STRONTIUM ISOTOPIC GEOCHEMISTRY OF OIL-FIELD BRINES BINDLEY FIELD, HODGEMAN COUNTY, KANSAS

by

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INTRODUCTION

The chemistry of oil-field water has been studied to determine the chemical evolution and the migration and accumulation history of water (White, 1965; Clayton et al., 1966; Hanshaw and Hill, 1969; Hitchon et al., 1971; Kharaka and Berry, 1974; Collins, 1975). Fluid-rock interactions play key roles in the compositional development of subsurface water. These interactions are complex and require several lines of investigation to uncover fully the nature and extent to which host rocks have influenced the composition of the presently entrapped water. Stable isotopic data have been useful in obtaining information concerning possible fluid-rock interactions and the source of waters (Clayton et al., 1966). More recently, the potential use of Sr isotopes as indicators of the source of salinity and migration route of oil-field brine has been recognized (Chaudhuri, 1978; L. Nicastro, R. Robinson and C. Bias, personal communications, 1982).

The knowledge of the extent to which the host rocks have influenced the Sr isotopic composition of the water is critical to the interpretation of the Sr isotopic data. Carbonate rocks form nearly half of all the oil reservoirs known throughout the world. Carbonate rocks generally contain significant amounts of Sr, and they have natural tendencies to exchange Sr with associated water. These carbonate rocks can greatly influence the Sr isotopic composition of the entrapped water. When the isotopic composition of the reservoir water is influenced by the isotopic composition of the reservoir rock, the Sr isotopic data can be of limited value in deciphering

the origin of the water. On the other hand, if the local reservoir rocks have had a minimal effect in controlling the Sr isotopic composition of the associated water, the isotopic data can provide helpful clues to the present hydrologic state that exists in the oil field. The data can also provide information about the migration history of the oil-field water.

Scope of the Study

This paper reports the results of Sr isotope determinations integrated with chemical and stable isotopic data of oil-field water associated with carbonate reservoir rocks of Mississippian age in Bindley field of Hodgeman County, Kansas. The purpose of the study was to determine the extent to which the present carbonate reservoir rocks influence the Sr isotopic composition of the oil-field water. Knowledge of the reservoir rock's influence can be applied toward the resolution of the role of the water in governing the present reservoir hydrologic properties. The extent of the carbonate rock's interaction with the water provides useful information concerning the chemical and migration history of the oil-field water. An explanation of the chemical symbols used in this report is given in the Appendix.

Previous Studies

Four investigations have involved the application of Sr isotopic data to studies of oil-field water. Chaudhuri (1978) suggested that Sr isotopes could be used to define the lateral limits of a hydrologic

system. His study revealed incompatible Rb/Sr and $^{87}Sr/^{86}Sr$ ratios between oil-field waters and their associated reservoir rocks in Kansas and Colorado. The incompatible data indicate that the waters migrated into the present reservoirs. Migration of the water through Rb-rich clays surrounding the reservoir rocks was a possible explanation for the Sr isotopic ratios of the waters. Sunwall and Pushkar (1979), in their study of southeastern Ohio brines, reaffirmed Chaudhuri's suggestion that Sr isotopic ratios may be useful in determining the extent of the water-rock interactions. The Sr isotopic compositions of reservoir waters, including several water samples that were collected from wells that were old and had unknown production histories, were similar to the Sr isotopic compositions of local meteoric water.

Two concurrent studies of oil-field water are in progress at Kansas State University. These studies include investigation of Sr isotopes in oil-field water from sandstone reservoirs of Middle Pennsylvanian "Cherokee" age from Ness County, Kansas. The Sr isotopic character of the water has developed during interactions outside the present sandstone reservoirs (L. Nicastro and C. Bias, personal communications, 1982).

Selection of Study Area

The Bindley field of Hodgeman County, Kansas was selected for this isotopic study because of the availability of oil-field water, cores, cuttings and electrical log data for many wells. Bindley

field is in north central Hodgeman County in T21S and T22S, R24W (Fig. 1).

The oil-field water is being produced from the Upper Mississippian Warsaw Limestone at depths between 4,606 feet and 4,689 feet below the surface. As production has continued for a sufficient period of time (5 - 7 years), the assumption that contamination from drilling operations is no longer present may be valid. Secondary recovery treatments were not applied on the wells of Bindley field prior to collection so the water samples may be considered to be representative of the naturally occuring subsurface fluids.

Acknowledgements

I would like to thank Drs. Sambhudas Chaudhuri, Robert Cullers, Claude Shenkel, Jr., and Robert Fry for serving as members of the advisory committee for this thesis. This research project has been supported by a Grant-In-Aid of Research from Sigma Xi, the Scientific Society, and by National Science Foundation Grant EAR-7920070.

Cores were made available for use in this study by the Kansas Geological Survey in Lawrence, Kansas. Oxygen and hydrogen isotopic compositions were determined at the United States Geological Survey facilities in Menlo Park, California. The Kansas State University Chemistry Department provided access to equipment for chloride analyses. Bromide analyses were conducted by Dr. D. Whittemore at the Kansas Geological Survey in Lawrence, Kansas.

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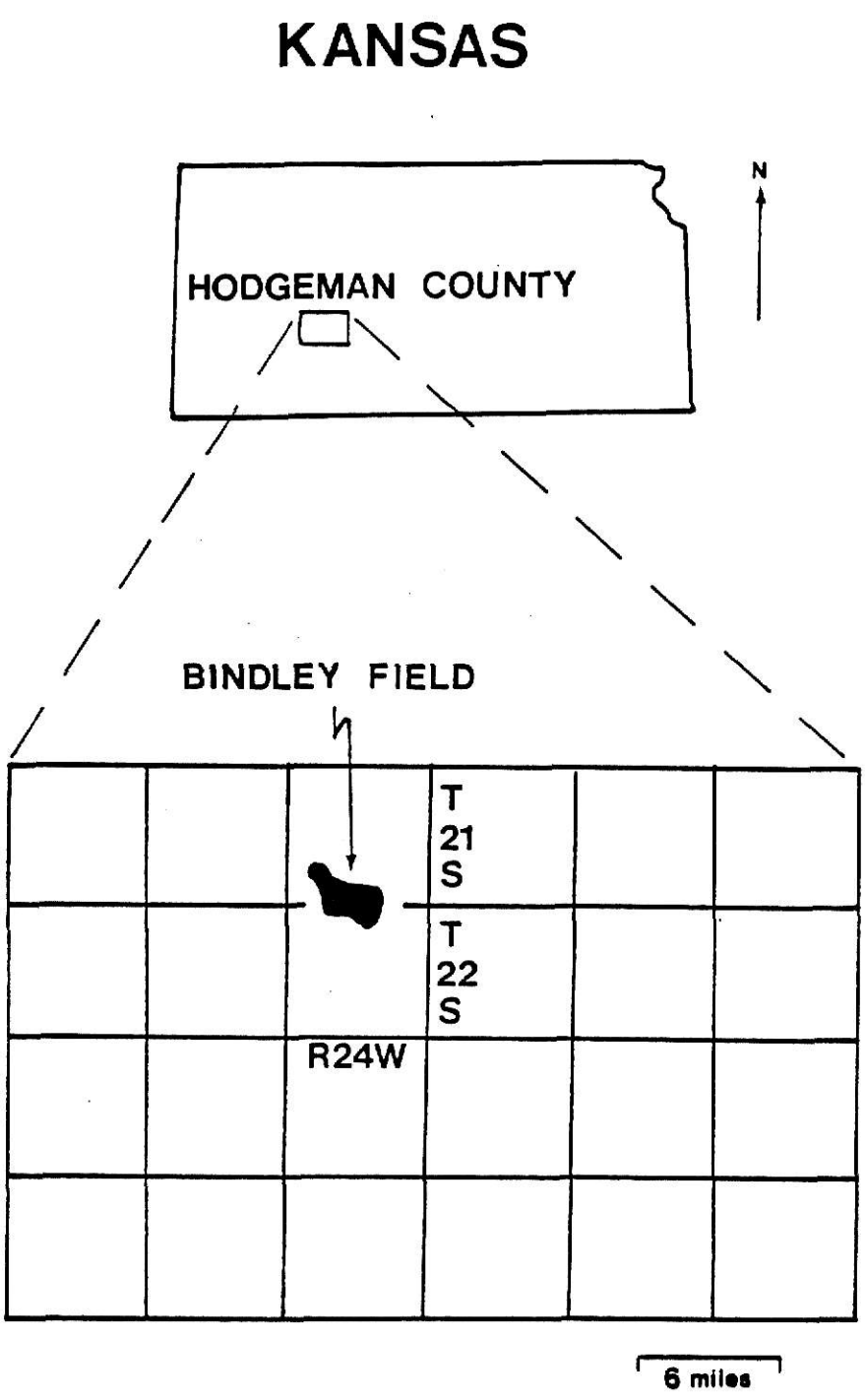

Figure 1. Location of Bindley field in Hodgeman County, Kansas.

GEOLOGY

Regional Geology

Bindley field is on the southwestern flank of the Central Kansas uplift (Fig. 2). Structural development of the uplift commenced during early Paleozoic time, the most intense period of uplift occurred from mid-Mississippian through Early Pennsylvanian and resulted in the absence of the Mississippian rocks on the uplift. Lower Mississippian and older rocks were upturned and truncated by erosion (Merriam, 1963; Ebanks et al., 1977).

Contemporaneously, Mississippian deposition occurred in the downwarping Hugoton Embayment south and west of the uplift. Sediments thickened to a maximum of 880 feet both toward the embayment's axis and southward into the Oklahoma Anadarko Basin (Merriam, 1963; Goebel, 1968). Widespread distribution of oölitic and fossil-fragmental limestone verify the dominance of a shallow and warm epicontinental sea in the shelf region of the Hugoton Embayment. Minor sandstone and shale deposits formed from the clastic detritus derived from the uplifted areas.

Cambarian through Devonian rocks lie unconformably beneath Mississippian rocks in western Kansas. Unconformably overlying the Mississippian rocks are Early-late Pennsylvanian units (Fig. 3). The Kinderhookian, Osagian, Meramecian and Chesteran stages of the Mississippian System consist of limestone or dolomite that is generally white, dense, and cherty or oölitic (Geobel, 1968). The Mississippian formations in the subsurface of western Kansas are

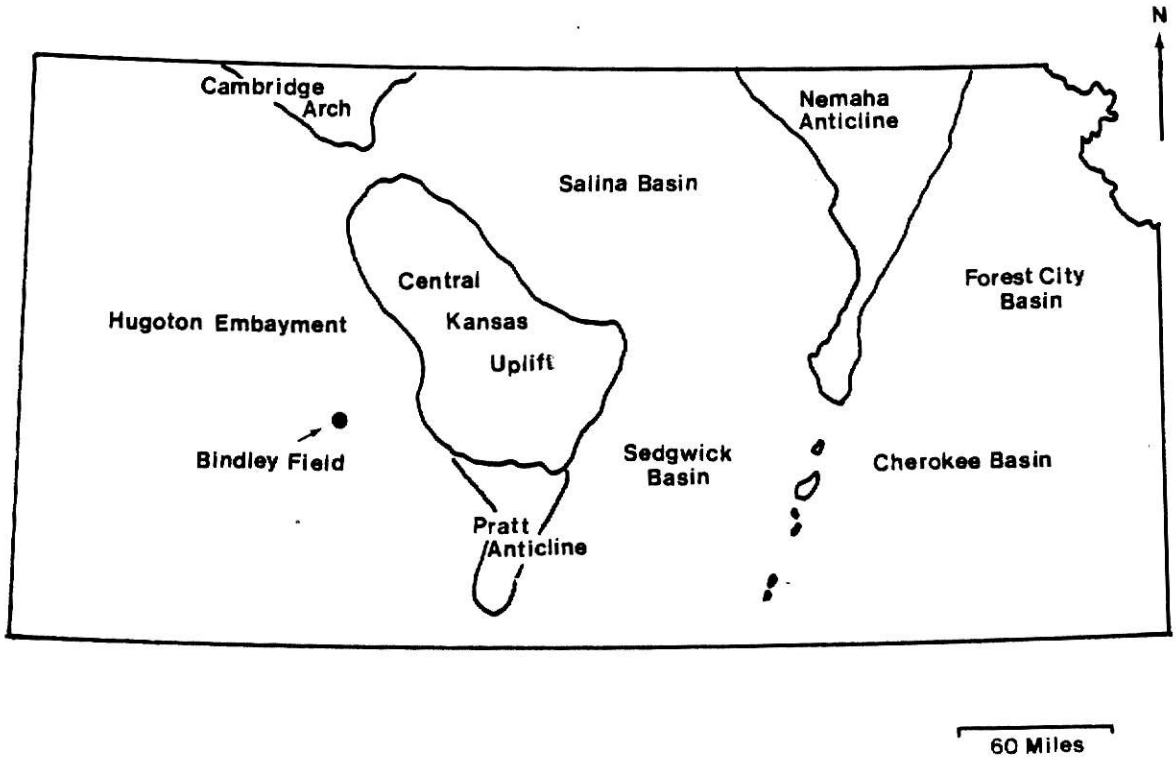

Figure 2. Principal structural features of Kansas during the pre-Desmoinesian post-Mississippian (modified from Merriam, 1963).

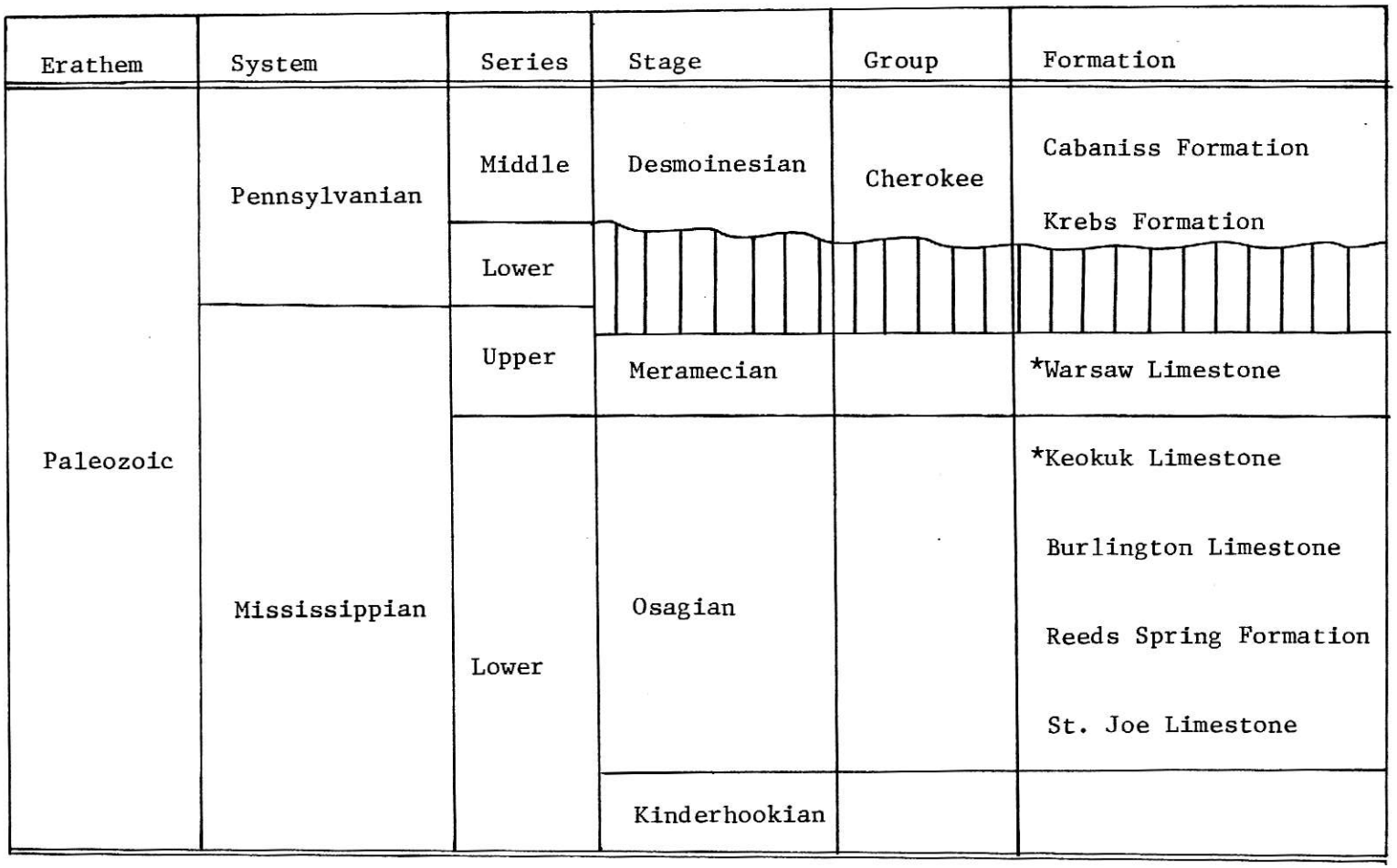

Figure 3. Generalized Mississippian and Lower-Middle Pennsylvanian stratigraphic sequence of Bindley field area. *Rock units involved in this study of Bindley field.

