic exchange between the seawater and minerals depleted in D and ^{18}O , 3) formation of hydrated minerals, 4) isotopic fractionation by shale-membrane filtration, 5) exchange with organic constituents, or 6) a combination of all these processes.

The isotopic composition of oil-field waters, in some instances, has been related to the isotopic composition of the local meteoric water. Clayton et al. (1966) noted a positive correlation of δD and TDS in oil-field brines from the Illinois and Alberta basins and a positive correlation between $\delta^{18}O$ and TDS in these and other basins (Table 8). Extrapolation of the data back to low TDS intersected a point corresponding to the local meteoric water

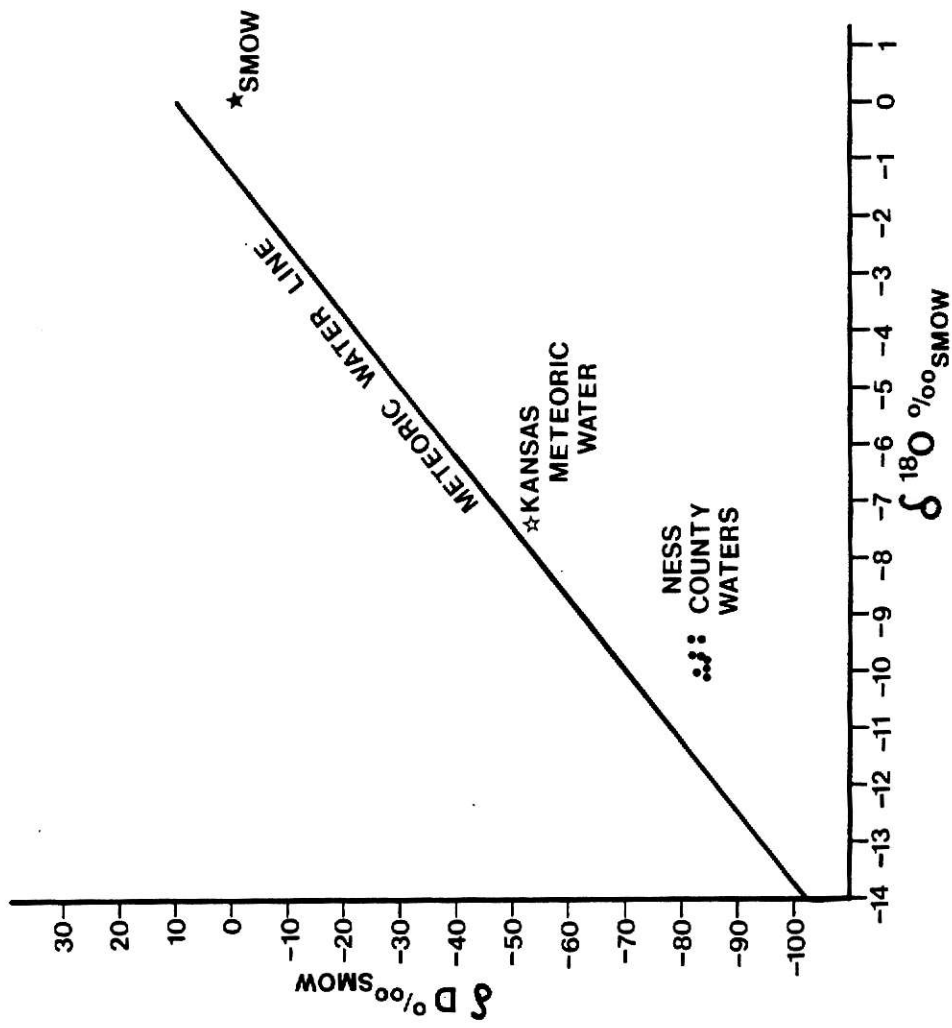


Figure 16. Relation of δD and $\delta^{18}O$ in oil-field waters, Miner field, Ness County, Kansas to meteoric water line and Kansas meteoric water (adapted from Craig, 1961a).

Table 8. Correlation coefficients of data from Clayton et al.
(1966) and this study.

CLAYTON ET AL. (1966)

δ D versus TDS	*Significant	$\delta^{18}\text{O}$ versus TDS	*Significant
(I) 0.812	Yes	0.867	Yes
(M) 0.592	Yes	0.901	Yes
(G)-0.112	No	0.629	Yes
(A) 0.846	Yes	0.915	Yes
THIS STUDY			
0.761	Yes	0.567	No

* 95% confidence level

I Illinois Basin

A Alberta Basin

M Michigan Basin

G Gulf Coast

isotopic composition, which led them to conclude that the brines were of local meteoric origin.

The water from Ness County may be compared to Kansas meteoric water to test whether the waters indeed have a meteoric contribution. If the oil-field waters had developed their stable isotopic character by mixing of seawater with local meteoric water, the resulting ratios would be intermediate between the values of seawater ($\delta D = 0$, $\delta^{18}O = 0$) and those of meteoric water. The meteoric water values for Ness County can be taken as -52.57 per mil δD and -7.38 per $\delta^{18}O$ (SMOW), which are the values obtained for a sample of meteoric water from Riley County in eastern Kansas, equivalent in latitude to Ness County. As the observed values in the oil-field waters are more negative than these values, dilution of marine connate water by meteoric water seemingly cannot account for the highly negative isotopic character of the saline oil-waters.

Isotopic exchange between water and clay minerals may also be a factor for the observed isotopic character of the saline waters. The effect of clay mineral-water interaction was investigated by Savin and Epstein (1970), who reported that the clay mineral hydroxyls are enriched in ^{18}O by 26 per mil and depleted in D by 30 to 70 per mil at 25°C, relative to the water with which they are in equilibrium. They noted very little isotopic exchange between seawater and clay minerals, but O'Neil and Kharaka (1976) reported the occurrence of extensive hydrogen isotopic exchange and negligible oxygen isotopic exchange between clay minerals and water at temperatures as low as 100°C.

Speculation regarding the origin of clay minerals may be necessary to explain the isotopic composition of the Miner field waters. If the clay minerals in the late Paleozoic rocks in Kansas are detrital in origin and

were derived from higher latitudes as far away as 1000 km, for example, these clay minerals could possess δD as low as -150 per mil but a $\delta^{18}O$ only of about -1 per mil (SMOW). Reaction of these detrital clay minerals with local meteoric waters may explain the negative δD values in the oil-field waters but would not explain the negative $\delta^{18}O$ values. Some controlling factor other than the clay mineral-water reactions will be necessary to produce the D- and ^{18}O -depleted waters of the Miner field.

Interlayer water present in clay minerals is uniformly arranged and thought to have a structure similar to that of ice (Grim, 1968). Ice has a δD that is 20 per mil higher and a $\delta^{18}O$ of 3.1 per mil higher than the water from which it forms (O'Neil, 1968). Neo-formation of clay minerals containing interlayer water with an ice-like structure would cause the surrounding water to be lowered in the D and ^{18}O content. In a highly compacted rock, the volume of free water is small, and the structural water in the neo-formed clay minerals will now have considerable influence on the isotopic composition of the free water. This free water, which is depleted in D and ^{18}O , could form a part of the oil-field waters.

Isotopic compositions of oil-field waters have been influenced by various diagenetic reactions. Clayton et al. (1966), in studying water from several sedimentary basins, demonstrated that reaction of waters with carbonate minerals is a factor in determining the variation of the oxygen isotopic composition of these waters.

Marine carbonate rocks have a $\delta^{18}O$ of +20 to +30 per mil (SMOW) (Faure, 1977). Any reaction of the marine carbonate rocks in the vicinity of the reservoir rocks in the Miner field with meteoric water, seawater, or a mixture of the two waters, can only increase the $\delta^{18}O$ values without changing the δD values. Because the Miner field waters are depleted in ^{18}O and D

relative to local meteoric waters, the carbonate-water interaction is not a dominant factor in controlling the H and O isotopic composition of the oil-field waters.

Anhydrite is known to be interbedded within the Permian salt beds in the subsurface in the area of the oil field (Merriam, 1963). Anhydrite is commonly formed from the dehydration of gypsum, and water produced from this process could come into contact with salt beds, thereby raising the salinity of the waters. However, the isotopic composition is not explained by this process. The isotopic fractionation factor (α) for gypsum at 40°C has been reported as $\alpha^{18}\text{O} = 1.0040$, and $\alpha \text{ D} = 0.980$ (Sofer, 1978). The water produced by crystallization of gypsum would thus be enriched in ^{18}O by +4 per mil and depleted in D by -20 per mil relative to seawater (Fig. 17). If the anhydrite in the Permian units was formed from dehydration of gypsum, the waters released from this process would have this isotopic composition, i.e. enriched in ^{18}O and depleted in D. The Miner field waters could not have been produced in this manner, because their $\delta^{18}\text{O}$ values of approximately -9.0 per mil and $\delta \text{ D}$ values of approximately -85.0 per mil (SMOW) are far more negative than values of gypsum hydration waters. Therefore, dehydration of gypsum that was originally formed by precipitation from evaporating seawater can be confidently ruled out as a major factor in determining the H and O isotopic character of the oil-field waters.

Isotopic fractionation by shale-membrane filtration is another possible mechanism by which waters may become depleted in D and ^{18}O . Graf et al. (1965) found that isotopic fractionation by shale-membrane filtration may occur in subsurface environments. Coplen and Hanshaw (1973) reported a depletion of D by 2.5 per mil and of ^{18}O by 0.8 per mil in the filtered solution during a membrane-filtration experiment. As membrane filtration

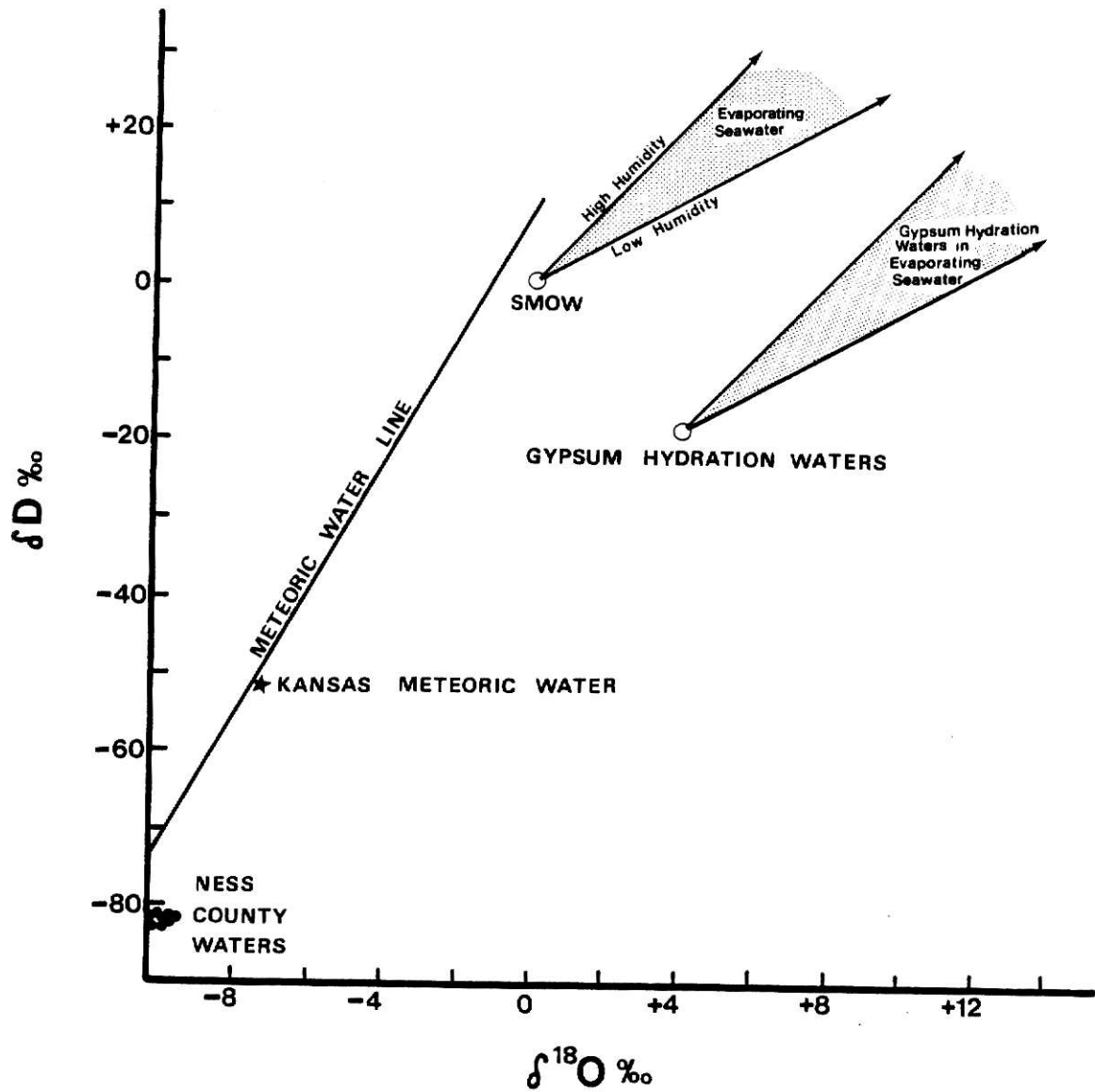


Figure 17. Relation of δD and $\delta^{18}O$ in oil-field waters, Miner field, Ness County, Kansas to O and D shifts exhibited during evaporation of normal seawater and seawater containing hydration waters of gypsum (adapted from Sofer, 1975).

does produce water that becomes depleted in both D and ^{18}O , a meteoric water, seawater, or a mixture of the two, when membrane-filtered, could explain the highly negative δD and $\delta^{18}\text{O}$ values of the Miner field waters. The Miner field waters, however, are likely to be membrane-concentrated, as pointed out in the discussion on the major chemistry of the waters. Membrane-concentrated waters would be expected to be enriched in heavier isotopes, which the Miner field waters are not. Therefore, isotopic fractionation by shale-membrane filtration alone has not produced the light isotopic enrichment in the oil-field waters. Mixing of a concentrated water with some other filtered water, however, could produce light-isotope enrichment in the oil-field waters.

Exchange of D between water and other hydrogen compounds such as methane and H_2S has been cited as a possible mechanism for lowering the δD in oil-field waters (Clayton et al., 1966). The δD in biogenic gases has been reported to vary from -175 to -250 mil (SMOW) (Schoell, 1980). Mixing of water with biogenic CH_4 could cause H exchange between the two, thus lowering the δD of the water.

Hitchon and Friedman (1969) suggested that exchange with biogenic H_2S may be another factor in D depletion. Because the exchange of D between water and H_2S takes place readily, introduction of light H from H_2S would lower the D value of the waters, which may then account for some of the depletion of D for the Miner field water. Considering the solubility of H_2S in water, the exchange alone may not be sufficient to lower the D values of the local meteoric water from -52.57 per mil to -80.0 per mil or less. Factors operating in addition to exchange of D between H_2O and H_2S must have caused the lowering of the D content of the Miner field waters.

The foregoing discussions are all based upon the assertion that the

isotopic composition of Kansas meteoric waters has been similar to present-day values since the late Paleozoic. One fact supporting this is that Kansas has never been further from the equator than it is today (Dott and Batten, 1981; Levin, 1978). Any variations in the isotopic character of meteoric waters caused by changes in latitude since the Paleozoic would only have served to increase the D and ^{18}O content, as Kansas has been closer to the equator. Inasmuch as this may be true, the possibility still exists that the H and O isotopic composition of Kansas meteoric water in the past could have deviated from the "normal" meteoric values expected in temperate latitudes by becoming even more negative than the present-day meteoric values and the Miner oil-field waters. A plot of δD and $\delta^{18}\text{O}$ versus TDS could possibly yield a positive correlation, as in Clayton et al. (1966), and extrapolation of these data back to low salinity (for meteoric water) could give these abnormally negative values. The plot of δD versus TDS of the Miner field waters yields a correlation coefficient of 0.761, which is significant at the 95 percent confidence level, and a similar plot of $\delta^{18}\text{O}$ versus TDS values of the waters yields a correlation coefficient of 0.542, which is not significant at the 95 percent confidence level. The $\delta^{18}\text{O}$ value of meteoric water obtained by extrapolation of these data to low salinity can be regarded with much less confidence than the δD value for meteoric water obtained by the same method. Nevertheless, the $\delta^{18}\text{O}$ value will be obtained by this method and discussed here, although it must be borne in mind that the value may not be as valid as the D value.

Extrapolation of the best-fit line drawn among the points to low TDS (3000 mg/l or less, that of most meteoric waters), intersects corresponding isotopic values at a D of -97.76 per mil and a $\delta^{18}\text{O}$ of -12.65 per mil (Fig.18). The values plot within the ranges of Craig's (1961a) meteoric line and are

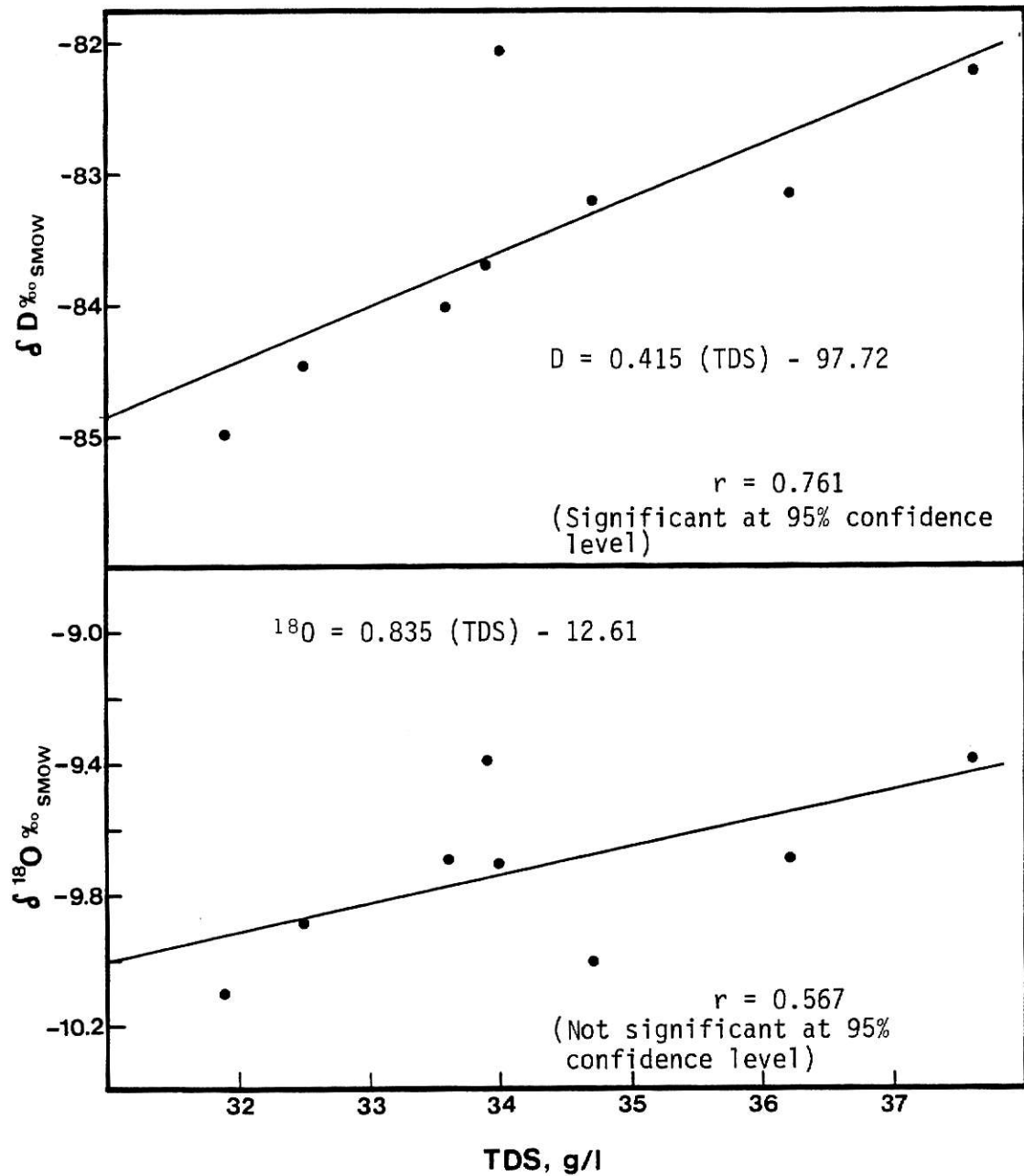


Figure 18. Isotopic composition of oil-field waters, Miner field, Ness County, Kansas in relation to TDS.

reasonable values for a meteoric water derived from latitudes of about 50° to 52°. Clayton et al. (1966) were led to the conclusion that the origin of the oil-field brines that they investigated was local meteoric water, as extrapolation of their δD and $\delta^{18}O$ versus TDS plots intersected isotopic values of present meteoric waters in the general latitude from which the brine and meteoric water samples were obtained. By applying this line of reasoning to the Miner field waters, it may be concluded that any meteoric water involved in the evolution of these formation waters had a δD of -97.76 per mil and a $\delta^{18}O$ of -12.65 per mil (SNOW).