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identified by their fossils and insoluble residues. One of the most distinctive units of the Upper Mississippian Series is the Warsaw Limestone of the Meramecian Stage (Merriam, 1963). The Warsaw contains distinctive microfossiliferous chert that allows the Warsaw to be differentiated from the underlying Osagian and other Mississippian limestone units.

Geology of the Study Area

The Mississippian sequence in Bindley field unconformably overlies the Viola Limestone of Middle Ordovician age. The Mississippian Warsaw Limestone lies unconformably beneath the Middle Pennsylvanian Cherokee and Marmaton groups that contain "alternating shale and limestone beds" (Ebanks et al., 1977, p. 313). The Pennsylvanian basal conglomerate is the lowest section of Pennsylvanian rock in contact with the Mississippian rock. The basal unit is composed of "vari-colored shale and chert- or mixed-lithoclast conglomerate" (Ebanks et al., 1977, p. 313).

The Warsaw Limestone of the Meramecian Stage is the youngest Mississippian unit in the study area. Osagian and Kinderhookian limestone formations lie conformably beneath the Warsaw Limestone. The wells in Bindley field were drilled through 60 to 70 feet of the Warsaw Limestone and into the upper 20 feet of the Keokuk Limestone of the Osagian Stage.

Ebanks et al. (1977) studied in detail the cores that were cut through the Warsaw and Keokuk limestone intervals. According

to their description (p. 313):

> The 'Warsaw' Formation in the Bindley field area... comprises three main rock types. The main reservoir rock of the field is a brown or greenish-gray sucrosic dolomite with fossil-mold and intercrystalline porosity and moderate permeability. Interbedded with this dolomite is gray, crinoid-bryozoan lime grainstone or packstone with very low porosity and permeability. Gray or tan, cherty, glauconitic, very fine, sucrosic dolomite with spicule-mold porosity and very low permeability underlies the other two rock types in most wells.
>
> In contrast, 'Osage' rocks beneath the spicule dolomite are monotonously similar, gray or tan, cherty dolomite. The chert is nodular, white or blue-gray, and opaque.

The oil trap of Bindley field is "localized in the highly porous, low-relief, bryozoan-mound facies of the Warsaw Formation" (Ebanks et al., 1977, p. 309). Several other less common rocks interbedded with the bryozoan-dolomite of the main reservoir facies are thin beds of "fine, greenish-gray, very argillaceous dolomite... light-gray, fine dolomite with... silica nodules... and green, waxy shale or dark-gray, cherty, calcareous shale" (Ebanks et al., 1977, p. 319).

COLLECTION OF SAMPLES

Samples of oil-water mixture from 13 wells drilled into the Warsaw Limestone (Fig. 4), were collected in precleaned polyethylene bottles. The bottles were cleaned in concentrated HCl, followed by several rinsings with deionized distilled water. Each sample was collected at the well head; flow lines were flushed prior to each collection. Nearly one liter of sample was taken from each well, and a second liter, collected from some of the wells, was acidified for cation determinations. Sample bottles were sealed and labeled in the field.

Separation of the oil-water mixture occurred during storage in the laboratory. After an adequate volume of water had separated at the bottom of the bottle, the water was removed by puncturing a hole in the side of the bottle near the bottom. The waters were filtered and stored for chemical analysis.

Cores of dolomite and shale from five wells (Everton 1, Bindley 2, Deustch 1, Schauvliege 1, Dixon 1) were available at the Kansas Geologic Survey. Rock samples representing both producing and non-producing zones in these wells were selected for the isotopic and mineralogic investigation.

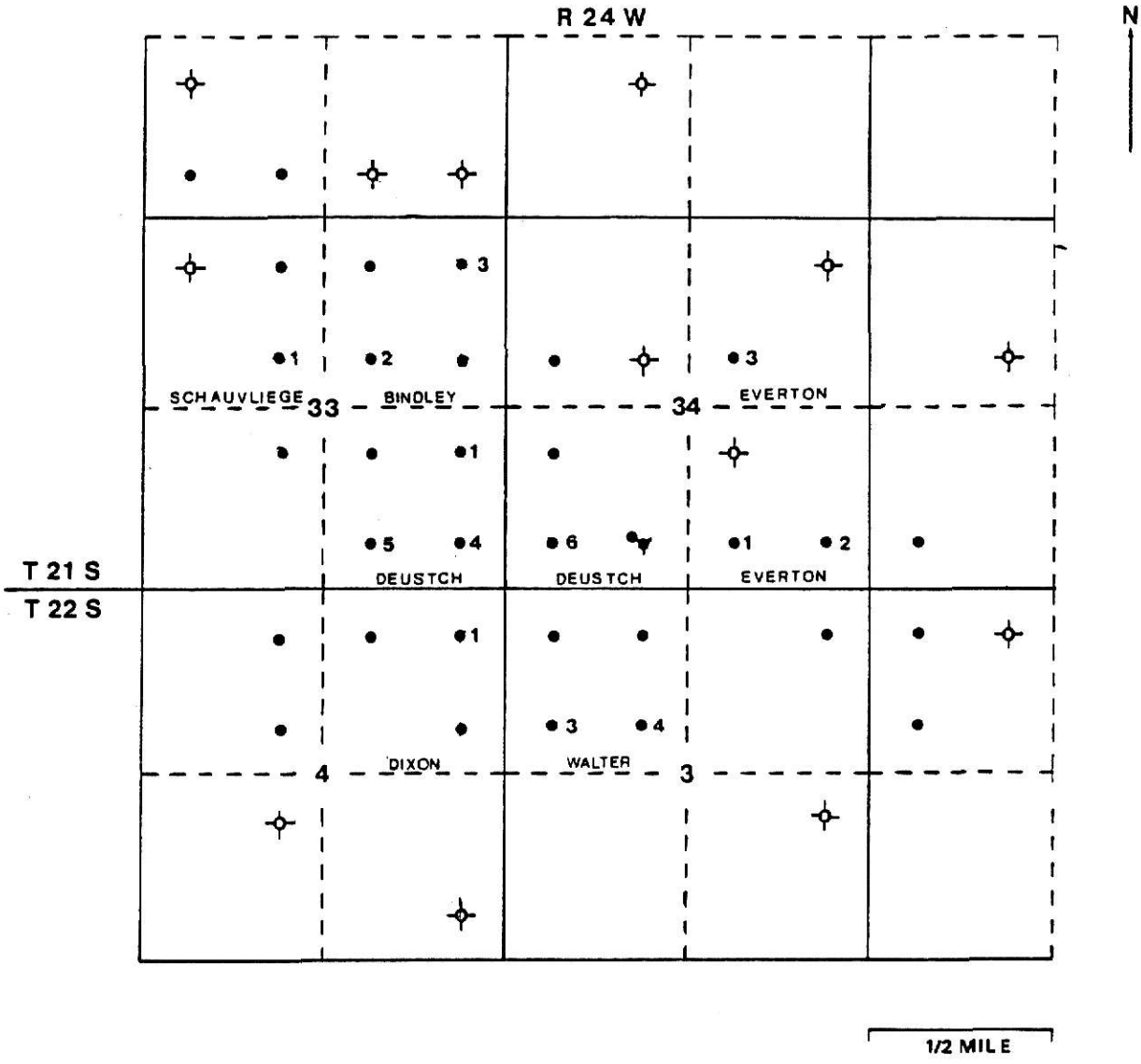

Figure 4. Location of wells in Bindley field, Hodgeman County Kansas. Wells sampled in this study are identified by names and numbers.

ANALYTICAL PROCEDURES

X-Ray Diffraction

Beds of shale which are interbedded with dolomites above and below the oil-water contact within the Warsaw Limestone of Bindley field, were analyzed for their clay mineral content. Shales were rinsed with distilled water to remove residual drilling mud. The samples were air dried and then crushed by steel mortar and pestle. The powdered shale samples were separated by centrifugation techniques into slurries of 2-0.5 μm and less than 0.5 μm size fractions.

Oriented slides were prepared by placing a fraction of the clay slurry on glass slides. After the clay slides were air dried, they were used for clay mineral identification by X-ray diffraction. Selected slides were treated with ethylene glycol, other with hydrazine, and heated to 490° C for one hour. The remaining slurries were dried and ground to powders for Rb/Sr ratio determinations by X-ray fluorescence.

X-ray diffraction was obtained using a Norelco Wide Range Diffractometer using nickel-filtered Cu-K alpha radiation. This instrument was equipped with a proportional-counter detector and a pulse-height analyzer. The goniometer-slit system included a 1° divergent slit, a 1° anti-scatter slit, and a 0.003-inch receiving slit. Chart speed was 30 inches per hour with the time constant set at 2 seconds. The scanning speed for the diffraction was 1° per minute. The 2θ scanning ranges were as follows:

$46^{\circ}- 2^{\circ}$ = untreated clays

$28^{\circ}- 2^{\circ}$ = glycolated clays

$30^{\circ}- 2^{\circ}$ = hydrazined clays

$32^{\circ}- 2^{\circ}$ = heated clays.

Major Chemistry

Cation concentrations were determined by spectrophotometry using a Perkin Elmer Model 305 B spectrophotometer. Oil-field waters were diluted with deionized distilled water to obtain concentrations that were within the linear detection limits of the instrument. Stock solutions of each cation were diluted from 1,000 ppm to produce standards that bracket the detection limits of the cation solutions being analyzed. Chemical interferences were eliminated by the addition of 0.1 percent La-solution to Ca, Mg, and Sr standards and samples. Ionization during K and Na determinations was minimized by the addition of excess (1,000 mg/l) Na in K standards and excess K in Na standards and samples.

Sulfate concentrations in the waters were determined by turbidometric methods as described in the fourteenth edition of Standard Methods for the Examination of Water and Wastewater by the American Public Health Association (1975). A Na_2SO_4 stock solution was made by dissolving 147.9 mg of Na_2SO_4 in 1 liter of deionized distilled water, thus creating a 100 mg/l solution. Standard solutions were made by diluting the Na_2SO_4 stock to concentrations that bracketed the SO_4 detection range.

A salt-acid glycerol solution was prepared by first dissolving 75 g of NaCl in 300 ml of distilled water, then adding 30 ml of concentrated 12 N HCl, 100 ml of 95-percent isopropyl alcohol, and 50 ml of glycerol. To each standard, blank, and water sample, a predetermined volume of the salt-acid glycerol solution was added. At the time of SO_4 analyses, $BaCl_2$ crystals were dissolved into the samples. Within 5 minutes of the $BaCl_2$ addition, samples were poured into precleaned cuvettes, then placed into a Coleman Model 14 Universal Spectrophotometer which measured the percent transmittance of the sample. Concentrations in ppm were obtained using conversion graphs.

Immediately following the original opening of the collected water samples and filtration, HCO_3 analyses were conducted. The waters were titrated against Na_2CO_3 using standard titration techniques. Titration endpoints were detected using a pH meter at a pH = 4.5. The values for HCO_3 concentrations may not be the true values of the waters while they were in residence. Changes in physical parameters between the subsurface and surface can greatly alter carbonate solubility.

A Buchler Digital Chloridometer was used to obtain the Cl concentration for each of the waters. The titration method employed is based on the coulometric generation of silver ion <u>in situ</u> and the amperometric detection of the endpoint. The silver ion that is generated at an anode consumes the Cl ions in solution. The time elapsed during electrolysis is proportional to the amount of Cl precipitated. The endpoint is marked after all Cl is consumed when there is a rapid rise in silver-ion concentration. A gelatin-supporting

electrolyte solution was used as a blank solution. Sample waters were diluted with distilled water, then mixed with the electrolyte solution prior to testing. Procedures used for the Cl analysis are the same as those taught in Chemical Analysis in the Chemistry Department at Kansas State University.

The total dissolved solids (TDS) in the brines were measured by weighing 1 ml of each sample, evaporating the samples to dryness on a hotplate, heating the samples in a 200° C oven for more than one hour to remove the water of crystallization, then weighing the residual salt. Samples were reheated and reweighed to check that the evaporation was complete. The quotient of the salt weight over the water weight equals the TDS value for each sample. The measured TDS contents of the brines are within the percent error of the TDS contents that were calculated by summing the concentration of each of the constituents of the samples.

The precision of these chemical procedures during the analysis of the oil-field brine is presented in Table 1. Precisions that are indicated in the table are the average of the relative deviations from the mean of each set of duplicate or triplicate analysis for 60 percent of the samples investigated.

Strontium Isotopic Determination

Isotopic values were determined using mass spectrometric techniques. Mass spectrometric analyses were made on a 15-cm radius, 60° magnetic sector, Nier-type instrument (Nuclide Corporation Model

Table 1. Analytical precision of chemical data of oil-field brines from Bindley field, Hodgeman County, Kansas.

	Precision (Percent)
Li	2
Na	5
K	2
Rb	1
Mg	6
Ca	4
Sr	4
Cl	6
SO_4	3
TDS	5

6-605), which was equipped with a solid source in single-filament configuration and a Faraday cup ion-collection system. Ion currents were enhanced by a Cary vibrating reed electrometer. Ion intensities were recorded on a strip chart modified with expanded-scale circuitry.

Strontium samples were separated from the sample waters by cation-exchange techniques. Columns of Dowex 50W-X8 cross-linked resin in bead form, used for cation-exchange separations, were calibrated then cleaned with 2 N Vycor-distilled HCl. An amount of sample water containing approximately 30 micrograms of Sr was pipetted into clean teflon beakers and evaporated to dryness. The salts were redissolved with a few ml of 2 N HCl, then carefully loaded into the columns. Each column was eluted with a predetermined volume of 2 N HCl. Strontium chloride was collected in teflon beakers at appropriate elution intervals and evaported to dryness. Salts were redissolved in 3 N HNO_3 and evaporated. Heating the dryed samples over a bunsen flame oxidized organic residues. The $Sr(NO_3)_2$ was mounted on precleaned Ta filaments prior to mass spectrometric analysis.

Rubidium separation involved the formation of insoluble $RbClO_4$. A few drops of double-distilled $HClO_4$ were added to a reduced volume of sample waters that contained 15-20 micrograms of Rb. Solutions were placed in a freezer for 24 hours where $RbClO_4$ precipitation occurred. The supernatant liquid was decanted and the residual crystals were rinsed several times with distilled deionized water to remove excess salts. Next methanol was added to the crystals. After the solution

was stirred, settling was allowed to take place. Residual fluid was decanted and distilled deionized water was added. Sample solutions were evaporated to a mushy mass, redissolved in methanol, and evaporated to dryness. Rb-perchlorate salts were converted to $RbNO_3$ by dissolution with 3 N HNO_3. Rubidium nitrate salts were mounted for mass spectrometric analyses.

Isotopic ratios were calculated from sets of 6 peaks with a single sample analysis consisting of the average of 7 to 13 such sets. All Sr analyses have been corrected for fractionation. The $^{87}Sr/^{86}Sr$ values were normalized to $^{86}Sr/^{88}Sr = 0.1194$. The Elmer and Amend $SrCO_3$ standard had a $^{87}Sr/^{86}Sr$ ratio of 0.7081 ± 0.0003 at a 95 percent confidence level.

Rubidium and strontium concentrations were measured by isotopic dilution. Strontium concentrations were obtained during a ^{84}Sr-enriched spike. Samples were spiked to give a $^{84}Sr/^{86}Sr$ ratio of approximately 1.0. A ^{87}Rb-enriched spike solution was used for determining Rb concentrations of the waters. Samples were spiked to give a sample-spike mixture $^{87}Rb/^{85}Rb$ of 1.0. Isotopic ratios obtained in each sample analysis were the average value from 6 to 10 sets of 6 peak measurements.

RESULTS

X-ray Diffraction Data

X-ray diffraction studies reveal the predominance of well-crystallized illite in four clay-mineral samples made from shales collected at various depths within the Warsaw Limestone. Negligible amounts of quartz, feldspar, and dolomite are present in the 2-0.5 μm size fractions. Quartz appears in the <0.5 μm fraction in two samples. Chlorite is also a minor mineral present in the larger size fractions of two samples and in both size fractions of one sample. Essentially no shift in d-spacings occurred for any diffraction maxima following ethylene glycol solvation, hydrazine solvation, or heating at 490° C for an hour after either solvation treatment. Figure 5 contains the diffraction patterns of sample Deustch 1 - 4670, which is representative of the other clay-mineral samples, after various treatments.

Illite (001) reflections occur between 10.00 Å and 10.16 Å. The higher order illite reflections and corresponding d-spacings are (002) at 4.98-5.03 Å, (003) at 3.35-3.31 Å and (004) at 2.5 Å. The illite (001) peak is the most intense of all the diffraction maxima. The (002) and (003) illite reflections are the next intense peaks. The illite reflections remain sharp, narrow, and symmetrical even after various solvation and heat treatments which indicates that the illites in the clay samples are well-crystallized. The only asymmetry in the illite peaks is on the low-Å side of the

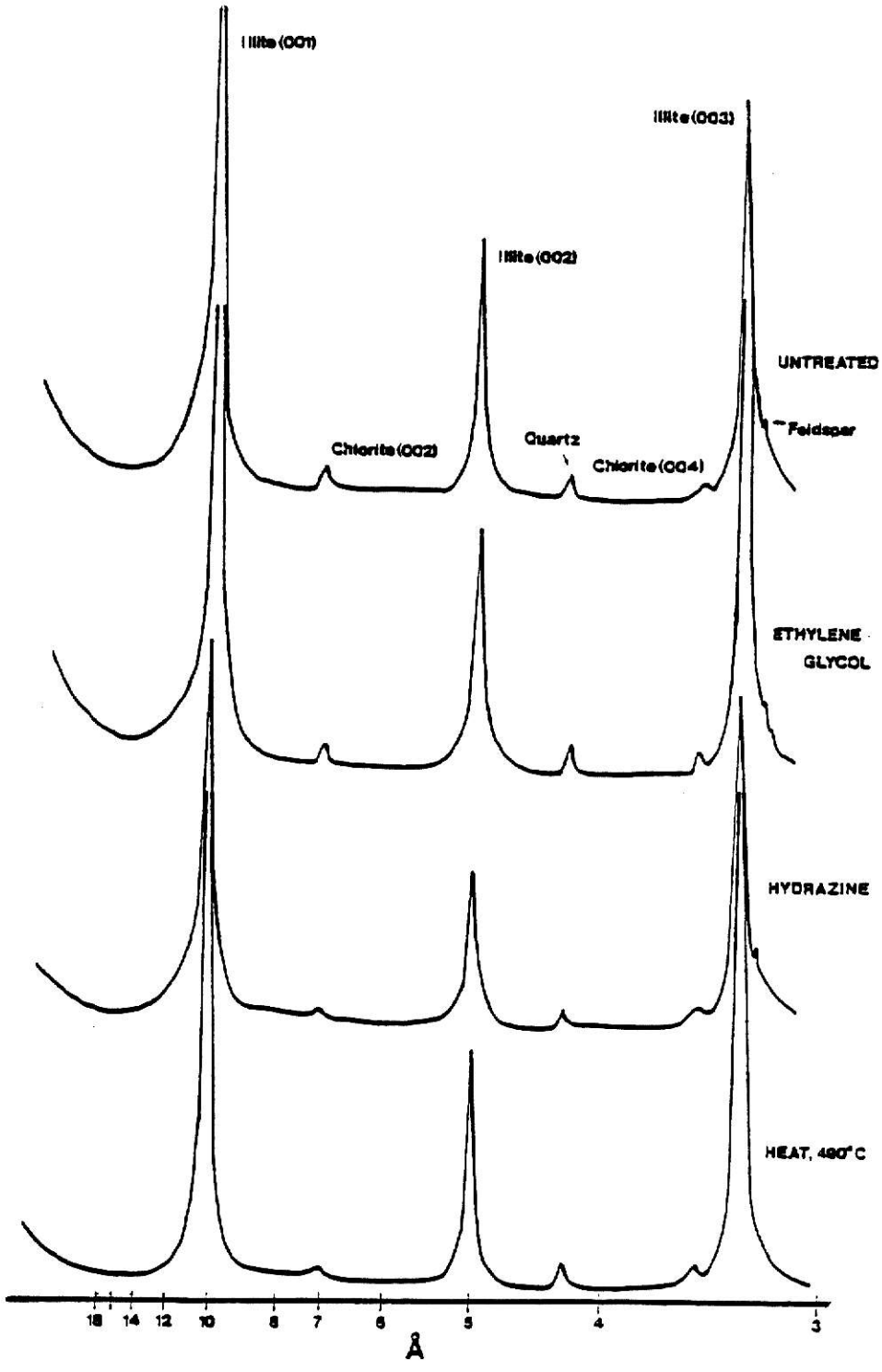

Figure 5. X-ray diffraction patterns identifying clay minerals present in the 2-0.5 μm clay fraction of Deustch 1 - 4670.

illite (003) reflections where an overlap with a feldspar reflection occurs.

Diffraction patterns from three clay samples indicate the presence of a 14-Å mineral with strong even reflections and weak or absent odd reflections. The strength of the (002) and (004) reflections, occurring at 7.02-7.14 Å and 3.50-3.56 Å respectively, are characteristic of iron enrichment in the octhedral layer of the clay mineral. The (001) and (003) reflections at 14.29 Å and 4.73 Å are present on diffraction patterns of only one sample. The determination of the abundance of this mineral as compared to illite, using the area underneath the (001) peaks, revealed that there is less than one percent of this 14-Å mineral in the clay samples. As the sharp, short, symmetrical reflections for this mineral remained unchanged upon ethylene glycol, hydrazine, and heat treatments, this mineral was identified as an iron-rich chlorite.

Quartz occurring at 4.26 Å, is in minor amounts in the larger size fractions of all four samples and the smaller size fractions of two clay-mineral samples. A second quartz peak may be a part of the low-Å asymmetry of illite (003) together with feldspar that occurs at 3.26 Å. The minor feldspar reflections appear in only the larger size fractions. Dolomite occurs at 2.89 Å in the larger size fractions of two clay-mineral samples.

Chemical Data

Some chemical constituents in oil-field water can be used to classify the water. Also, the interpretation of the chemical data can establish possible origins and modes of evolution of the subsurface waters.

Major constituents measured in this study are Na, K, Ca, Mg, SO_4, HCO_3, and Cl. Minor elements analyzed are Li, Rb, Sr, and Br. The concentrations of these constituents are presented in Table 2. The relative abundances of the ions among the oil-field waters are very similar as shown in a Schoeller diagram (Fig. 6). The abundance of the ions, in decreasing order, is Cl, Na, SO_4, Ca, Mg, K, HCO_3, Sr, Br, Li, and Rb. Relative enrichments and depletions in the oil-field brines, compared to average seawater, are displayed in Table 3. The brines are enriched in Na, Cl, Ca, Sr, and Rb, and they are depleted in Mg, HCO_3, K, SO_4, and Br relative to average seawater.

Seawater contains approximately 35,000 Mg/l of total dissolved solids (TDS). Waters containing more than 35,000 mg/l TDS are classified as brines by Krieger (1963). Waters having 10,000 to 100,000 mg/l TDS are considered to be saline waters by Davis (1963). Davis (1963) reserved the term brine for waters containing more than 100,000 mg/l TDS. The oil-field waters collected from the Warsaw Limestone in Bindley field contain between 40,300 and 45,350 mg/l TDS and will called brines, following Krieger's definition.

Table 2. Chemical constituents of oil-field brines from Bindley field, Hodgeman County, Kansas

(concentrations expressed in mg/l)

Well	Na	K	Rb	Li	Mg	Ca	Sr	Cl	SO_4	HCO_3	Br	TDS
EVERTON 1	13,500	320	0.9	11.7	410	1540	43	22,900	2310	53	31	41,300
EVERTON 2	13,300	340	0.9	12.0	410	1530	43	23,000	3150	35	—	42,400
EVERTON 3	14,550	330	0.9	12.2	500	1670	46	24,500	2660	53	—	42,500
BINDLEY 2	13,510	320	0.8	11.6	420	1440	42	23,000	2080	82	30	42,500
BINDLEY 3	13,500	330	0.9	12.1	460	1450	41	22,500	2380	56	32	42,000
WALTER 3	12,280	310	0.8	12.6	390	1520	41	23,000	2090	44	—	44,500
WALTER 4	13,350	320	0.9	12.2	440	1450	43	21,800	2880	73	39	40,300
DEUSTCH 1	14,460	330	0.9	12.4	420	1580	42	23,900	2870	79	—	44,700
DEUSTCH 4	14,180	350	0.8	11.9	460	1450	40	23,400	—	—	38	42,600
DEUSTCH 5	13,410	320	0.8	12.0	420	1450	42	21,600	3000	64	—	42,700
DEUSTCH 6	13,830	330	0.9	12.2	430	1560	42	24,300	2660	70	34	45,400
SCHAUVLIEGE 1	13,640	310	0.9	12.1	400	1510	43	22,700	2600	73	—	42,100
DIXON 1	13,890	320	0.9	12.2	430	1550	41	23,200	2940	73	29	43,400

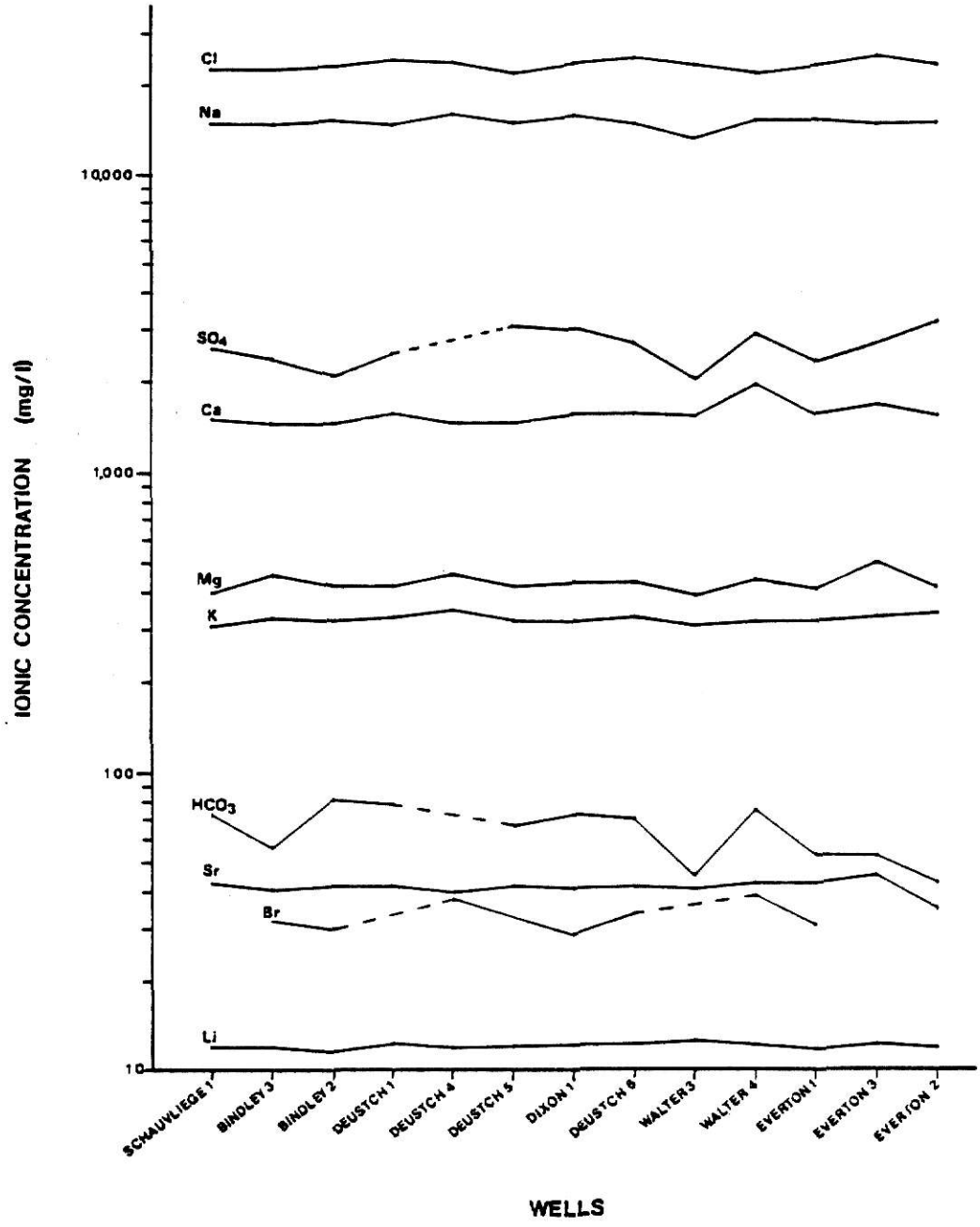

Figure 6. Variation of constituents among the oil-field brines from Bindley field, Hodgeman County, Kansas.

Table 3. Comparison of average constituent concentrations between seawater and the brines from Bindley field, Hodgeman County, Kansas, showing relative enrichments and depletions (concentrations expressed in mg/l).

	Seawater*	Bindley Field Brines
Li	0.2	12
Na	11,000	13,600
K	350	325
Rb	0.1	0.9
Mg	1,300	430
Ca	400	1,520
Sr	7	42
Cl	19,000	23,000
Br	65	33
SO_4	2,670	2,290
HCO_3	400	58
TDS	35,000	42,800

* Collins, 1975

Several systems of chemical classification exist for water (Palmer, 1911; Sulin, 1947; Schoeller, 1955; Ostroff, 1967; Collins, 1975). Concentrations of constituents and ratios between various constituents may suggest the origin of a water. Four classes of water have been defined based on the composition of dissolved salts in the waters, and these compositions are related to the origin of the waters (Sulin, 1947). In the Sulin genetic classification scheme, ionic compositions are expressed in milligram-equivalents of each ion (Table 4), and ratios are expressed in a percent-equivalent form (Table 5). In the following equations, Na and Cl are used to represent all the alkalies and all the halides, respectively.