Factors that generally affect the isotopic composition of meteoric waters are latitude, climate, elevation, and geographic distribution of land and ocean. Latitude, climate, and elevation all involve temperature differences, as temperature affects the fractionation factor. Fractionation is greater at low temperatures than at high temperatures (Faure, 1977).

Effect of the distribution of land and ocean on the isotopic composition of meteoric water is not as temperature-dependent as latitudinal, climatic, and elevation effects. As an air mass containing water vapor moves inland and farther from the ocean, the vapor will become progressively lighter in its isotopic composition, because the first water to condense will be enriched in heavy isotopes.

Graf et al. (1965) suggested that the distribution of D in pre-Pleistocene meteoric water may have differed from that of the present because of changes in land-surface elevation, climate, and areal extent of oceans extending into North America. Clayton et al. (1966) explained the existence of low-salinity waters that were depleted in $\delta^{18}O$ and D relative to present-day local precipitation as originating as meteoric water of Pleistocene age. A parallel argument may be made here: the Miner field waters contain a component of

meteoric water that had an isotopic character such as would result from precipitation during an earlier, colder climate, although not necessarily the Pleistocene. The time that has passed since the Pleistocene is not sufficiently long for the water to migrate deeply into the reservoir rocks. A period of glaciation in the Southern Hemisphere during the Permo-Pennsylvanian time may have affected the climate, but the effect, if any, is not well understood.

If these isotopic values ($\delta D = -97.76$ and $\delta^{18}O = -12.65$) are taken as representative of the meteoric water, then the Miner field waters can be explained by mixing of this isotopically-negative meteoric water with seawater or evaporated seawater under arid conditions (the evaporation line would have a slope of 3.5) (Sofer, 1978). The $\delta^{18}O$ and δD values of this evaporated seawater would be +20 per mil and +90 per mil, respectively. The corresponding salinity of the evaporated seawater would be in the proximity of 300,000 mg/l. This is slightly above the point of gypsum precipitation. A mixture of approximately 90 percent of the meteoric water and about 10 percent of evaporated seawater could produce isotopic values such as those observed in the Miner field waters. This proportion of mixing of evaporated seawater and the negative meteoric water would explain the observed salinities of the Miner field waters.

If, on the other hand, the meteoric water is mixed with normal seawater with an isotopic composition of SMOW, 80 percent seawater and 20 percent meteoric water are necessary to produce the observed TDS in the oil-waters. This resulting mixture, however, does not explain the δD and $\delta^{18}O$ values in the Miner field waters, as the mixture would be more enriched in D and ^{18}O . Other processes mentioned earlier must again be invoked to lower the isotopic values to those of the Miner field water.

The stable H and O isotopic composition of the Ness County oil-field waters can best be explained by:

- (1) Mixing a highly negative meteoric water with evaporated seawater.
- (2) Neo-formation of clay minerals bearing water in an ice-like arrangement.

The processes that cannot account for both the D and ^{18}O depletions of the Miner field waters relative to seawater or present-day meteoric water are:

- (1) Isotopic exchange with clay minerals.
- (2) Water released from conversion of gypsum into anhydrite.
- (3) Isotopic exchange between water and methane of H_2S .
- (4) Reaction with marine carbonate rocks.
- (5) Isotopic fractionation by shale-membrane filtration.

Strontium Isotopic Composition

Strontium isotopic composition of oil-field waters may be useful as a tracer in the origin and evolution of their chemical character. It may be used to distinguish between Sr from a continental source and that from a marine source. In general, continent-derived Sr is enriched in ^{87}Sr relative to marine-derived Sr. The isotopic composition of marine Sr is limited between 0.7068 and 0.7091, which are the values of seawater during the Phanerozoic (Peterman et al., 1970; Burke et al., 1982).

The $^{87}\text{Sr}/^{86}\text{Sr}$ values of the Miner field waters range from 0.7254 to 0.7277, which are much higher than the ratio for seawater at any time during the Phanerozoic. If the saline oil-waters originated as seawater, then the Sr isotopic composition of the former suggests that the waters have acquired Sr from a source enriched in ^{87}Sr . This means that the waters must have reacted with a source high in Rb/Sr ratio, which had a high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. An evaporated seawater will have an isotopic composition identical to that

of normal seawater. As the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the oil-field waters are higher than those of seawater, evaporation of seawater cannot explain the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the oil-field waters.

Many oil-field waters are depleted in Mg and enriched in Ca and Sr. This has been attributed to dolomitization of carbonate rocks. The process of dolomitization, according to some investigators, requires the influx of Mg-rich brine, which may be considered to be marine in origin, through limestone (Beales and Hardy, 1980; McKenzie et al., 1980; Friedman, 1980). Therefore, any fluid involved in dolomitization resulting from interaction between Mg brine and carbonate rocks, both of marine origin, would have an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio very close to seawater values. As the oil-field waters have considerably higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than those in seawater, dolomitization by a marine-derived Mg brine could not possibly produce the high $^{87}\text{Sr}/^{86}\text{Sr}$ values. Dolomitization of limestone by an Mg-rich solution could be a factor in producing high isotopic ratios in the Miner field waters, provided the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in this Mg-rich solution is higher than that of the Miner field waters. This Mg-rich solution must then be of continental origin. The highest known $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of any continental waters or brines is about 0.7350, as reported by Chaudhuri (1978). Mixture of water containing an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.735 with Sr having an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.709 from the limestone, can produce water with Sr isotopic ratios close to the ratios observed in the Miner field waters.

Chloritization has been suggested as a possible cause for Mg depletion in the waters. If chlorite is formed from direct precipitation from any water, it cannot be detected by $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the water as this process has no effect on the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the water. Conversion of smectite, vermiculite, or biotite into chlorite could also account for Mg depletion.

Conversion of smectite will generally release Sr with low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, possibly from 0.7080 to 0.7119 (Chaudhuri and Brookins, 1978). Thus it is highly unlikely that this can account for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios observed in "Cherokee" waters, if the water originally possessed primarily marine isotopic ratios. Chloritization of vermiculite is a common process, and vermiculite commonly has a high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio because of a high Rb/Sr ratio. Therefore, chloritization of vermiculite could have caused the high ratios of the oil-waters. Biotite is known to have a high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. Conversion of biotite to chlorite could also account for the observed high ratios of the oil-field waters. Although biotite and vermiculite are not known to be present in the vicinity of the reservoir rocks, chloritization of these minerals could have occurred somewhere outside of the reservoir system and the waters associated with this reaction migrated into the reservoirs.

Dissolution of minerals in evaporite deposits has been suggested as the process involved in influencing the chemical character of oil-field waters. Evaporite minerals precipitated from seawater will inherit their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from the seawater present at the time of precipitation. A. Clayton (pers. comm., 1982) has determined that the Sr isotopic ratios in samples of Permian gypsum and halite range between 0.7080 and 0.7090, which is within the range for marine Sr isotopic ratios. If the waters from the Miner field wells originated from dissolution of evaporite beds, the $^{87}\text{Sr}/^{86}\text{Sr}$ value of the waters would be very close to these evaporite Sr isotopic values. As the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the formation waters are higher than the $^{87}\text{Sr}/^{86}\text{Sr}$ in any evaporite deposits, dissolution of evaporite minerals is not a major controlling factor for the observed $^{87}\text{Sr}/^{86}\text{Sr}$ values.

Because the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the oil-field waters are considerably higher than those of any marine carbonate rocks, at least a part of the Sr

in these waters must be considered to have been derived from a Rb-rich phase. Reaction between waters, having Sr of marine isotopic values, and K-feldspars, which are common silicate minerals in crustal rocks, can be a possible explanation for the observed high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the oil-field waters. To assess the magnitude of the influence of feldspars on the Sr isotopic composition of the feldspar and the fraction of Sr in the waters derived from the feldspars must be available.

Assuming that only five percent of the total Sr in the waters, having a Sr content of 46 mg/l and an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7265, is derived from K-feldspars, the calculated $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the feldspars becomes 1.059. This ratio is possible for feldspars in many Precambrian alkalic igneous rocks, as supported by unpublished data of Chaudhuri on K-feldspars from alkalic plutonic rocks of about 1100 m.y. old. However, a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 1.059 is probably a high value for average feldspars in crustal rocks. An assumption of 10 percent of the Sr being derived from K-feldspars leads to a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.884 for the minerals. This ratio is not at all uncommon for the Sr isotopic composition of feldspars (Brooks, 1968). Thus, 10 percent of the total Sr in the oil-field waters could be attributed to a K-feldspar source. Any $^{87}\text{Sr}/^{86}\text{Sr}$ ratio less than 0.884 would require that more than 10 percent of the Sr in the waters be derived from feldspars. In this case, any K released during feldspar dissolution must be taken up by another process, as the waters are depleted in K.

Although K-feldspar dissolution in general can increase the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, the question can be raised as to whether the feldspars in the reservoir rocks could have an influence on raising the ratios of the waters. Potassium-feldspar abundance of one percent (see Appendix) was determined for the "Cherokee" sandstone. The available core sample was not

large enough to separate and analyze the feldspar for its $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. If the ratio of the feldspar was very high, this abundance could account for the $^{87}\text{Sr}/^{86}\text{Sr}$ in the water, but the influence of these feldspars in controlling the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is doubtful. Feldspar from another "Cherokee" reservoir not far from this study area was analyzed for its $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, which is 0.7259 (Bias, pers. comm., 1982). This ratio is too low to produce the similar ratios in the waters, if mixed with water having marine Sr isotopic values.

Other minerals present in the sandstone that are known to contain high Rb/Sr ratios, and would provide ^{87}Sr to raise the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the waters, are glauconite/celadonite and clay minerals. Ratios were not obtained from these minerals because sample size was too small. The non-exchangable Sr in glauconite has been found to possess $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from 0.7107 to 4.0195 (Morton and Long, 1980). No data are available on the Sr isotopic composition of exchangeable Sr from glauconite, but the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio would very likely be lower than these values, as Chaudhuri and Brookins (1978) found that exchangeable Sr from clay minerals is generally lower in $^{87}\text{Sr}/^{86}\text{Sr}$ ratio than non-exchangable Sr.