The q Na/ q Cl ratio of a water, the first parameter used in the Sulin classification, determines which ion dominates. When this ratio is greater than 1.0, Na is the dominant or excessive ion available to combine with sulfate or bicarbonate in the water. Sodium will combine with sulfate creating a sulfate-sodium water if (q Cl - q Na)/q SO_4 is less than one. When this second equation is greater than one, bicarbonate-sodium waters are formed by excess sodium combining with bicarbonate in the water. Excess chloride ions may combine with calcium or magnesium depending on the (q Cl - q Na)/q Mg ratio. For waters which this quotient is greater than one, chloride-calcium waters are formed, and for those in which it is less than one, cloride-magnesium waters form.

Table 4. Chemical constituents of oil-field brines from Bindley field, Hodgeman County, Kansas (concentrations expressed in equivalents per mil)

Well	Na	K	Rb	Li	Mg	Ca	Sr	Cl	SO_4	HCO_3	Br
EVERTON 1	587	8.2	0.01	1.7	33.7	76.8	0.98	646	48	1.8	0.39
EVERTON 2	578	8.7	0.01	1.7	33.7	76.3	0.98	649	66	1.2	—
EVERTON 3	633	8.4	0.01	1.8	41.1	83.3	1.05	691	55	1.8	—
BINDLEY 2	587	8.2	0.01	1.7	34.6	71.9	0.96	649	49	2.7	0.38
BINDLEY 3	587	8.4	0.01	1.7	37.9	72.4	0.94	635	49	1.9	0.40
WALTER 3	534	7.9	0.01	1.8	32.1	75.8	0.94	649	44	1.5	—
WALTER 4	580	8.2	0.01	1.8	36.2	72.4	0.98	615	60	2.4	0.49
DEUSTCH 1	629	8.4	0.01	1.8	34.6	78.8	0.96	674	60	2.6	—
DEUSTCH 4	617	9.0	0.01	1.7	37.9	72.4	0.91	660	—	—	0.48
DEUSTCH 5	583	8.2	0.01	1.7	34.6	72.4	0.96	609	63	2.2	—
DEUSTCH 6	601	8.4	0.01	1.8	35.4	77.8	0.96	685	55	2.3	0.42
SCHAUVLIEGE 1	593	7.9	0.01	1.7	32.9	75.3	0.98	640	54	2.4	—
DIXON 1	604	8.2	0.01	1.8	35.4	77.3	0.94	654	61	2.4	0.36

Table 5. Chemical constituents of oil-field brines from Bindley field, Hodgeman County, Kansas (concentrations expressed in percent of the sum of the equivalents)

Well	q Na	q K	q Rb	q Li	q Mg	q Ca	q Sr	q Cl	q SO_4	q HCO_3	q Br
EVERTON 1	82.9	1.16	0.001	0.24	4.8	10.8	0.14	92.8	6.9	0.26	0.06
EVERTON 2	82.7	1.24	0.001	0.24	4.8	10.9	0.14	90.6	9.2	0.17	—
EVERTON 3	84.4	1.12	0.001	0.24	5.5	11.1	0.14	92.4	7.4	0.24	—
BINDLEY 2	83.3	1.16	0.001	0.24	4.9	10.2	0.14	92.6	7.0	0.38	0.05
BINDLEY 3	83.0	1.18	0.001	0.24	5.3	1 .2	0.13	92.7	7.2	0.18	0.06
WALTER 3	83.2	1.20	0.001	0.28	4.9	11.6	0.14	93.5	6.3	0.22	—
WALTER 4	82.9	1.17	0.001	0.26	5.2	10.3	0.14	90.8	8.8	0.35	0.07
DEUSTCH 1	83.5	1.12	0.001	0.24	4.6	10.5	0.13	91.5	8.1	0.35	—
DEUSTCH 4	83.5	1.22	0.001	0.23	5.1	9.8	0.12	—	—	—	—
DEUSTCH 5	83.2	1.17	0.001	0.24	4.9	10.3	0.14	90.2	9.3	0.33	—
DEUSTCH 6	82.9	1.15	0.001	0.25	4.9	10.7	0.13	92.3	7.4	0.31	0.06
SCHAUVLIEGE 1	83.3	1.11	0.001	0.24	4.6	10.6	0.14	92.0	7.7	0.34	—
DIXON 1	83.0	1.13	0.001	0.25	4.9	10.6	0.13	91.2	8.5	0.33	0.05

The classification of the oil-field brines from the Bindley field following the Sulin scheme is presented in Table 6. All thirteen of the waters are chloride-calcium type waters. Other studies have found oil-field brines to be most often chloride-calcium and chloride-magnesium waters (Sulin, 1947; Bojarski, 1970; Collins, 1975). Sodium-sulfate and sodium-bicarbonate waters are meteoric and artesian waters. Seawater and waters associated with evaporite sequences constitute the chloride-magnesium water type. Chloride-calcium waters describe waters from deep, stagnant environments.

Oxygen - Deuterium Isotopic Data

Oxygen and hydrogen isotope data are useful in determining the origin of oil-field brines from sedimentary rocks of marine origin. The isotopic compositions of O and H are expressed as per mil differences relative to standard mean ocean water (SMOW). The equations used in the calculations of $\delta^{18}O$ and δD are:

$$\delta^{18}O = \left[\frac{(^{18}O/^{16}O)_{spl} - (^{18}O/^{16}O)_{SMOW}}{(^{18}O/^{16}O)_{SMOW}}\right] \times 10^{3}‰$$

$$\delta D = \left[\frac{(D/H)_{spl} - (D/H)_{SMOW}}{(D/H)_{SMOW}}\right] \times 10^{3}‰$$

Positive $\delta^{18}O$ and δD values indicate enrichment of the brines in heavy isotopes compared to SMOW. Negative values imply depletion of

Table 6. Sulin classification of the oil-field brines from Bindley field, Hodgeman County, Kansas (values expressed in the percent-equivalent form).

	$\frac{Cl-Na}{Mg}$*	Genetic Water Type
EVERTON 1	1.8	Cl-Ca
EVERTON 2	1.3	Cl-Ca
EVERTON 3	1.2	Cl-Ca
BINDLEY 2	1.6	Cl-Ca
BINDLEY 3	1.6	Cl-Ca
WALTER 3	1.8	Cl-Ca
WALTER 4	1.2	Cl-Ca
DEUSTCH 1	1.4	Cl-Ca
DUESTCH 4	1.4	Cl-Ca
DEUSTCH 5	1.1	Cl-Ca
DEUSTCH 6	1.6	Cl-Ca
SCHAUVLIEGE 1	1.6	Cl-Ca
DIXON 1	1.6	Cl-Ca

* Final parameter used in the Sulin classification scheme

heavy isotopes relative to SMOW. Stable isotopic values of Bindley field waters, presented in Table 7, contain $\delta^{18}O$ values ranging between -8.38 and -8.91 per mil with δD values ranging from -70.1 to -80.2 per mil. Friedman et al. (1964) also reported similar D values for waters from the Kansas River near Topeka. The oil-field waters have been depleted in D and ^{18}O compared to SMOW.

Craig (1961) established the relationship between $\delta^{18}O$ and δD in meteoric water samples. The stable isotopic values from many areas of the world were plotted on a $\delta^{18}O$ versus δD graph. The line that the data created is described by the equation $\delta D = 8\ \delta^{18} + 10$ and refered to as the meteoric water line. Waters from closed basins in which evaporation is a dominant factor in controlling the isotopic composition of the waters, plot to the right of the meteoric water line (Craig, 1961).

Analysis of geothermal waters by Craig (1963) uncovered an 'oxygen-isotope shift' away from the meteoric water line (Fig. 7). More positive $\delta^{18}O$ values in the geothermal waters were attributed to a progressive equilibrium of the O in the waters and in silicate and carbonate reservoir rocks. Silicate rocks have an average $\delta^{18}O$ of $+10.0 \pm 5$ per mil. Average Paleozoic marine carbonate rocks have $\delta^{18}O$ ranges between +18.0 and +28.0 per mil.

Clayton et al. (1966) determined the ^{18}O and D isotopic composition of several oil-field brines from Illinois, Michigan, Gulf Coast, and Alberta that were collected from oil pools in sedimentary rocks of marine origin. The isotopic data from these

Table 7. Oxygen and hydrogen isotopic data on oil-field brines from Bindley field, Hodgeman County, Kansas.

	δD	$\delta^{18}O$
EVERTON 1	-70.1	-8.78
EVERTON 2	-76.8	-8.78
EVERTON 3	-73.3	-8.81
BINDLEY 2	80.2	-8.91
WALTER 3	-74.8	-8.62
WALTER 4	-77.5	-8.61
DEUSTCH 1	-73.3	-8.82
DEUSTCH 5	-79.6	-8.43
SCHAUVLIEGE 1	-76.6	-8.64
DIXON 1	-70.5	-8.38
SMOW	0	0
KANSAS METEORIC	-52.3	-7.38

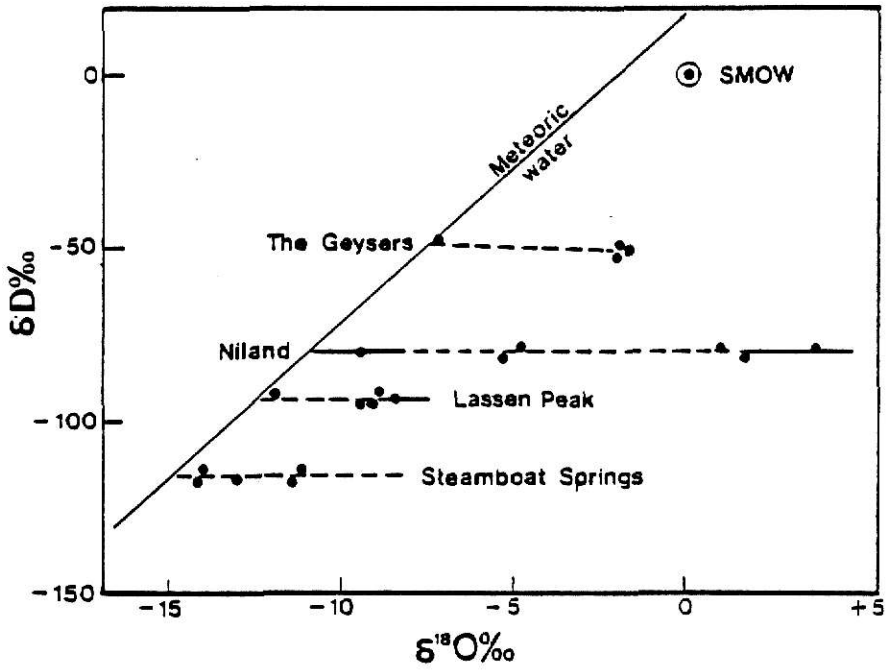

Figure 7. Oxygen-isotope shift displayed by geothermal waters (copied from Faure, 1977).

areas were plotted on the $\delta^{18}O$ versus δD graph with Craig's meteoric water line. Positive sloping lines extending away from the meteoric water line resulted, showing both $\delta^{18}O$ and δD enrichment in the brines compared to meteoric water (Fig. 8). The H-isotope shift may be due to isotopic exchange between the hydrogen in the brines and in hydrocarbons, hydrogen sulfide, or hydrated minerals (Clayton et al., 1966). None of the brine lines converge on SMOW, therefore, a marine origin for the brines was not substantiated. The brine lines intersect the meteoric water line, thus revealing compatible isotopic compositions between the brines and present meteoric waters.

The $\delta^{18}O$ and δD values obtained on the waters from Bindley field are plotted on the $\delta^{18}O$ versus δD graph together with the meteoric water line, SMOW, and a local Kansas meteoric water. (Fig. 9). The Bindley field brines cluster to the right of the meteoric water line. The brine values are depleted in $\delta^{18}O$ and δD relative to SMOW and Kansas meteoric water. From this figure, the relationship between meteoric water, seawater, host rocks, and the brines is not apparent.

Strontium Isotopic Data

Strontium isotopic compositions of Bindley field waters are presented in Table 8. The isotopic values, expressed in terms of $^{87}Sr/^{86}Sr$ ratios, range between 0.7231 and 0.7254. Strontium isotopic ratios increase due to the beta-decay of ^{87}Rb to ^{87}Sr. The concentration of Rb in the oil-field brines is 0.8 to 0.9 mg/l

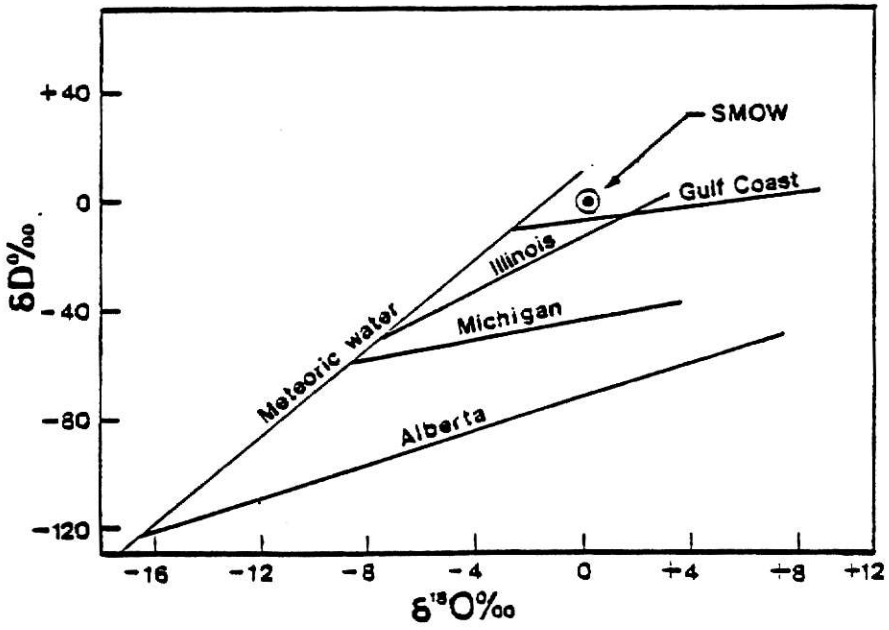

Figure 8. Relationship between the δD and $\delta^{18}O$ in brines from Gulf Coast, Illinois, Michigan, and Alberta sedimentary basins (modified from Clayton et al., 1966).

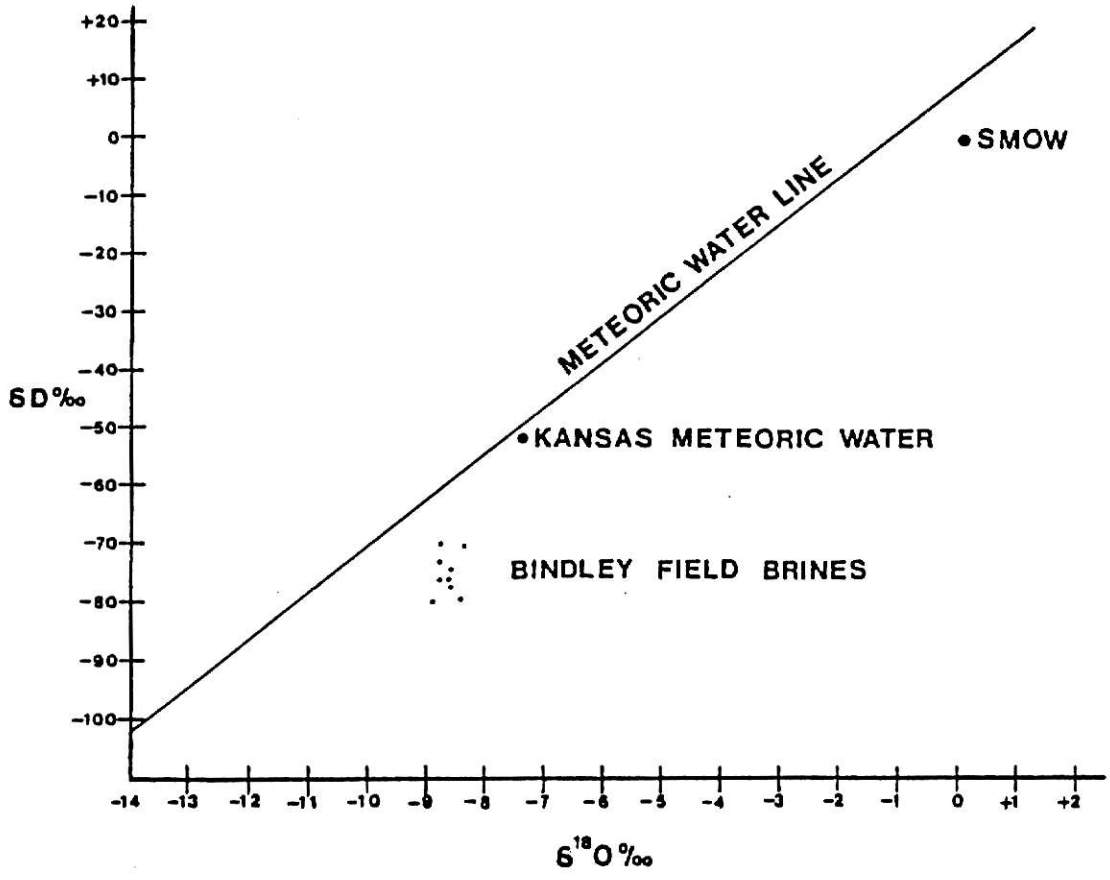

Figure 9. Oxygen and deuterium isotopic compositions of the oil-field brines from Bindley field, Hodgeman County, Kansas.

Table 8. Rubidium - strontium data on brines and clay fraction of a shale from Bindley field, Hodgeman County, Kansas.

BRINES	$^{87}Sr/^{86}Sr$*	Rb/Sr
EVERTON 1	.7232	.021
EVERTON 2	.7253	.021
EVERTON 3	.7233	.020
BINDLEY 2	.7241	.019
BINDLEY 3	.7241	.022
WALTER 3	.7254	.018
WALTER 4	.7236	.021
DEUSTCH 1	.7249	.021
DEUSTCH 4	.7242	.020
DEUSTCH 5	.7231	.019
DEUSTCH 6	.7239	.021
DIXON 1	.7245	.022
CLAY FRACTION FROM SHALE		
DEUSTCH 1 - 4670 (2-.05μm)	.7950	—

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

Data plotted on Bindley field maps, Figures 21-22, p. 76-77.

and the Rb/Sr ratios range between 0.018 to 0.022. Because Rb values and Rb/Sr ratios are low, there has been practically no increase in the $^{87}Sr/^{86}Sr$ values of the waters due to radioactive decay of ^{87}Rb in the waters. Assuming that a closed system has existed with respect to Rb and Sr, the $^{87}Sr/^{86}Sr$ ratios of the waters can be considered to be the initial values.

The strontium isotopic values of waters from some wells in Bindley field are different from others, therefore, isolated existence among these waters is a strong possibility. The water from the Deustch 5 well has a $^{87}Sr/^{86}Sr$ ratio of 0.7231, whereas that from the Walter 3 well has a $^{87}Sr/^{86}Sr$ ratio of 0.7254. The isotopic compositional difference is well outside the range of experimental error ($\pm$ 0.0003), hence these two waters are isolated from each other in the subsurface.

The $^{87}Sr/^{86}Sr$ ratio of the host carbonate rock is much lower than that of the reservoir waters. The host carbonate rock of Mississippian age has a Sr isotopic value of approximately 0.7080 as determined by Peterman et al. (1970). The clay fraction from one of the shale beds has a $^{87}Sr/^{86}Sr$ ratio of 0.7950. These values are significantly different from those of the oil-field brines and thus suggest that an isotopic equilibrium between the rocks and the waters of Bindley field does not exist.

DISCUSSION

Chemical evolution of oil-field water generally results from the interactions of many complex processes. The origin of the water at the time of sediment deposition together with the chemical modifications that occur during residence in the subsurface govern the evolution of the oil-field water. Mineral dissolution and precipitation, ion exchange, ultrafiltration through clay-shale membranes, and infiltrating water are some of the mechanisms that can alter the original composition of the water. Chemical parameters individually can result from specific chemical or physical processes, thus the discussion of the chemical composition of the oil-field waters from Bindley field explores the plausible mode(s) of evolution, either of the individual or of the group elemental characteristics. The isotopic data also suggest different interpretations, which are not necessarily contradictory, of the processes by which the waters acquired their present chemical characters. Hence, the data of Sr and stable isotopes are discussed separately. The information derived from the chemical and isotopic data are then integrated to provide some plausible modes of chemical evolution of the waters.

Chemical Composition

Total Dissolved Solids and Bromide.--The TDS content in the oil-field brines from Bindley field (40,300 to 45,400 mg/l) are greater than that in seawater (35,000 mg/l). Assuming that the waters had a marine origin, on the basis that the rocks were deposited in a

marine environment, the higher salinity of the oil-field water could be related to either evaporation of the seawater, varied fluid-rock interactions, or concentration through clay-shale membrane effects.

Rittenhouse (1967) subdivided oil-field water into five groups based on their Br versus TDS content. Water with a Br and TDS content lying along the concentration curve for seawater belong to Group I. The water may have formed from the concentration of seawater by evaporation or from being diluted by low Br and TDS fresh water. Group II water has similar TDS values to those of Group I but has higher Br contents. The enrichment of Br is possibly due to decomposition of organic matter. Water of Group III has greater TDS content and lesser Br content than that of the water expected from concentrated seawater. Solution of halite evaporite sequences or halite in salt domes will result in a great increase in the TDS values with little rise in Br content. Group IV water contains less Br and TDS than expected from dilution of seawater by fresh water Dilution or mixing of Group III water may create the water belonging to Group IV. The last group contains water that results from extensive concentration of seawater by evaporation. The TDS content of Group V water is very high, and the Br content increases rapidly due to halite precipitation.

The Br and TDS data from Bindley field brines, plotted in Figure 10, lie in the Group III region. The oil-field brines are depleted in Br compared to concentrated seawater at equivalent TDS values.

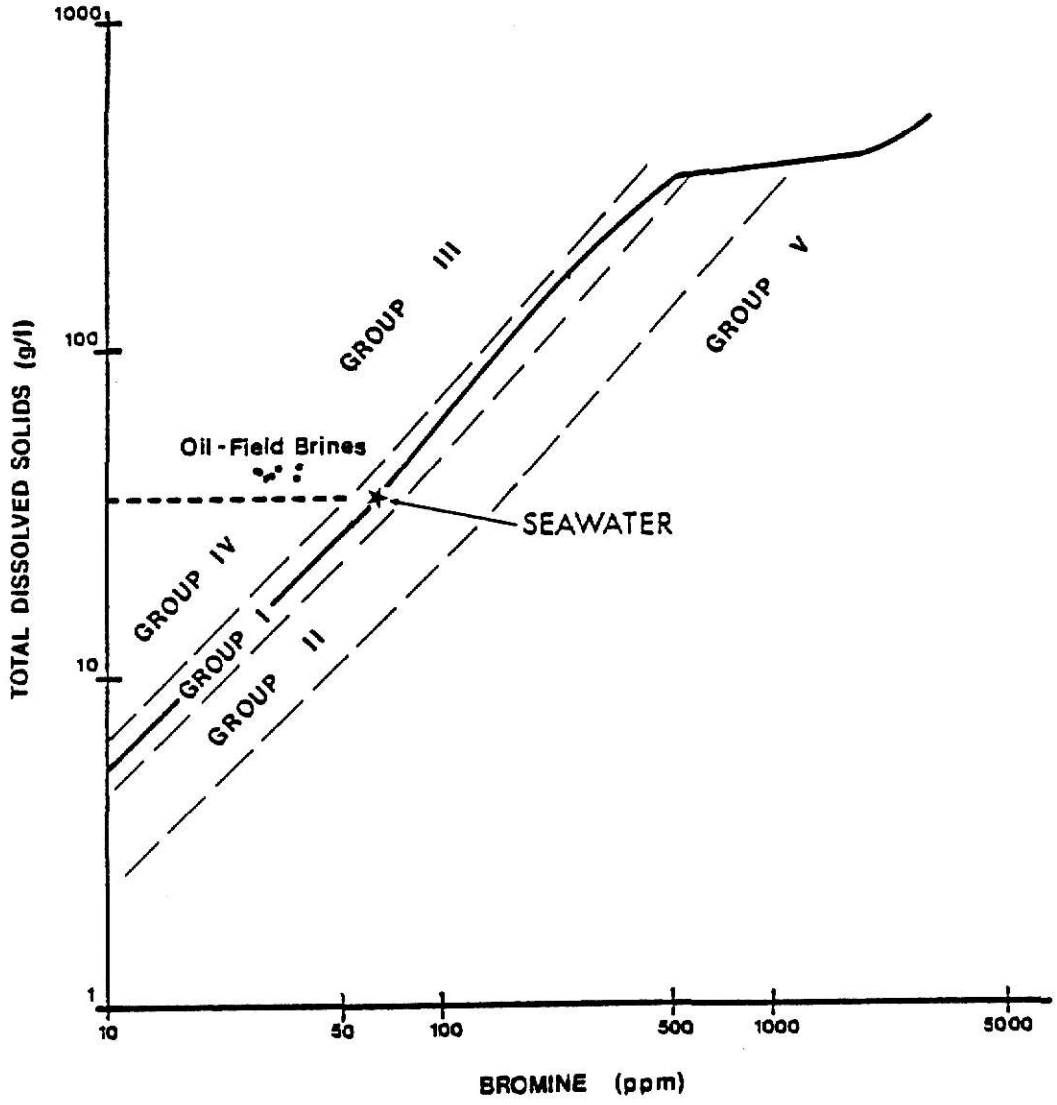

Figure 10. Comparison of Br and TDS concentrations of oil-field brines from Bindley field, Hodgeman County, Kansas, with evaporating seawater (modified by Rittenhouse, 1967).

Many histories of evolution exist that could cause the brines to attain their present Br and TDS values. Four of the simplest evolutionary paths by which the brines could have formed from seawater are shown in Figure 11. These processes include: (1) seawater slightly diluted by fresh water, than dissolving halite, (2) seawater dissolving halite, then being diluted, (3) a concentrated seawater dissolving halite, then being diluted, or (4) a diluted seawater dissolving halite, then being concentrated (Rittenhouse, 1967). In all of these paths, the Br and TDS contents of the brines were created by mixing a fresh water with seawater or a concentrated seawater, and dissolution of halite.

Divalent Cations.--Comparison of the concentration of Mg, Ca, and Sr relative to Cl values of the oil-field brines indicates that the waters are enriched in Ca and Sr and depleted in Mg compared to the concentrations at equivalent Cl levels of evaporated seawater (Figs. 12-14). The Ca and Sr enrichment and Mg depletion in other oil-field waters have been explained by dolomitization (Bentor, 1969; Rittenhouse et al., 1969; Collins, 1975). Dolomitization may occur when Mg-bearing water comes into contact with calcium carbonate phases. Magnesium exchange with the Ca in the carbonates results in the water losing Mg and gaining Ca and Sr. The waters of Bindley field are produced from Mississippian dolomitic carbonate rocks, thus dolomitization of the reservoir carbonate rocks could be the cause for the Ca and Sr enrichment and Mg depletion of the waters from Bindley field.

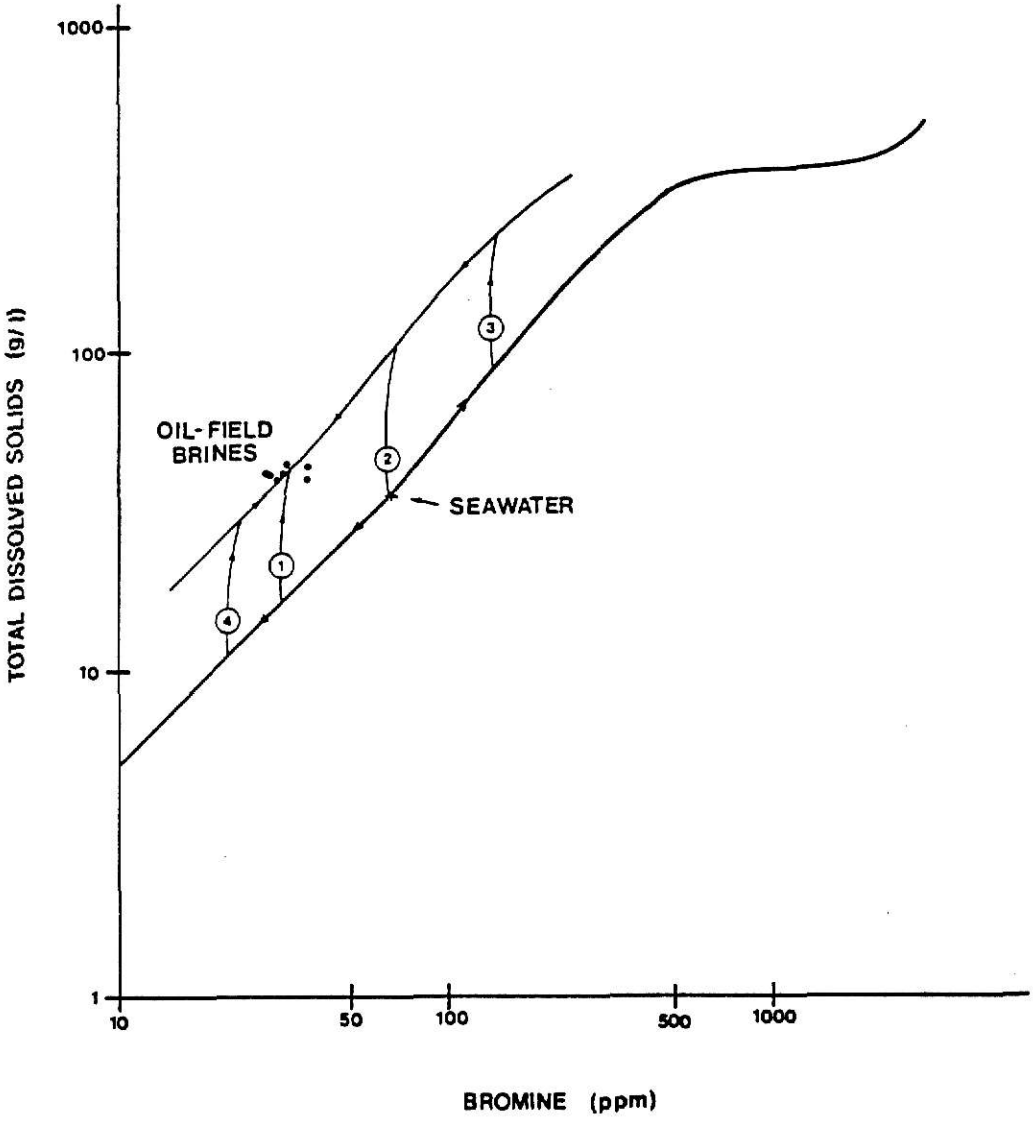

Figure 11. Evolutionary paths by which the oil-field brines from Bindley field, Hodgeman County, Kansas, could have formed from seawater (modified after Rittenhouse, 1967).