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios were obtained for waters produced from the Mississippian carbonate reservoir rocks. The "Warsaw" units have been noted to contain glauconite (Nodine-Zeller, 1981). It is possible that the glauconite had some influence on the high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the water. However, the amount of leachable Sr that could come from the glauconite would be quite low, compared to the amount that would come from the limestone; therefore, the ratio would be dominated by marine Sr isotopic ratios from the limestone. Also, the amount of glauconite in the sandstone units (see Appendix) could not be expected to contribute enough Sr to the waters to raise the isotopic ratios considerably. Thus, glauconite cannot be a major contributor to the high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the present formation waters.

Membrane filtration has been previously suggested in this report as one of the plausible mechanisms that can account for the chemical character of the Miner field waters, although it may not be the sole cause. Ion exchange with clay minerals during membrane filtration could account for a high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the water. Illite, among all the clay minerals, contains the most Rb and high Rb/Sr ratios. As ^{87}Rb decays to ^{86}Sr , the decay will impart a high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio to the Sr in illite. Chaudhuri and Brookins (1978) noted that exchangeable Sr in illite is high in $^{87}\text{Sr}/^{86}\text{Sr}$, as high as 0.7277, but less than the ratio of the non-exchangeable Sr. Thus, ion exchange with illite in the shale during membrane filtration could account for high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the waters. The problem to be addressed here is whether the clay minerals within and immediately surrounding the reservoir rocks are responsible for raising the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios to those observed in the Ness County waters.

Illite is present in the "Cherokee" shale. It would seem possible that as water flowed through the illitic shale, ion exchange could increase the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the waters. However, the Sr isotopic ratio of the clay minerals in the "Cherokee" shale is 0.7191, which is lower than this ratio in the water. Therefore, ion exchange by the water with the clay minerals in the "Cherokee" shale, at least immediately above and below the reservoir sandstones, is not apparently responsible for the present $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the waters. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the clay minerals in the "Cherokee" sandstone is 0.7193 (Bias, pers. comm., 1982), which also renders clay-mineral ion exchange in the host rocks an unlikely factor responsible for the present ratio in the waters.

Stable isotopic data, as well as some of the chemical data, point to a mixing of different water types, one component of which is meteoric, and the other a seawater that is somewhat concentrated. A mixing relationship

between two chemically separate waters, which can explain the chemical characteristics of the oil-field waters, is also evident when the Sr isotopic data are compared with the corresponding chloride content. Suggestion of a slight inverse trend between these two parameters is illustrated in Figure 19. The correlation coefficient is -0.409, which is not significant at the 95 percent confidence level. Although the possibility of a very weak relationship seems to be indicated here, a similar study of oil-field waters from "Cherokee" reservoirs has yielded data with an inverse relationship. Data from Bias (pers. comm., 1982) yielded a correlation coefficient of -0.891, which is significant at the 95 percent confidence level. The mixing of two waters, a high-Cl and low- $^{87}\text{Sr}/^{86}\text{Sr}$ water, characteristic of marine waters, and a low-Cl and high- $^{87}\text{Sr}/^{86}\text{Sr}$ water, characteristic of continental water, can explain this inverse relationship.

Several mixing models can be devised by utilizing limits on the proportional amounts, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, TDS, and Sr contents of the two components, one of which is a seawater source and the other a continental-derived source. In the previous discussion on the stable isotopic data, it has been pointed out that mixing 10-20 percent concentrated seawater with 80-90 percent continental water could explain the TDS and stable isotopic composition of the oil-waters. This range of mixing proportions will be considered here in devising the models that can explain the Sr isotopic composition of the waters. Two mixing models are envisioned: (1) mixing a slightly concentrated marine water and a continental water, accompanied by membrane filtration, and (2) mixing a slightly evaporated marine water with a diagenetically modified continental water. Variations of these models are summarized in Table 9.

In model 1, 80 percent continental water is mixed with 20 percent

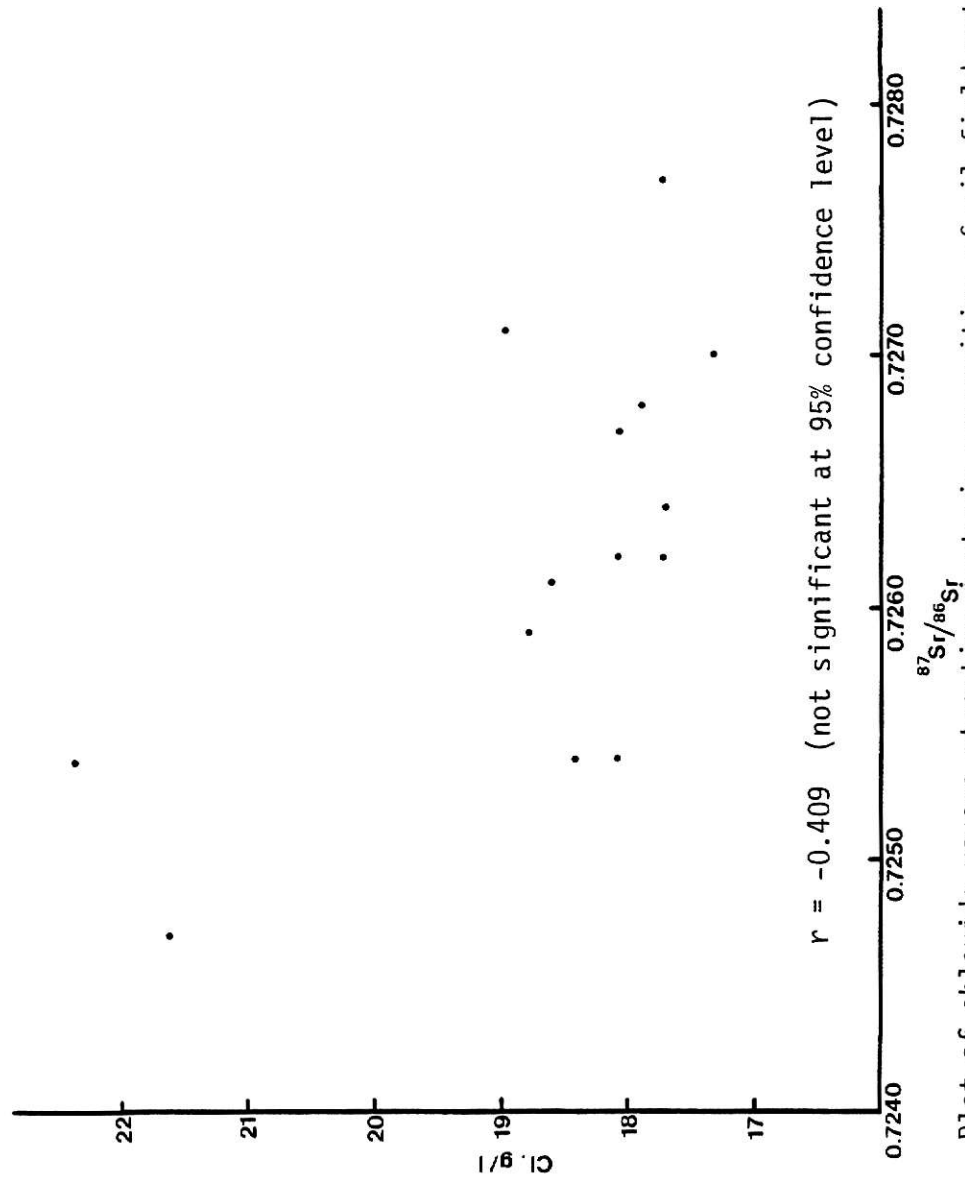


Figure 19. Plot of chloride versus strontium isotopic composition of oil-field waters, Miner field
Ness County, Kansas.

MIXING:			PRODUCES WATER WITH:	
<u>1</u>	80% continental	20% marine		
$^{87}\text{Sr}/^{86}\text{Sr}$	0.730	+	0.709	→
Sr	0.1 mg/l	+	25 mg/l	→
TDS	1,00 mg/l	+	120,000 mg/l or less	→
				Then membrane filtration to concentrate and raise TDS and Sr content
<u>2a</u>	80% diagenetically modified continental water	20% concentrated marine water		
$^{87}\text{Sr}/^{86}\text{Sr}$	0.7290	+	0.799	→
Sr	51 mg/l	+	25 mg/l	→
TDS	11,250 mg/l	+	120,000 mg/l	→
				33,000 mg/l
<u>2b</u>	90% diagenetically modified continental water	10% concentrated Marine water		
$^{87}\text{Sr}/^{86}\text{Sr}$	0.7280	+	0.709	→
Sr	48.3 mg/l		25 mg/l	→
TDS	23,000 mg/l		120,000 mg/l	→
				33,700 mg/l
<u>2c</u>	90% diagenetically modified continental water	10% evaporated marine water		
$^{87}\text{Sr}/^{86}\text{Sr}$	0.729	+	0.709	→
Sr	45 mg/l	+	55 mg/l	→
TDS	6,700 mg/l	+	270,000 mg/l	→
				46 mg/l
				33,030 mg/l

Table 9. Summary of mixing models between continental water and seawater.

concentrated marine water. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7258 in the resulting water explains similar ratios in the Miner field waters, but neither the Sr content of 46 mg/l, nor the TDS of 32-33,000 mg/l in the Miner field waters is explained by this combination. The Sr concentration and TDS contents of this mixture must be raised without seriously affecting the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio by concentrating this mixture, possibly by membrane filtration.

In model 2a, 80 percent continental water, whose Sr and TDS contents have been raised by such diagenetic processes as membrane filtration or dissolution of minerals, mixes with 20 percent concentrated marine water. The water thus produced as a result of this mixture will have an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7250 and Sr and TDS contents of 45.8 and 33,000 mg/l respectively. These values are very similar to the values of these parameters in the Ness County waters; therefore, mixing of these two water types could account for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios as well as the Sr and TDS contents of the Ness County waters.

Models 2b and 2c are similar to models 1 and 2a, but the proportions are changed to 90 percent diagenetically-modified continental water and 10 percent evaporated marine water. The marine water in model 2c is evaporated to a point slightly below that of gypsum precipitation. Both of these mixing models, 2b and 2c, also produce water similar to the Ness County waters in both chemical and isotopic character.