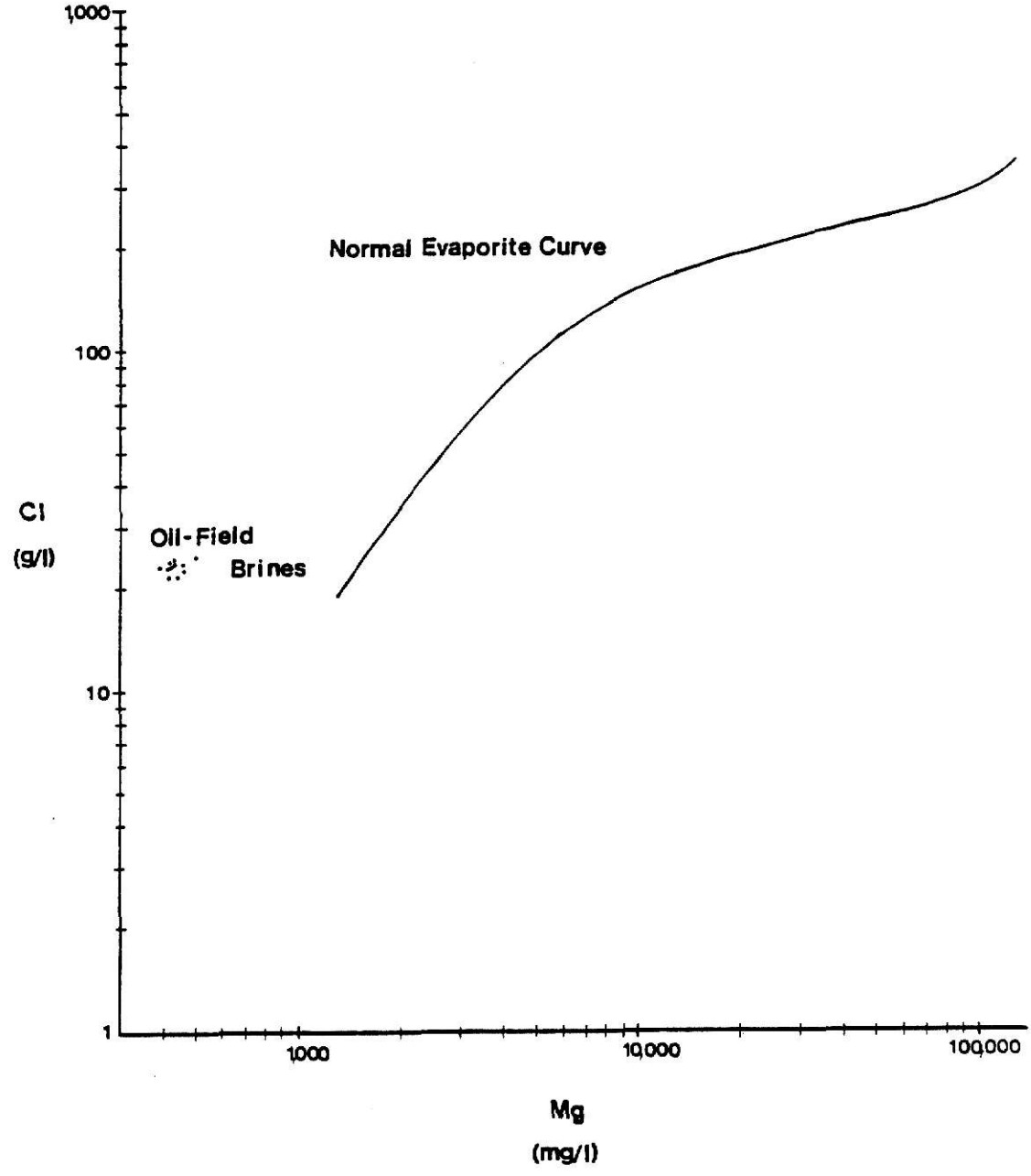

Figure 12. Comparison of the Mg concentrations of oil-field brines from Bindley field, Hodgeman County, Kansas, with evaporating seawater.

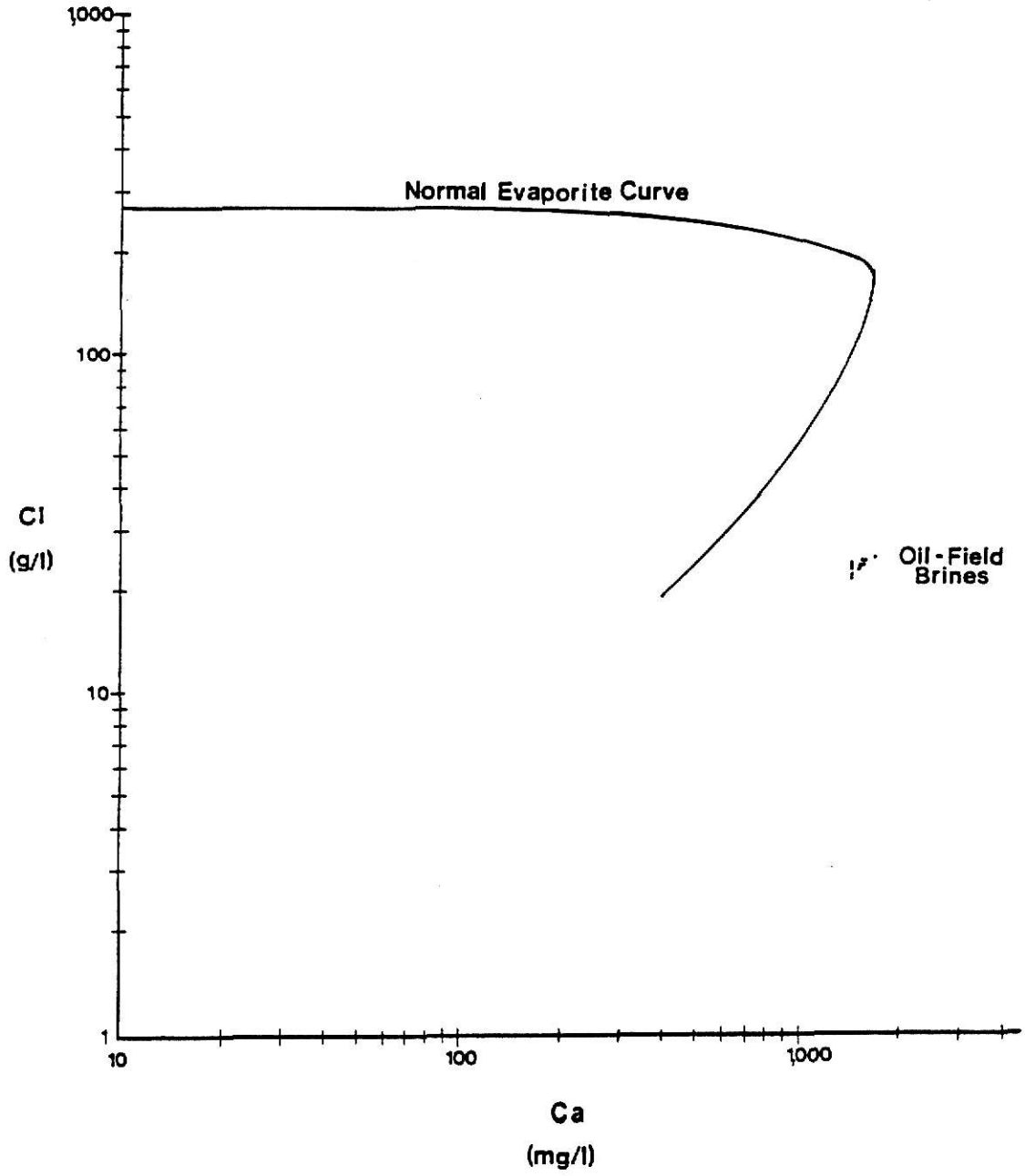

Figure 13. Comparison of the Ca concentrations of oil-field brines from Bindley field, Hodgeman County, Kansas, with evaporating seawater.

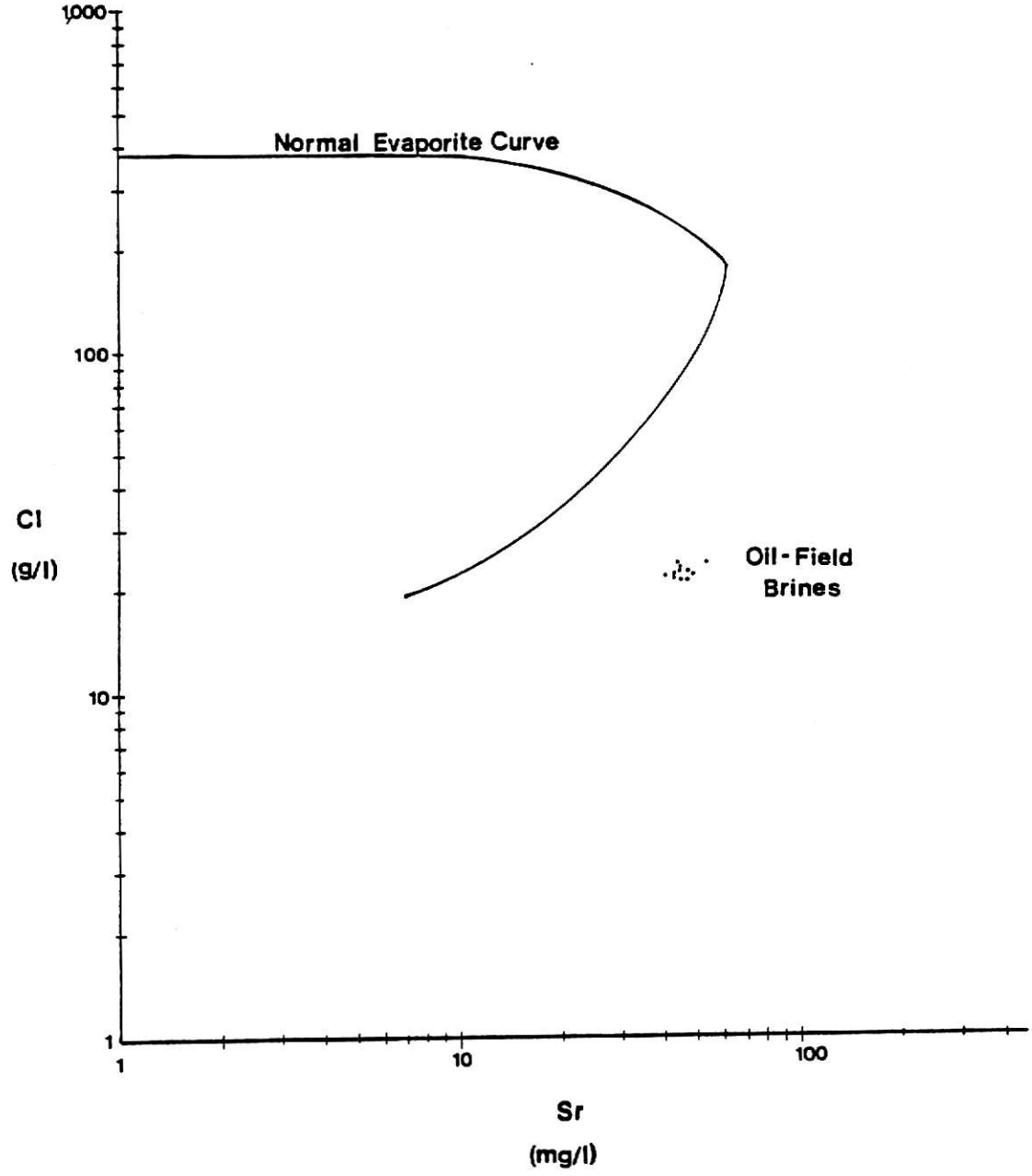

Figure 14. Comparison of the Sr concentrations of oil-field brines from Bindley field, Hodgeman County, Kansas, with evaporating seawater.

Alternately, Collins (1975) suggested that chloritization of smectite or degraded illite may account for the Mg depletion and Ca and Sr enrichment of brines. As chlorite is absent or present in small amounts (<2 percent) in the clay fraction of the interbedded shale of the carbonate reservoir rock, at least the chloritization of the reservoir rocks is not a significant factor controlling the observed chemical trend.

Ultrafiltration through clay-shale membranes may also explain the relative trend of Ca, Sr, and Mg concentrations of Bindley field waters. Natural clay-shales behave as non-ideal membranes. The membrane property arises from the negatively charged outer surface of the clay minerals. The negative electrical field in the pore volume of clay particles will cause repulsion of the incoming anions. Thus, the movement of water through the membrane will cause the salinity of the out-flowing water to be less than the incoming water (DeSitter, 1947; McKelvey and Milne, 1962; Kharaka and Berry, 1974; Kharaka and Smalley, 1976). Clay-shale membrane-filtered waters will be characterized by the following decreasing order of divalent cation retardation: Sr>Ca>Mg. The enrichment ratios (concentration of an element in the water divided by the concentration of the element in seawater) of Mg, Ca, and Sr for the oil-field brines from Bindley field are 0.3, 3.8, and 6.0, respectively. The sequence of relative order of enrichment is Sr>Ca>Mg, which indicates that the waters are being, or have been, membrane concentrated rather than membrane-filtered.

As discussed in the preceding paragraphs, dolomitization and

filtration by clay-shale membranes can account for the observed Ca and Sr enrichments and Mg depletions in the oil-field brines from Bindley field. Strontium isotopic data that will be discussed later, show that dolomitization could not have caused the Ca, Sr, and Mg compositions of the brines. As the Sr isotopic data do not impose any constraint on the membrane filtration, this process is likely the one responsible for developing the observed Ca, Sr, and Mg trends in the oil-field brines.

Monovalent Cations.--The chemical data show that in the brines Rb and Li are enriched and K is slightly depleted with respect to the normal evaporite curve (Figs. 15-17). This pattern of relative concentration among monovalent cations has been reported in studies of other subsurface water (Collins, 1975). Collins (1975) considered the depletion of K in oil-field water to have occurred during diagenesis as K is preferentially absorbed by associated sediments, especially by ion-exchange with illitic clay minerals. The Warsaw Limestone in Bindley field contains abundant illitic shale, so the K depletion of the brines may be related to ion-exchange with the shale. However, the depletion of K by illitic adsorption is difficult to explain when the Rb enrichment of the brines is considered. The uptake of K by clay minerals is accompanied by a concomitant uptake of Rb. The clay minerals, however, preferentially adsorb Rb over K (Collins, 1975). Thus the adsorption by clay minerals will result in a greater depletion of Rb than K in the water. Because the oil-field brines are enriched in Rb and depleted in K

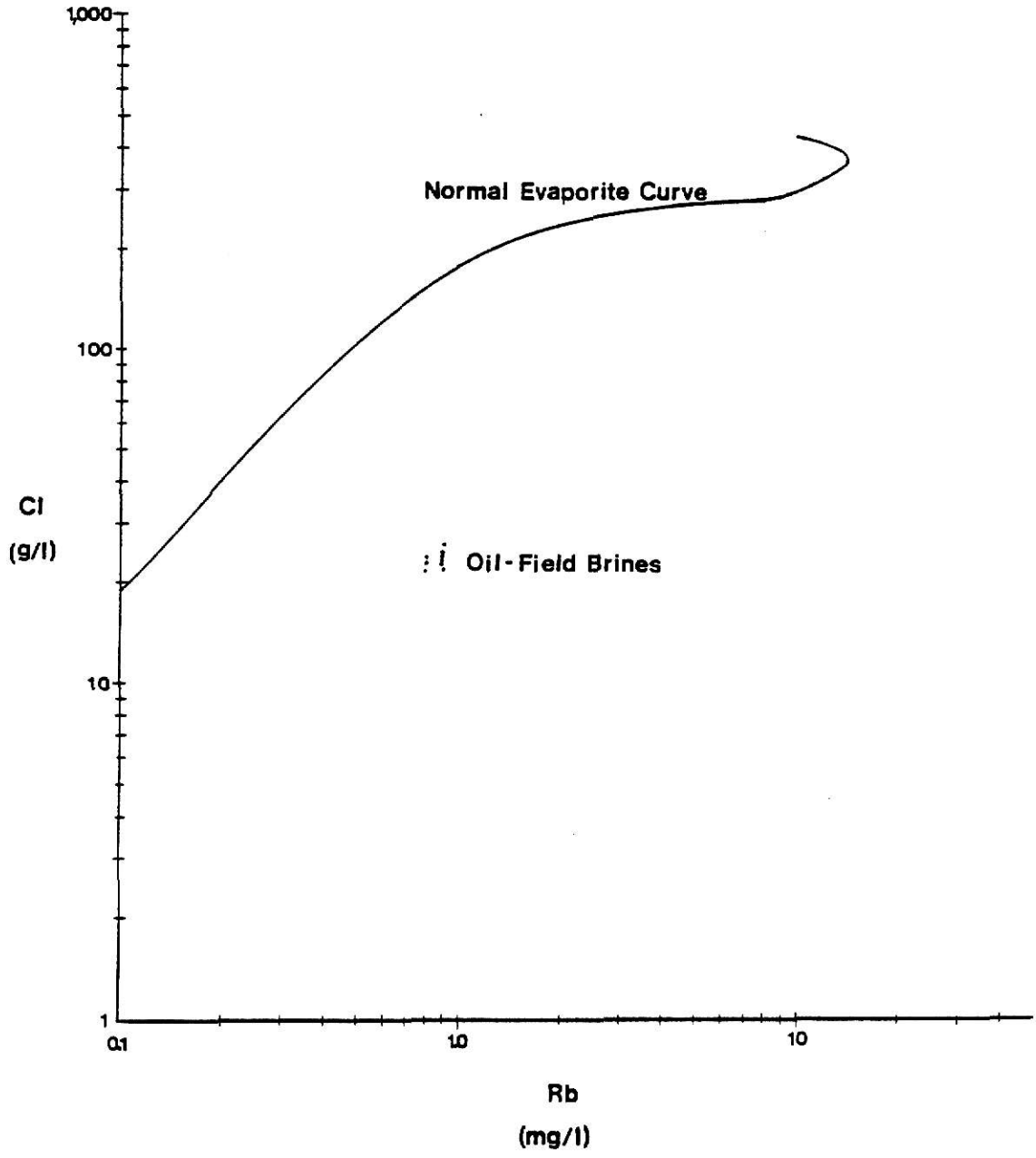

Figure 15. Comparison of the Rb concentrations of oil-field brines from Bindley field, Hodgeman County, Kansas, with evaporating seawater.

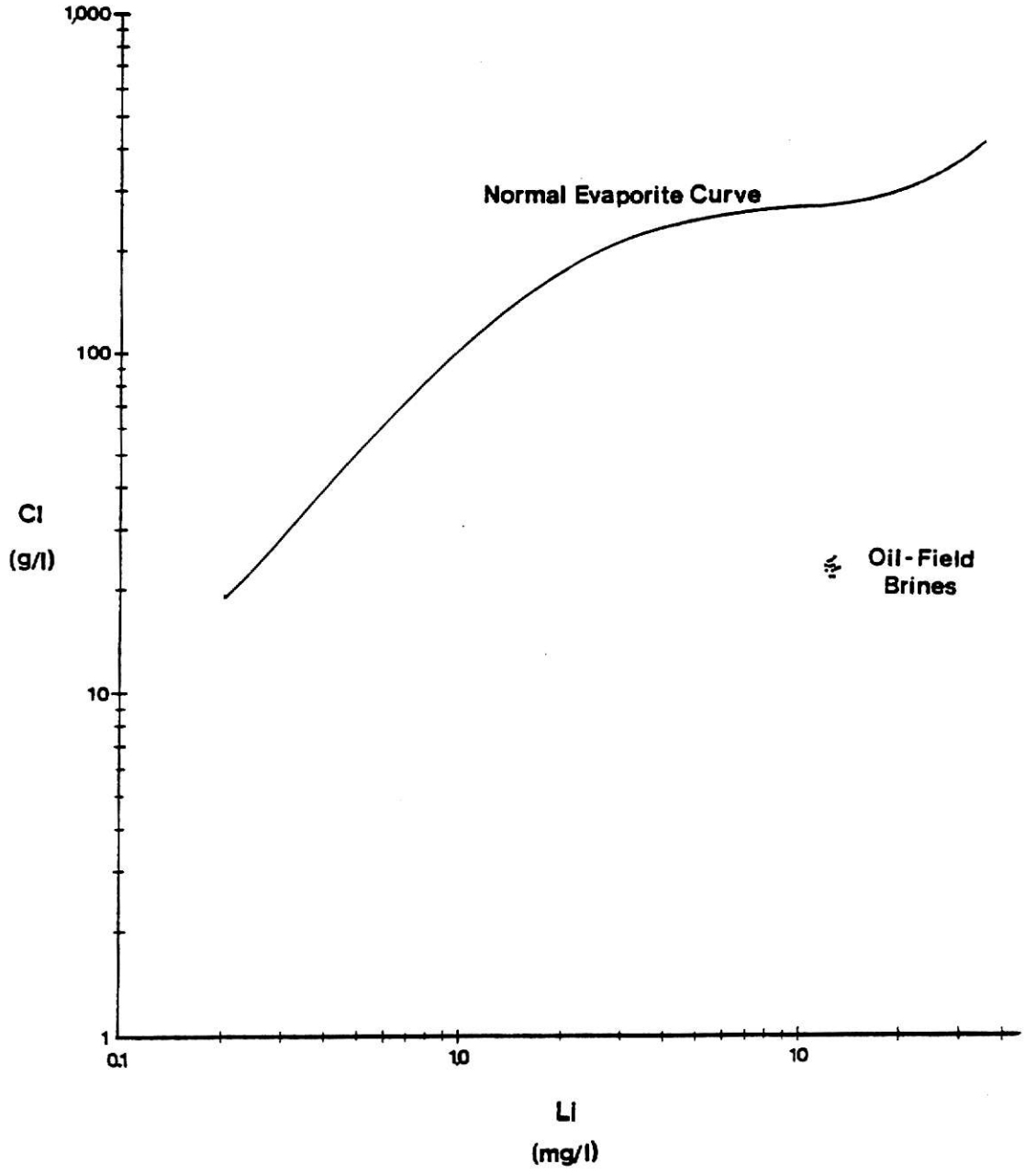

Figure 16. Comparison of the Li concentrations of oil-field brines from Bindley field, Hodgeman County, Kansas, with evaporating seawater.

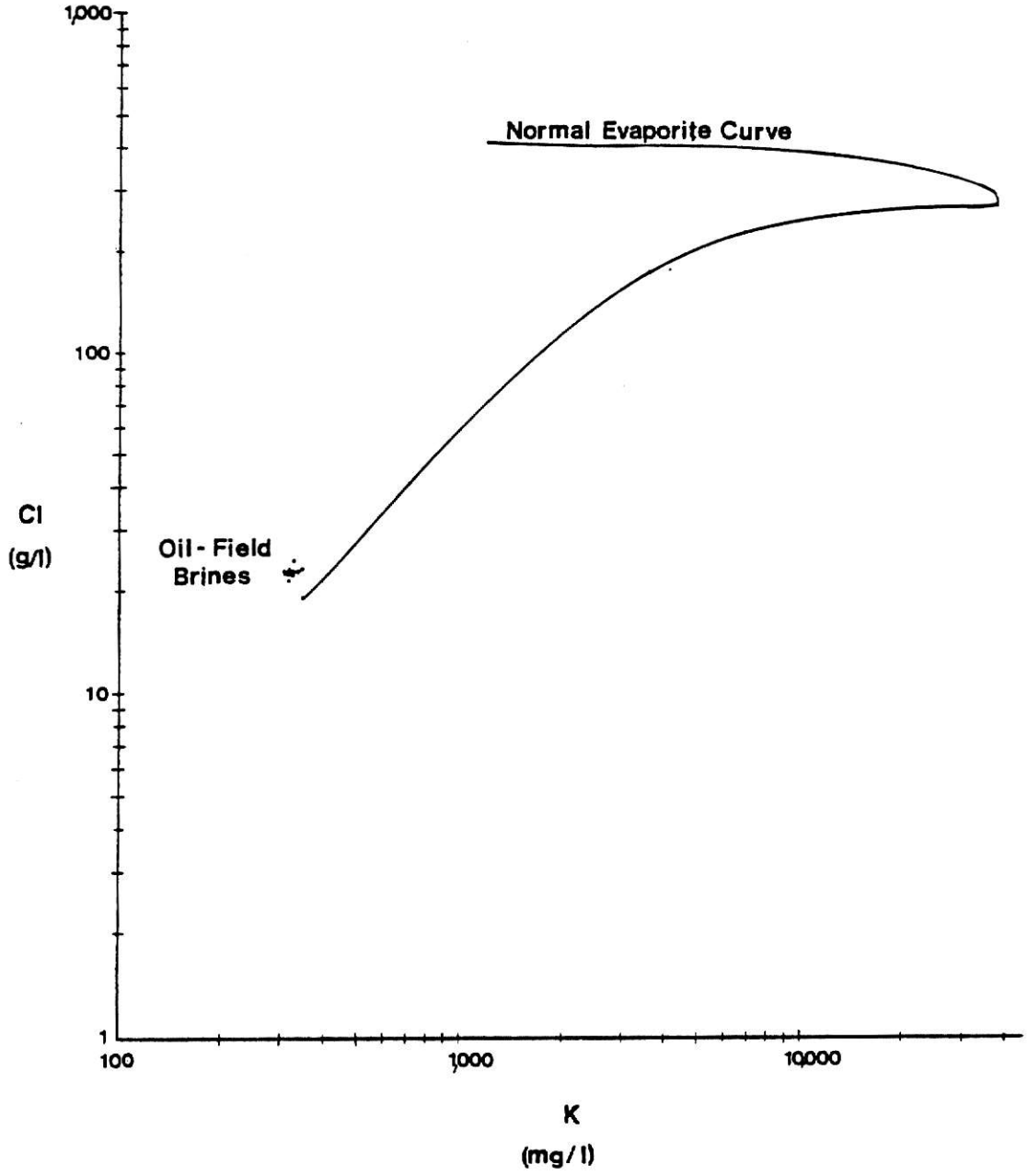

Figure 17. Comparison of the K concentrations of oil-field brines from Bindley field, Hodgeman County, Kansas, with evaporating seawater.

relative to a seawater, adsorption by clay minerals does not appear to be a major factor controlling the concentrations of K and Rb in the oil-field brines.

Potassium is a major constituent in potash feldspar, thus the formation of authigenic feldspar may cause a depletion of K in water from which the mineral formed. For the lack of complete chemical data, such as Al and SiO_2 contents in brines, the formation of K-feldspar from the brines cannot be established. The K/Rb ratios of the waters could have been influenced by the formation of feldspar. Unfortunately, the partitioning factor of K/Rb between the K-feldspar and the water in equilibrium with the solid in a sedimentary environment is not known. Thus, any role of feldspar formation governing the composition of the oil-field brines cannot be determined.

The K/Rb ratios of the oil-field brines range between 356 and 437; seawater K/Rb ratio is 3,500 and river water K/Rb ratio is 1,500. A simple mixture of the waters will not generate the K/Rb values of the brines. An extensive reaction of a seawater with silicate rocks and minerals, which make up K/Rb crustal materials having an average K/Rb ratio of 250, can generate the observed K/Rb ratios of the brines.

Potassium and rubidium data on different mineral phases that form from evaporation of seawater are sparse. In a geochemical study of Permian evaporite deposits of Kansas, A. Clayton (personal communication, 1982) observed that carbonates and sulfates have K/Rb ratios between 40 and 250 and chlorides have K/Rb ratios between 200 and 900.

Reactions between evaporite minerals and seawater or fresh water can also result in K/Rb ratios similar to those of the oil-field brines.

The enrichment of Rb and depletion of K relative to seawater at equivalent chloride levels can also be explained by filtration of seawater through clay-shale membrane. The ion retardation sequence for the alkali elements is Rb > K > Na > Li (Kharaka and Berry, 1974). According to this sequence, the oil-field brines represent membrane-concentrated water, which would also result in increased TDS content.

In the preceding discussion of the K and Rb contents of the oil-field waters, these elemental compositions have been attributed to dissolution of evaporite minerals and silicates by a seawater and filtration of a seawater by clay-shale membranes. In view of the Sr and stable isotopic data that will be discussed later, the dissolution of evaporite minerals probably is not the major process controlling the K and Rb contents of the waters.

The concentration of Li (11.6 to 12.4 mg/l) in the oil-field brines is greater than Li in evaporated seawater at equivalent Cl levels. Even the most evaporated seawater whose Li content may be as high as 34 mg/l (Collins, 1975), when mixed with any less concentrated seawater or fresh water, cannot generate the observed Li-Cl relationship of the oil-field brines. The dissolution of halite beds, with Li contents generally between 1 to 2 ppm, also cannot account for the excess Li in the brines.

The enrichment ratio of Li is 60 and is greater than that for the other alkali elements. If the Li concentration is the result of

filtration by clay-shale membranes then, following the ion retardation sequence of alkali elements the waters would be the membrane-filtered water. The concept of a membrane-filtered water is contrary to the concept of membrane-concentrated water as suggested by the Rb and K contents. To be compatible with the idea of the membrane-concentrated water, excess Li must have been added to the waters. Selective expulsion of Li from clay minerals during ion-exchange or from the decomposition of Li-bearing silicate minerals, as suggested by Collins (1975), can supply the excess Li of the brines.

In summary, simple evaporation of seawater, mixing of seawater and meteoric water, or halite dissolution cannot account for the Li contents of the oil-field brines. Ion exchange with clay minerals and decomposition of Li-bearing silicate minerals may have had a major role in governing the observed distribution of Li in the brines.

The Na-Cl compositions of the waters lie close to the seawater evaporite curve, before the precipitation stage of gypsum (Fig. 18). The close proximity of the Na and Cl concentrations to the seawater evaporite curve is a chemical characteristic that is common to many oil-field waters (Collins, 1975). The Na and Cl enrichments, relative to normal seawater, in the oil-field brines from Bindley field can develop by concentration of seawater through evaporation, dilution of concentrated seawater by meteoric water, dissolution of halite beds, or filtration of water by clay-shale membranes.