A varied mixing of two water components will display a linear trend in their $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/\text{Sr}$ values. The $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/\text{Sr}$ data for the Miner field waters are scattered, implying the presence of more than two sources of Sr (Fig. 20). The correlation coefficient is 0.492, which is not significant at the 95 percent confidence level. This scattering can be explained by having an additional source of Sr.

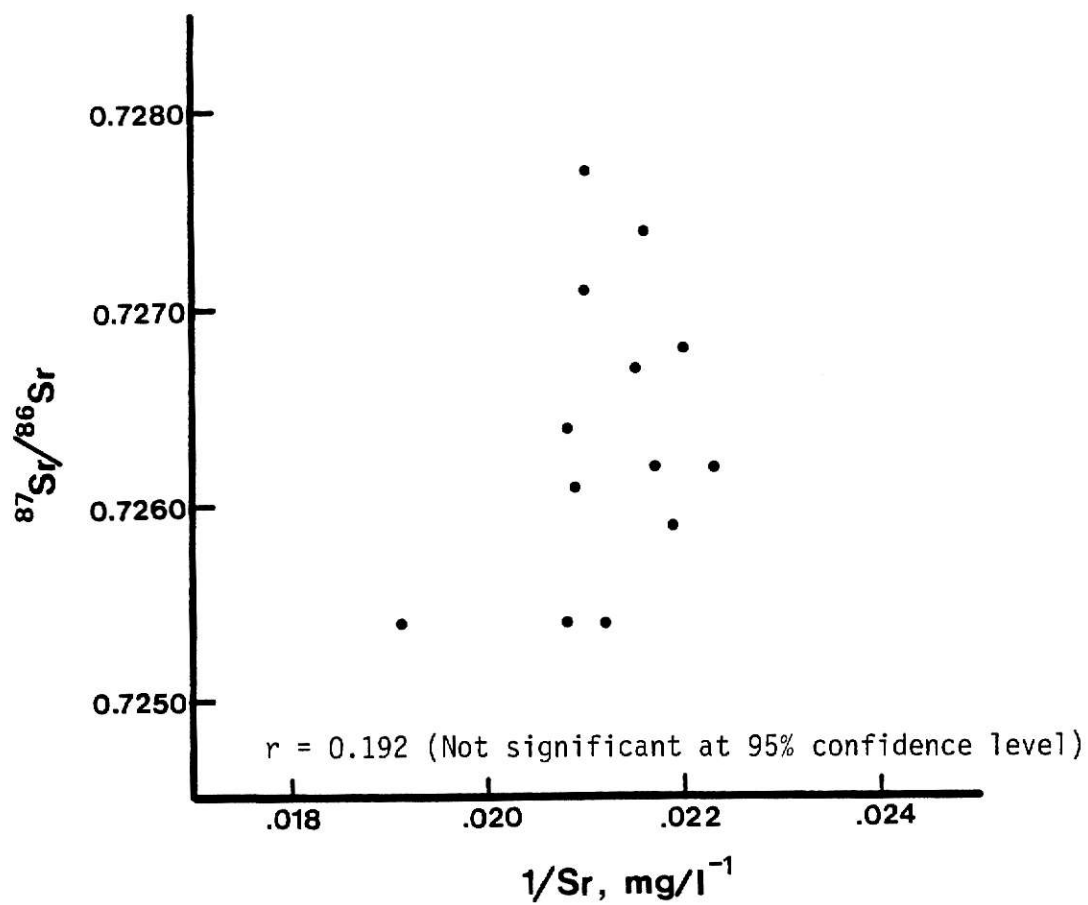


Figure 20. Scatter-plot of strontium isotopic composition versus reciprocal of strontium content in oil-field waters, Miner field, Ness County, Kansas.

In summary, the factors most likely to be involved in controlling the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the Ness County waters are:

- (1) Interaction with silicate minerals, such as chloritization of vermiculite and biotite, dissolution of feldspars, and ion exchange with illite.
- (2) Mixing of continental or diagenetically modified continental water with an evaporated marine water.

The local reservoir rocks and the immediate enclosing rocks had very little influence on the Sr isotopic characters of the water. The Ness County waters inherited their Sr isotopic composition largely from outside the vicinity of the "Cherokee" reservoir rocks.

Hydrologic Relationships Among the Reservoirs

Figure 21 is a plot of the wells and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the waters from them. Any difference outside of experimental error in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios among individual reservoirs cannot be maintained unless the reservoirs are separated by an impermeable barrier. However, similarity in isotopic ratios does not necessarily indicate hydrologic connection.

Three isotopically distinct groups of waters can be recognized. Waters from Wells 4, 5, and 11, all with the lowest ratio of 0.7254, constitute one group. Similarly, another group is formed by waters from Wells 1, 6, 8, and 12, which have ratios averaging 0.7262. Waters in the third group, from Wells 9, 10, and 13, have the highest ratios, averaging 0.7274. Waters from Wells 2 and 7 may be produced from the same sandstone body, as they are close to one another and their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7268 and 0.7267 are nearly identical. It is difficult to assign these waters to one of the two groups whose $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are 0.7262 and 0.7274, because the $^{87}\text{Sr}/^{86}\text{Sr}$ values of waters from the two wells overlap the values for the two groups

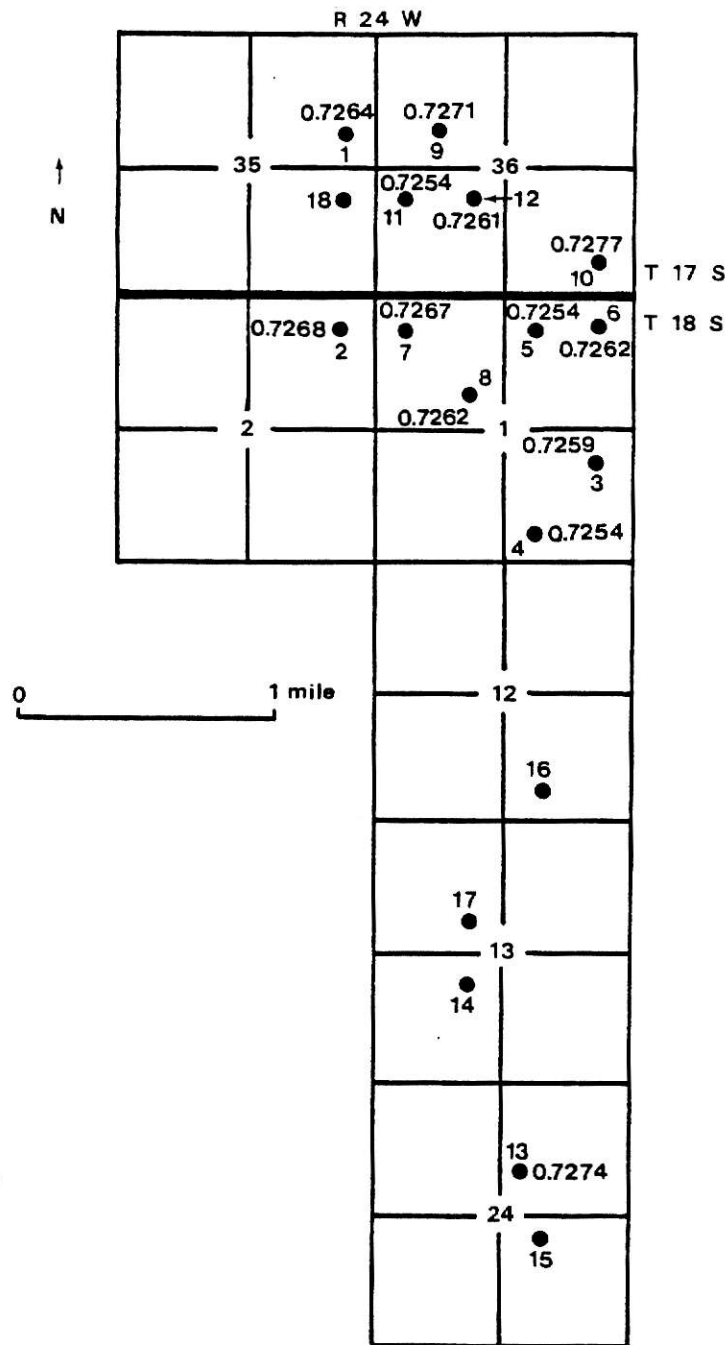


Figure 21. Location of wells and the strontium isotopic composition of the water samples from each well. (● *location of well*)

when the error of 0.0003 is considered. Similar uncertainty exists for Well 3 water, whose isotopic composition overlaps the two groups with ratios of 0.7254 and 0.7262. No hydrologic connection can exist among the reservoir rocks of these three isotopically distinct groups of waters. Strontium isotopic data cannot establish whether or not hydrologic continuity exists among the reservoir rocks within each group.

Explanation for the variations in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio among the groups of wells lies in the inherently complex migrational paths of the waters prior to their introduction into the reservoir rocks. If the waters had encountered rocks composed of different amounts of carbonates, evaporites, clay minerals, and other silicates, or reactions of waters with these rocks took place to different degrees, it is highly conceivable that the waters would then acquire slightly different $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from these rocks. The waters then entered the reservoirs bearing these dissimilar $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, and these ratios could have remained unchanged until the present.

Another possible cause for the differences in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios among the groups of waters may lie in the isotopic nature of waters present in the reservoirs prior to introduction of fluids that now constitute the formation waters. During carbonate rock formation, little or no isotopic diffusion takes place between the residual pore fluids and any unconsolidated mass or its associated fluids; therefore, the isotopic composition of a carbonate rock unit and its associated waters varies even on a small scale (Ramakrishnan, 1983). Mixture of these isotopically heterogeneous waters to varying degrees with later-infiltrating waters could produce the small differences in the Sr isotopic composition observed in the present oil-field waters.

The calcite cements from two "Cherokee" sandstone bodies analyzed in this study do not possess identical $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.7142 and 0.7216).

The differences in the ratios could be caused by leaching radiogenic ^{87}Sr from feldspar or glauconite in the sandstone during dissolution of the cements. However, the abundances of these minerals are quite low compared to the amount of calcite cement, so the contribution of radiogenic ^{87}Sr from feldspar or glauconite is probably negligible. Considering the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the cements as their true ratio, the ratio may support the possible existence of Sr isotopic heterogeneity in waters residing in different sandstone units as well as in the "carbonate" units. Mixing of these residual waters with infiltrating waters bearing much radiogenic ^{87}Sr can produce the small but significant Sr isotopic differences in the present oil-field waters.

It must be emphasized that the effects of the host and immediate enclosing rock units in raising the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the present waters is minimal. The waters now present in the reservoirs must have migrated into the reservoirs bearing Sr having high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios very similar to these ratios seen today.

Origin of the Carbonate Cement

Carbon isotopes.--Stable isotopes of carbon, ^{12}C and ^{13}C , can be helpful in the determination of the origin of carbonate rocks. Marine carbonate rocks are generally close to zero on the PDB scale in $\delta^{13}\text{C}$ content (Degens and Epstein, 1962). Freshwater carbonate rocks are more enriched in ^{12}C and are more varied in their $\delta^{13}\text{C}$ values. This ^{12}C enrichment and greater $\delta^{13}\text{C}$ variability is largely attributable to the presence of ^{12}C -enriched CO_2 gas derived from plant respiration and oxidation of plant debris (Faure, 1977). Average $\delta^{13}\text{C}$ values of -4.93 ± 2.75 per mil (PDB) for marine carbonates have been reported by Keith and Weber (1964). The $\delta^{13}\text{C}$ in freshwater mollusks is -0.6 to -15.2 per mil (PDB) and in marine mollusks is $+4.2$ to -1.7 per mil (PDB) (Keith et al., 1964). Although the

$\delta^{13}\text{C}$ of marine and freshwater carbonate rocks may serve to differentiate their environment of deposition, diagenetic changes of carbonate rocks and cements can alter the original $\delta^{13}\text{C}$ values, making interpretation uncertain.

The calcite cement from one of the "Cherokee" sandstone reservoirs has a $\delta^{13}\text{C}$ value of -11.84 per mil (PDB), and a $\delta^{18}\text{O}$ value of +22.55 per mil (SMOW). The $\delta^{13}\text{C}$ value indicates that the cement is more enriched in ^{12}C than marine carbonate rocks. Examination of the thin section of the sandstone reveals that the CaCO_3 is secondary. Apparently, the carbonate cement had been isotopically equilibrated by isotopic exchange with, or precipitated from, fresh meteoric water containing CO_2 enriched in ^{12}C . The $\delta^{18}\text{O}$ of the cement is on the low end for marine carbonate rocks, which are as low as +20 per mil (SMOW). This low value is attributed by Keith and Weber (1964) to oxygen isotope exchange with water depleted in ^{18}O relative to seawater. Another possibility is that the cement was precipitated from fresh waters at the time of initial lithification of the sandstone units, with the grain boundaries displaying the characteristics of secondary cementation. This would also explain the observed C and O isotopic values. Whichever occurred, this is evidence of meteoric waters in the sandstone reservoirs during their diagenetic history.

The precipitation of the calcite cement could also have been caused biologically. The dominant fractionation process for carbon is biological, that is, living organisms will concentrate the lighter isotope in their metabolic functions. Sulfate-reducing bacteria widely present in petroleum reservoirs utilize oxygen from SO_4 to oxidize CH_4 , producing H_2S and isotopically light CO_2 . This CO_2 then reacts with Ca in the water to precipitate secondary CaCO_3 , which will be enriched in ^{12}C . Several $\delta^{13}\text{C}$ values have been reported that are unusually negative. Aragonite was found to possess $\delta^{13}\text{C}$ values ranging from -23.1 to -60.6 per mil (PDB), and an average $\delta^{13}\text{C}$

value of -36.2 ± 6.2 per mil (PDB) for CaCO_3 from cap rocks in salt domes was reported. Calcite from the Wind River Formation has an average $\delta^{13}\text{C}$ of -22.5 ± 4.0 per mil (PDB), and sulfur-bearing limestone from Sicily was reported to have a $\delta^{13}\text{C}$ of -28.7 ± 8.9 per mil (PDB) (Faure, 1977). In all these examples, the CaCO_3 may have precipitated with CO_2 derived from inorganic or bacterial oxidation of CH_4 , which is strongly ^{12}C -enriched relative to all other organic matter in sedimentary rocks. Although the $\delta^{13}\text{C}$ of the "Cherokee" carbonate sandstone cement is not as low as the above-mentioned values, it is possible that the low carbon isotopic value in the sandstone is a result of some biogenic influence. Although a biogenic cause is possible for the ^{12}C enrichment in the "Cherokee" sandstone cement, the enrichment is better explained by the mixing of two waters, at least one of which is continentally derived. A continental source for the ^{12}C enrichment is preferred, as it is supported by the Sr isotopic composition of the cement.

Strontium isotopic composition.--Comparison between the Sr isotopic composition of the waters and that of the calcite cement in the "Cherokee" reservoir rock units will aid in understanding the role of the present water in the diagenetic history of the rocks. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of cements from the sandstone samples from two cored holes are 0.7142 and 0.7216, which are significantly lower than the Sr isotopic ratios (0.7268 and 0.7264) observed in the waters from the same two wells. Carbonates will inherit their $^{87}\text{Sr}/^{86}\text{Sr}$ character from the water from which they precipitate. As pointed out previously, the sandstone units may have had a history of association with marine conditions. Although the original pore water in the sandstone reservoirs may have had a freshwater component, the amount of Sr (0.1 mg/l) delivered to the oceans is small compared to the concentration of

Sr in seawater (8 mg/l); therefore, the Sr would retain a marine isotopic character. The carbonate cement precipitated from such waters would be expected to exhibit nearly the range of marine Sr isotopic character (0.7068 to 0.7090). Because the cements possess higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than marine Sr isotopic values, they could not have formed from such water. As these cements must have formed from water that was highly enriched in ^{87}Sr relative to seawater, precipitation of carbonate cements of these sandstone units must have occurred upon introduction of continental waters that were high in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Furthermore, the cements cannot be genetically related to the present oil-field waters, because the ratios in the waters are higher than those of the cements.

The following conclusions are supported by the results of this study:

1. According to Sulin's classification, the oil-field waters are all chloride-calcium type.
2. Major chemical data are explained primarily by:(a) mixing of seawater and meteoric water,(b) concentration by shale-membrane filtration, and(c) ion exchange or reaction with clay minerals.
3. Stable isotopic data are best attributed to:(a) mixing of light-isotope enriched meteoric water with evaporated seawater, and(b) neo-formation of clay minerals that contain water with an ice-like crystalline structure.
4. Strontium isotopic composition of the Miner field waters indicates that development of their Sr isotopic character can be limited to:(a) mixing of marine-derived and continental-derived waters and(b) interaction with certain silicate minerals, i.e. biotite, vermiculite, and K-feldspar.
5. Gypsum dehydration and dissolution, halite dissolution, dolomitization, and reaction with hydrocarbons or H_2S are among the processes that can be considered minor in the development of the chemical isotopic character of the oil-field waters.
6. Carbon, O, and Sr isotopic data of cements of the "Cherokee" sandstone reflect introduction of ^{87}Sr -, ^{16}O -, and ^{12}C -enriched waters, possibly of continental origin, during the initial lithification or diagenesis of the rocks. However, the cements are not genetically related to the present oil-field waters.
7. Three isotopically distinct groups of reservoirs are recognized on the basis of $^{87}Sr/^{86}Sr$ data of the waters. Possible causes of variation among these groups are: (1) slightly different paths of migration, or (2) presence of isotopically heterogeneous waters in the reservoirs prior to infiltration of the water that now composes the oil-field waters.

REFERENCES

- Barnes, H. L., 1979, *Geochemistry of hydrothermal ore deposits*: New York, John Wiley and Sons, 798 p.
- Beales, F. W. and Hardy, J. W., 1980, Criteria for the recognition of diverse dolomite types with an emphasis on studies of host rocks for Mississippi Valley-type ore deposits, in D. H. Zenger, J. B. Dunham, and R. L. Ethington, eds., *Concepts and models of dolomitization*: SEPM Spec. Pub. No. 28, p. 197-213.
- Bias, C., Kansas State University, Manhattan, Kansas, 1982.
- Billings, G. K., Hitchon, B., and Shaw, D. R., 1969, Geochemistry and origin of formation waters in western Canada sedimentary basin, 2. Alkali metals: *Chem. Geol.*, v. 4, p. 211-224.
- Bredehoeft, J. D., Blyth, C. R., White, W. A., and Maxey, G. B., 1963, Possible mechanism for concentration of brines in subsurface formations: *Am. Assoc. Petroleum Geol. Bull.*, v. 47, No. 2, p. 257-269.
- Brooks, C., 1968, Relationship between feldspar alteration and the precise post-crystallization movement of rubidium and strontium isotopes in a granite: *Jour. Geophys. Research*, v. 73, p. 4751-4757.
- Burke, W. H., Denison, R. E., Hetherington, E. A., Koepnick, R. B., Nelson, H. F., and Otto, J. B., 1982, Variation of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ throughout Phanerozoic time: *Geology*, v. 10, p. 516-519.
- Chaudhuri, S., 1978, Strontium isotopic composition of several oilfield brines from Kansas and Colorado: *Geochim. et Cosmochim. Acta*, v. 42, p. 329-331.
- Chaudhuri, S. and Brookins, D. G., 1978, The Rb-Sr systematics in acid-leached clay minerals, *Chem. Geol.*, v. 24, p. 231-242.
- Chebotarev, I. I., 1955, Metamorphism of natural waters in the crust of weathering: *Geochim. et Cosmochim. Acta*, v. 8, nos. 1-4, p. 22-48, 137-170, and 198-212.
- Clayton, A., Kansas State University, Manhattan, Kansas, 1982.
- Clayton, R. N., Friedman, I., Graf, D. L., Meyeda, T. K., Meents, W. F., and Shimp, N. F., 1966, The origin of saline formation waters 1. Isotopic composition: *Jour. Geophys. Research*, v. 71, No. 16, p. 3869-3881.
- Collins, A. G., 1972, Geochemical classification of formation waters for use in hydrocarbon exploration and production: Unpublished Master's thesis, University of Tulsa, Tulsa, Oklahoma, 63 p.
- _____, 1974, Geochemistry of liquids, gases, and rocks from the Smackover Formation: BuMines Report RI 7897, 84 p.
- _____, 1975, Geochemistry of oilfield waters: *Developments in Petroleum Science* 1, Amsterdam, Elsevier, 496 p.

- Coplen, T. B. and Hanshaw, B. B., 1973, Ultrafiltration by a compacted clay membrane-1. Oxygen and hydrogen isotopic fractionation: *Geochim. et Cosmochim. Acta*, v. 37, p. 2295-2310.
- Craig, H., 1961a, Isotopic variations in meteoric waters: *Science*, v. 133, p. 1702-1703.
- Craig, H. 1961b, Standard for reporting concentration of deuterium and oxygen-18 in natural waters: *Science*, v. 133, 9. 1833-1834.
- Dansgaard, W., 1961, The isotopic composition of natural waters with special reference to the Greenland ice cap: *Medd. Grønland*, v. 165, p. 1-120.
- Davis, S. N., 1963, Discussion of papers: The chemistry of saline waters: *Groundwater*, v. 1, p. 51.
- Deer, W. A., Howie, R. A., and Zussman, J., 1962, Rock-forming minerals, vol. 3-Sheet silicates, New York, John Wiley and Sons, 270 p.
- Degens, E. T. and Epstein, S., 1962, Relationship between $^{18}\text{O}/^{16}\text{O}$ ratios in coexisting carbonates, cherts, and diatomites: *Am. Assoc. Petroleum Geol. Bull.*, v. 46, p. 534-542.
- Degens, E. T., Hunt, J. M., Teuter, J. H., and Reed, W. E., 1964, Data on the distribution of amino acids and oxygen isotopes in petroleum brine waters of various geologic ages: *Sedimentology*, v. 3, p. 199-225.
- DeSitter, L. U., 1947, Diagenesis of oilfield brines: *Am. Assoc. Petroleum Geol. Bull.*, v. 31, No. 11, p. 2030-2040.
- Dott, R. H. and Batten, R. L., 1981, *Evolution of the earth*: New York, McGraw-Hill, 503 p.
- Ebanks, W. J., Brady, L. L., Heckel, P. H., O'Connor, H. G., Sanderson, G. A., West, R. R., and Wilson, R. W., 1979, The Mississippian and Pennsylvanian (Carboniferous) systems in the United States-Kansas, *Kans. Geol. Surv. Prof. Pap.* 1110-Q, 30 p.
- Faure, G. and Powell, J. L., 1972, *Strontium isotope geology*: New York, Springer-Verlag, 188 p.
- Faure, G., 1977, *Principles of isotope geology*: New York, John Wiley and Sons, 464 p.
- Friedman, G. M., 1980, Dolomite is an evaporite mineral: Evidence from the rock record and from sea-marginal ponds of the Red Sea, in D. H. Zenger, J. B. Dunham, and R. L. Ethington, eds., *Concepts and models of dolomitization*: *SEPM Spec. Pub.* No. 28, p. 69-80.
- Friedman, I., Redfield, A. C., Schoen, R., and Harris, J., 1964, The variation of the deuterium content of natural waters in the hydrologic cycle: *Rev. Geophys.*, v. 2, p. 177-224.
- Friedman, I. and O'Neil, J. R., 1977, *Data of geochemistry*: U. S. Geol. Surv. Prof. Paper 440-KK, 12 p.

- Garrels, R. M., and MacKenzie, F. T., 1971, Chemical history of the oceans deduced from post-depositional changes in sedimentary rocks: Evolution of Sedimentary Rocks, New York, Norton and Co., Inc., 397 p.
- Graf, D. L., Friedman, I., and Meents, W. F., 1965, The origin of saline formation waters 2. Isotopic fractionation by shale micropore systems: Illinois State Geol. Surv. Circ. 393, 32 p.
- Graf, D. L., 1982, Chemical osmosis, reverse chemical osmosis, and the origin of subsurface brines: *Geochim. et Cosmochim. Acta*, v. 46, p. 1431-1448.
- Grim, R. E., 1968, Clay mineralogy: New York, McGraw-Hill, 596 p.
- Hitchon, B., and Friedman, I., 1969, Geochemistry and origin of formation waters in the western Canada sedimentary basin-I. Stable isotopes of hydrogen and oxygen: *Geochim. et Cosmochim. Acta*, v. 33, p. 1321-1349.
- Hitchon, B., Billings, G. K., and Klován, J. E., 1971, Geochemistry and origin of formation waters in Western Canada sedimentary basin—III. Factors controlling chemical composition: *Geochim. et Cosmochim. Acta*, v. 35, p. 567-598.
- Jewett, J. M., and Merriam, D. F., 1959, Geologic framework of Kansas; a review for geophysicists: in Symposium on geophysics in Kansas, Kans. Geol. Surv. Bull., v. 137, p. 9-32.
- Keith, M. L., and Weber, J. N., 1964, Isotopic composition and environmental classification of selected limestones and fossils: *Geochim. et Cosmochim. Acta*, v. 28, p. 1787-1816.
- Keith, M. L., Anderson, G. M., and Eichler, R., 1964, Carbon and oxygen isotopic composition of mollusk shells from marine and fresh-water environments: *Geochim. et Cosmochim. Acta*, v. 28, p. 1757-1786.
- Kharaka, Y. K., Berry, F. A. F., and Friedman, I., 1973, Isotopic composition of oil-field brines from Kettleman North Dome, California, and their geologic implications: *Geochim. et Cosmochim. Acta*, v. 37, p. 1899-1908.
- Kharaka, Y. K., and Berry, F. A. F., 1974, The influence of geological membranes on the geochemistry of subsurface waters from Miocene sediments at Kettleman North Dome in California: *Water Resources Research*, v. 10, p. 313-327.
- Kharaka, Y. K., and Smalley, W. C., 1976, Flow of water and solutes through compacted clays: *Am. Assoc. Petroleum Geol. Bull.*, v. 60, No. 6, p. 973-980.
- Krieger, R. A., 1963, The chemistry of saline waters: *Groundwater*, v. 1, No. 4, p. 7-12.
- Land, A. S., 1980, The isotopic and trace element geochemistry of dolomite: The state of the art. in D. H. Zenger, J. B. Dunham, and R. L. Ethington, eds., Concepts and models of dolomitization: SEPM Spec. Pub. No. 28, 320 p.

- Levin, H., 1978, *The earth through time*: Philadelphia, W. B. Saunders Company, 504 p.
- Lind, O. T., 1979, *Handbook of common methods in limnology*: St. Louis, The C. V. Mosby Company, 199 p.
- Lowenstam, H. A., 1961, Mineralogy, O-18/O-16 ratios, and strontium and magnesium contents of recent and fossil brachiopods and their bearing on the history of the oceans: *Jour. Geology*, v. 69, p. 241-260.
- McKelvey, J. G., and Milne, I. M., 1962, The flow of salt solutions through compacted clays: *Clays and Clay Minerals*, Proc. Natl. Conf. 9, Lafayette, Indiana, 1960, p. 248-259.
- McKenzie, J. A., Hsü, K. J. and Schneider, J. E., 1980, Movement of subsurface waters under the sabkha, Abu Dhabi, UAE, and its relation to evaporative dolomite genesis, in D. H. Zenger, J. B. Dunham, and R. L. Ethington, eds., *Concepts and models of dolomitization*: SEPM Spec. Pub. No. 28, p. 11-30.
- Merriam, D. F., 1963, The geologic history of Kansas: *Kans. Geol. Surv. Bull.*, v. 162, 317 p.
- Morton, J. P., and Long, L. E., 1980, Rb-Sr dating of Paleozoic glauconite from the Llano Region, central Texas: *Geochim. et Cosmochim. Acta*, v. 44, p. 663-672.
- Nodine-Zeller, D. E., 1981, Karst-derived Early Pennsylvanian conglomerate in Ness County, Kansas: *Kans. Geol. Surv. Bull.*, v. 222, 30 pp.
- O'Neil, J. R., 1968, Hydrogen and oxygen isotope fractionation between ice and water: *Jour. Phys. Chemistry*, v. 72, p. 3683-3684.
- O'Neil, J. R., and Karaka, Y. K., 1976, Hydrogen and oxygen isotope exchange reactions between clay minerals and water: *Geochim. et Cosmochim. Acta*, v. 40, p. 241-246.
- Ostroff, A. G., 1967, Comparison of some formation water classification systems: *Am. Assoc. Petroleum Geol. Bull.*, v. 51, p. 404-416.
- Palmer, C., 1911, *The geochemical interpretation of water analyses*: U. S. Geol. Surv. Bull., v. 479, 31 p.
- Peterman, Z. E., Hedge, C. E., and Tourtelot, H. A., 1970, Isotopic composition of strontium in seawater throughout Phanerozoic time: *Geochim. et Cosmochim. Acta*, v. 34, p. 105-120.
- Ramakrishnan, S., 1983, Geochemistry of carbonate rocks of Late Cambrian age, and inferences from strontium isotopic composition of Late Cambrian seawater: Kansas State University, M.S. Thesis, 101 p.
- Rittenhouse, G., 1967, Bromine in oilfield waters and its use in determining possibilities of origin of these waters: *Am. Assoc. Petroleum Geol. Bull.*, V. 51, p. 2430-2440.

- Savin, S. M., and Epstein, S., 1970, The oxygen and hydrogen isotope geochemistry of clay minerals: *Geochim. et Cosmochim. Acta*, v. 34, p. 25-42.
- Schoell, M., 1980, The hydrogen and carbon isotopic composition of methane from natural gases of various origins: *Geochim. et Cosmochim. Acta*, v. 44, p. 649-661.
- Schoeller, H., 1955, *Geochemie des eaux souterraines*: *Rev. Inst. Fr. Pet.*, v. 10, p. 181-213, 219-246, 507-552, and 823-874.
- Sofer, Z., 1975, Isotopic compositions of hydration water in gypsum: The Feinberg Graduate School Ph.D. Thesis (In Hebrew).
- Sofer, Z., 1978, Isotopic composition of hydration water in gypsum: *Geochim. et Cosmochim. Acta*, v. 42, p. 1141-1149.
- Sulin, V. A., 1946, Waters of petroleum formations in the system of natural waters: Moscow, Gostoptekhizdat, 96 p.
- Sunwall, M. T., and Pushkar, P., 1979, The isotopic composition of strontium in brines from petroleum fields of southeastern Ohio: *Chem. Geol.*, v. 24, p. 189-197.
- Swanson, D. C., 1979, Deltaic deposits in the Pennsylvanian Upper Morrowan Formation of the Anadarko Basin, in *Pennsylvanian Sandstones of the Mid-continent*: Tulsa Geol. Soc. Spec. Pub. No. 1, p. 115-168.
- Thompson, T. L. and Goebel, E. D., 1968, Conodonts and stratigraphy of the Meramecian Stage (Upper Mississippian) in Kansas: *Kans. Geol. Surv. Bull.*, v. 192, 56 p.
- Tien, P., 1970, Clay mineralogy of underclays in Cherokee Group (Middle Pennsylvanian), Kansas, (abstr.): Clay min. conf. 19th Ann., Clay Min. Soc. 7th Mtg., Oct 12-17, 1970, Miami Beach Fla., Prog. and Abstr.
- Walters, R. F., Gutru, R. J., and James III, A., 1979, Channel sandstone reservoirs of Pennsylvanian age in northwestern Ness County, Kansas, in *Pennsylvanian sandstones of the Mid-continent*: Tulsa Geol. Soc. Spec. Pub. No. 1, p. 313-326.
- White, D. E., 1965, Saline Waters of sedimentary rocks, in A. Young and J. E. Galley, eds., *Fluids in subsurface environments*: Am. Assoc. Petroleum Geol. Memoir 4, p. 342-366.

APPENDIX

Petrography of "Cherokee" sandstone

- I. Pennsylvanian, "Cherokee" Shale, Ness County, Kansas, on the western flank of the Central Kansas Uplift.
- II. Medium sandstone: calcitic submature quartzarenite
- III. Megascopic properties:
 - Hardness: fairly hard to friable
 - Grain size: 0.3 to 0.5 mm (1.5 to 1.0 ϕ)
 - Color: white to light brown
 - Sorting: moderately sorted
 - Orthochemical minerals: calcite cement, clay (illite?), glauconite, pyrite
- IV. Microscopic description: (1100 grains counted)
 - A. Summary: The sandstone is composed mainly of plutonic and some metamorphic quartz, generally 1.5 to 1.0 ϕ in size, although some grains are up to 0.5 ϕ and as small as 2.0 ϕ . The grains are subangular to sub-rounded and are moderately sorted. It is cemented by secondary calcium carbonate, which has replaced some of the quartz, and contains some authigenic clay, probably illite. The sandstone also contains some chert, feldspar, glauconite and pyrite, and has fair porosity.
 - B. Texture:
 1. Fundamental end members
 - a. 84% terrigenous
 - b. 14% orthochemical
 - c. Main rock group - terrigenous
 2. Fabric
 - a. Homogeneous
 - b. Packing-point contact, some whole-grain contact, some interpenetration at some grain contacts, some replacement of grains by calcite cement
 - c. 15-20% porosity before cementation
2-5% porosity after cementation
 - d. No preferred orientation of grains
 3. Grain size
 - a. Entire sediment: median 0.4 mm (1.25 ϕ); unimodal distribution, moderate sorting, no correlation of size with composition
 - b. Sand fraction: 79%, median 1.25 ϕ , range 0 ϕ to 3.5 ϕ moderate sorting
 - c. Textural name: medium sandstone

4. Grain shape
 - a. No idiomorphic grains
 - b. Low sphericity (not determined quantitatively), no variation of sphericity with composition
 - c. 2.0 to 4.0 ρ (subangular to subrounded), no variation of roundness with composition
5. Textural maturity: submature
6. Authigenic cements: calcite-11%, occurs in patches, moderately effective in holding sand grains together

B. Mineral Composition

1. Terrigenous minerals
 - a. Quartz
 1. Plutonic and metamorphic
 2. 79% by point count
 3. Uniformly distributed
 4. No preferred orientation
 5. 1.5 to 2.0 ϕ , unimodal
 6. Xenomorphic
 7. Low sphericity (not determined quantitatively)
 8. Subangular to subrounded with a continuous gradation
 9. Point contact, face contact, some grains indent each other
 10. Some silica overgrowths in optical continuity
 11. No cleavage
 12. No zoning
 13. Low relief, $n > \text{balsam}$
 14. White or transparent in reflected light
 15. Weak birefringence, undulose extinction
 16. Uniaxial positive, length-slow
 17. Inclusions: liquid-filled vacuoles in trains that do not extend across grain boundaries, $< 0.002 \text{ mm}$
 18. Relative abundance of each variety: 77% plutonic 2% metamorphic
 19. Grains are being replaced by calcite cement
 20. Source: granitic pluton or pre-existing sedimentary rocks
 - b. Chert
 1. 4% by point count
 2. Randomly scattered
 3. No preferred orientation
 4. 1.5 ϕ in size
 5. Moderate sphericity (not quantitatively determined)
 6. Subrounded (4.0 ρ)
 7. A few grains are indented by quartz grains
 8. No overgrowths
 9. White in reflected light
 10. Low relief, $n \approx \text{balsam}$; weak birefringence
 11. Usually length-fast

12. Interference figure indeterminable
13. No inclusions
14. No alteration visible
15. Varieties: microcrystalline quartz 98%
chalcedonic quartz 2%
16. Some grains are being replaced by calcite
17. Source: cherty Mississippian carbonates

c. Feldspar

1. Orthoclase, microcline, plagioclase
2. Identified by cleavage, sign, twinning
3. 1% in section by point count
4. Randomly scattered
5. No preferred orientation
6. Grain size -1.5 ϕ
7. Xenomorphic
8. Moderate sphericity
9. Subrounded
10. Cleavage-nearly right angles on (001) and (010)
11. No zoning
12. Low relief, $n < \text{balsam}$
13. Colorless to cloudy
14. Grid twinning in microcline, albite twinning in plagioclase, no twinning in orthoclase
15. Low birefringence, straight extinction, except for twinning
16. 10 $^{\circ}$ to 26 $^{\circ}$ extinction angle
17. Biaxial negative
18. No inclusions
19. Alteration taking place by vacuolization and sericitization
20. Source: granite or preexisting sedimentary rock

2. Orthochemical minerals

a. Clay minerals

1. Illite (?)
2. Identified by high birefringence, size
3. 3% by point count
4. Occurs in patches
5. No preferred orientation
6. Size; < 2 microns
7. It surrounds its neighbors and is not indented by other mineral grains
8. Low positive relief
9. Transparent, not pleochroic, clear in reflected light
10. High birefringence
11. Interference figure not obtained
12. Derived from illitization of sericites from weathered feldspars (some could be detrital)

b. Cement

1. Calcium carbonate
2. Identified by high birefringence, high relief
3. 11% in section by point count
4. Occurs in large patches
5. No preferred orientation
6. It contacts and replaces quartz and chert grains
7. No clastic nuclei present
8. Rhombohedral cleavage
9. No zoning
10. High positive relief
11. Colorless in reflected light
12. Some twinning
13. Extreme birefringence
14. Orientation not determined
15. Uniaxial negative
16. No inclusions
17. Fresh, unaltered
18. It is attacking and replacing quartz and chert grains
19. It has filled previous pore spaces by precipitation from waters entering the reservoir after deposition

c. Glauconite

1. Identified by green color under plane light
2. < 1% estimation
3. Randomly scattered
4. Size -.162 mm
5. Sphericity - good
6. Roundness - good
7. No clastic nuclei present
8. Cleavage perfect in 1 direction
9. No zoning
10. Moderate positive relief
11. Light olive green under plane light, pleochroic yellow to green
12. Moderate birefringence
13. Length-slow, $20-30^\circ$ extinction angle
14. Biaxial negative, $2v$ $16-30^\circ$
15. No inclusions
16. Fresh
17. Formed by alteration of other phyllosilicates

ISOTOPIC AND CHEMICAL STUDIES OF OIL-FIELD WATERS
ASSOCIATED WITH UPPER PALEOZOIC ROCKS, MINER FIELD,
NESS COUNTY, KANSAS

by

LUCY NICASTRO

B.A., State University of New York at Geneseo, 1977

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Chemical analyses and Sr, O, and H stable isotopic determinations were made on several oil-field water samples that were produced from the Middle Pennsylvanian "Cherokee" sandstone lenses and three oil-water samples that were produced from the Mississippian "Warsaw" Limestone in the Miner oil field in Ness County, Kansas. The TDS contents, which range from 31,900 to 37,600 mg/l, result from the predominance of Na and Cl ions. Sodium concentration ranges from 9090 to 11,840 mg/l and the Cl content varies from 17,200 to 22,400 mg/l. The Ca values lie within the range of 1150 to 1650 mg/l, Mg is from 405 to 493 mg/l, and the K concentration are from 209 to 265 mg/l. Strontium content ranges from 44.8 to 48.8 mg/l, except for one high value of 52.3 mg/l. Lithium concentrations are very similar, 11.7 to 12.8, except for one value of 37.7 mg/l, SO_4 ranges from 60 to 2160 mg/l; Rb contents are the lowest at 0.59 to 0.92 mg/l. Bromide values range from 32 to 43 mg/l. The oil-field waters are enriched in Li, Rb, Ca, and Sr relative to seawater, and are depleted in Na, K, Mg, Br, and SO_4 relative to seawater.

The δD of the waters ranges from -82.07 to -84.97 per mil and the $\delta^{18}\text{O}$ ranges from -9.39 to -10.10 per mil (SMOW). The waters are depleted in D and ^{18}O relative to local meteoric water with a δD of -52.27 and $\delta^{18}\text{O}$ of -7.38 per mil (SMOW). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the waters range from 0.7254 to 0.7277. Three isotopically distinct groups of waters can be recognized from the $^{87}\text{Sr}/^{86}\text{Sr}$ data.

Among the natural processes that have a major control in the development of the chemical and isotopic character of the waters are mixing of seawater and meteoric water, shale-membrane filtration, reaction with silicates, and interaction of the waters with clay minerals. Evaporation of seawater and mixing of seawater with meteoric water alone will not

explain the chemical and isotopic relationships of the elements in the waters. Strontium and stable isotopic data rule out some mechanisms that otherwise seem possible from chemical data alone. These mechanisms are: (1) dolomitization, (2) reaction with evaporite minerals, (3) isotopic exchange with carbonate rocks, H_2S , and hydrocarbons, and (4) halite dissolution. The host and immediate enclosing rocks have had little influence on the chemical and isotopic composition of the waters.

The $\delta^{13}C$ of -11.84 per mil (PDB) and $^{87}Sr/^{86}Sr$ ratios of 0.7142 and 0.7216 in the calcite cement of the "Cherokee" sandstone reflect the introduction of continental water into the sandstone at the time of precipitation of the cement. The cement is not genetically related to the waters now occupying the reservoirs.