The fact that Na and Cl of a vast majority of highly saline oil-field waters plot on, or close to, the evaporite curve is a strong

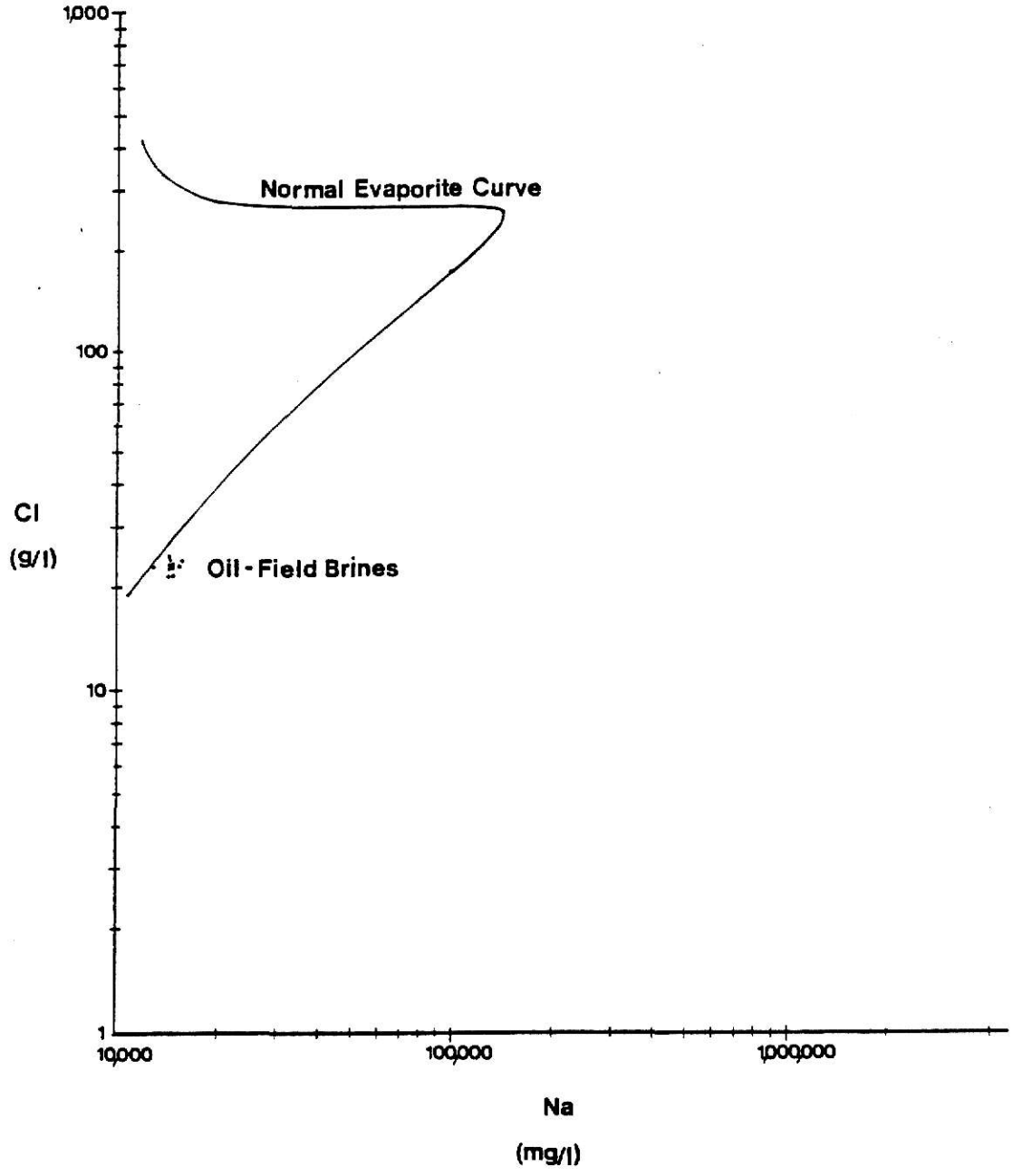

Figure 18. Comparison of the Na concentrations of oil-field brines from Bindley field, Hodgeman County, Kansas, with evaporating seawater.

indication that both Na and Cl are derived from the same source. Dissolution of Na-bearing silicates or ion exchange with Na-bearing clay minerals can alter the Na content of the waters without affecting the Cl composition. These reactions could be noted by a departure of the Na-Cl relationship from the Na-Cl evaporite curve. Possibly the effect of the release of Na to the waters by dissolution of silicate minerals may be partly compensated by neoformation of Na-bearing clay minerals that would remove Na from the waters. This coupled reaction of dissolution and precipitation could possibly produce such a small change in the Na content that the original Na/Cl ratios of the brines would remain nearly constant.

Halite crystals often adhere to the surface of mineral grains in shale and in carbonate rocks. As water moves through these rocks, the dissolution of halite will alter the Na and Cl composition of the water. The addition of these unknown quantities of Na and Cl may further mask the effects of the loss or gain of Na through clay-mineral reactions.

Filtration by clay-shale membranes can also account for the Na and Cl content in the oil-field brines. During filtration by the clay-shale membranes, Cl is concentrated more than Na on the inflow side of the membrane (Collins, 1975). The enrichment factors for Na and Cl in the brines from Bindley field are 0.81 and 0.83, respectively . The factors indicate that if a seawater had been filtered, the brines would represent the membrane-concentrated water. Similarly, the brines have been described as membrane-concentrated

waters on the basis of their divalent and other monovalent cations contents.

In summary, the Na-Cl relationship of the brines can be ascribed to: (1) dissolution of halite by meteoric water, seawater, or a mixture of these waters, (2) evaporation of seawater, (3) concentration of normal seawater by membrane filtration or (4) reactions between Na-bearing silicates and an evaporated seawater or a water that previously dissolved salt. Considering the stable isotopic data, which are discussed later, the evaporation of seawater is not a viable process for determining the observed Na-Cl relationship of the brines. Although the dissolution of halite can explain the Na-Cl relationship of the brines, it alone cannot explain the other chemical parameters.

Sulfate.--Except for two water samples, the SO_4 contents of Bindley field brines are less than the SO_4 content of seawater. Two water samples have SO_4 values very similar to the SO_4 content of seawater. Depletion of SO_4 could result from precipitation of SO_4 minerals, reduction of SO_4 by bacterial action, or filtration by clay-shale membranes.

Barite and celestite have low solubility products and could readily precipitate from solution causing a depletion of SO_4 in the residual water. Precipitation of gypsum can also cause depletion of SO_4. Because barium values were not determined and because the activity coefficients of Ca and SO_4 cannot be accurately determined

for such highly saline soluitons, the relative degrees of saturation of these brines with respect to barite, celestite, and gypsum cannot be calculated. Barite and celestite have not been identified in the reservoir rocks of Bindley field, therefore, formation of any barite and celestite within the Warsaw Limestone probably is not the cause of the SO_4 depletion of the oil-field brines. Ebanks et al., (1977) reported that discontinuous gypsum and anhydrite layers have been replaced by silica in the Warsaw Limestone in Bindley field. The dissolution of these SO_4 minerals would cause an increase in the SO_4 content of the brines rather than the observed depletion.

The reduction of SO_4 by bacterial action can also cause a depletion of SO_4 contents in brines. The equation which describes the reduction process is as follows:

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

The H_2S produced during this reaction could combine with Fe^{2+} in the water to precipitate as pyrite. Disseminated crystals of pyrite occur throughout the shale and dolomite in the reservoir unit in Bindley field. Sulfate reduction may thus be responsible for the depletion of SO_4 in the oil-field brines.

Filtration by clay-shale membrane can also be the cause for the depletion of SO_4 in waters. The passage of SO_4 is retarded compared to the passage of competing anions. The concentration of SO_4 will be relatively increased on the inflow side of the membrane compared to that on the outflow side. If Bindley field brines originated as seawater and later flowed through a clay-shale membrane,

then the SO_4-depleted water will represent the membrane filtered water. In contrast to this, all other chemical parameters have been earlier considered to be membrane-concentrated water. To be compatible with the concept of membrane-concentrated water, the incoming water must have had a SO_4 content sufficiently less than that of normal seawater so that the membrane-concentrated water remained low in SO_4.

The depletion of SO_4 content in the oil-field brines cannot be due to the formation or dissolution of SO_4 minerals within the present carbonate reservoir of Bindley field. However, it is possible that the brines became depleted through the formation or dissolution of SO_4 minerals before infiltrating the present reservoir. In order to have membrane filtration account for SO_4 content of the brines, the waters prior to filtration had to have been depleted in SO_4. Sufficient evidence in the form of pyrite exists to suggest that the reduction of SO_4 by bacterial action is a likely cause of the SO_4 depletion in the brines.

The overall chemical composition of the brines and most of the individual elemental concentrations can be explained by combinations of the following processes: (1) mixing of seawater and meteoric water, (2) dissolution of halite, (3) dissolution of alkali silicate minerals, (4) ion exchange with clay minerals, (5) filtration by clay-shale membranes and (6) sulfate reduction by bacterial action.

Oxygen - Deuterium Isotopic Composition

The present-day isotopic composition of ocean water is nearly uniform at $\delta D = 0$ per mil and $\delta^{18}O = 0$ per mil. The melting of all the ice sheets in the world would change the isotopic values of the oceans to $\delta D = -10$ per mil and $\delta^{18}O = -1$ per mil (SMOW) according to Taylor (1974). Studies on carbonate fossils have indicated that the oxygen isotopic composition of the ocean has not change at all since Mesozoic (Lowenstam, 1961). As the isotopic composition of the ocean controls the isotopic composition of all meteoric water, the position of the meteoric water line since the Mesozoic is thought to have remained within ± 1 per mil $^{18}O/^{16}O$ and ± 10 per mil for D/H of the present position. The isotopic composition of seawater probably has remained unchanged for even a longer period than the span of time since the Mesozoic. Taylor (1974), among many others, contended that the isotopic composition of the ocean water remained nearly constant through most of Phanerozoic time. Major disagreements exist as to the isotopic composition of seawater during the Precambrian. The isotopic composition of the oil-field brines from Bindley field will be compared to those of the present day seawater and the local meteoric water based on the premise that the $\delta^{18}O$ and δD values have remained nearly constant.

The oil-field brines have δD values ranging between -70.1 and -80.2 per mil and $\delta^{18}O$ values between -8.38 and -8.91 per mil relative to SMOW. If we assume that a fraction of these oil-field waters was of marine origin, and the assumption may be justified

on the basis that the rocks were deposited in a marine environment, then the depletion of D and ^{18}O can be explained by: (1) mixing or exchanging the seawater component with source(s) depleted in D and ^{18}O, (2) isotopic fractionation through filtration by clay-shale membrane, (3) neoformation of minerals, or (4) a combination of these factors in the subsurface.

The depletion of D and ^{18}O is especially remarkable in view of the high salinities of the oil-field brines (40,300 to 45,350 mg/l) compared to the salinity of normal seawater. Evaporation of seawater can account for the salinity but not the composition of the H and O isotopes of the brines. The evaporation will result in enrichment of both D and ^{18}O (Fig. 19). The dissolution of halite by seawater, meteoric water, or a mixture of the two waters can generate the high salinity of the brines, but the dissolution will not significantly change the isotopic composition of the brines.

Anhydrite beds are known to occur with salt beds in the vicinity of Bindley field (Merriam, 1963), and nodules of anhydrite occur within the reservoir rocks of the field (Ebanks et al., 1977). A process of formation of anhydrite is the dehydration of originally deposited gypsum. Water released during dehydration could have come into contact with salt beds and later have been released as highly saline waters. This may explain the salinity of the oil-field waters but not the isotopic composition of the waters. Sofer (1978) reported that the isotopic fractionation factors, α, for the gypsum-water system at about 40^{o} C. are $\alpha^{18}O = 1.004$ and $\alpha D = 0.980$.

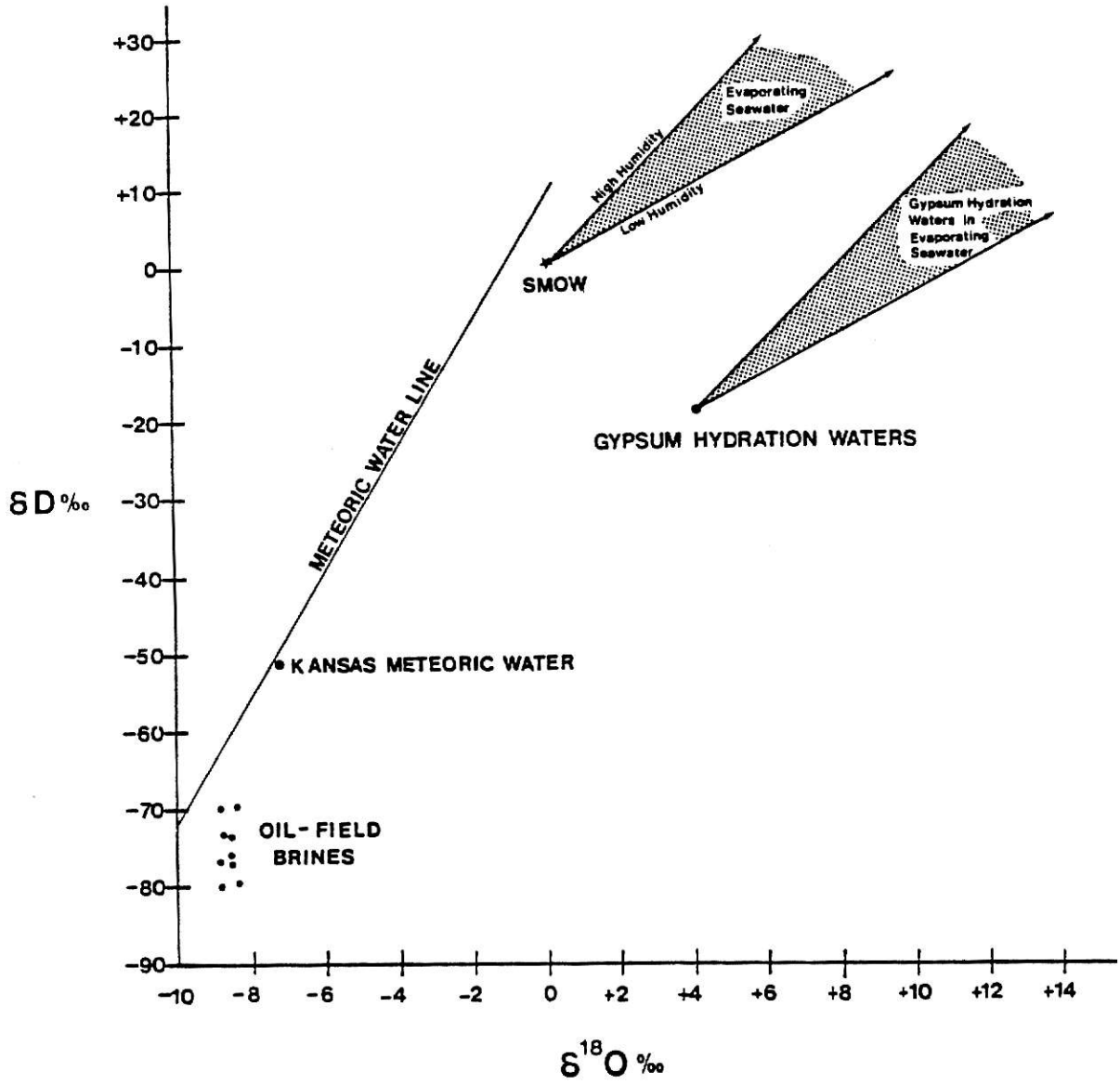

Figure 19. Oxygen and deuterium isotope shifts displayed during evaporation of normal seawater and seawater containing hydration waters from gypsum.

The water of crystallization of gypsum will be enriched in ^{18}O by about +40 per mil relative to seawater. Because of the $\delta^{18}O$ values of -8.38 to -8.91 per mil for the brines from Bindley field, it is highly unlikely that the hydration water in gypsum created the observed salinity.

Oil-field water have often been reported to be of meteoric origin. The original isotopic compositions are presumed to have been modified by reactions primarily with carbonate minerals (Clayton et al., 1966), by concentration through clay-shale membrane filtration (Graf et al., 1965: Kharaka and Berry, 1974), by mixing of the meteoric water with an assumed marine water (Degens et al., 1964), and by mixing of diagenetically modified seawater with fresh water (Hitchon and Friedman, 1969). In most cases, where meteoric water is considered, the isotopic composition of the meteoric water appears to be that of local atmospheric precipitation (Clayton et al., 1966; Kharaka and Berry, 1974). If the oil-field brines of Bindley field were largely meteoric in origin and were later isotopically modified by mixing with seawater or by reactions with the carbonate reservoir rocks, then the isotopic values that the water could attain would lie on a line that connects the local meteoric water with SMOW and with the carbonate rock values (Clayton et al., 1966; Kharaka and Berry, 1974).

Meteoric surface water from the Tuttle Creek Reservoir in Riley County, Kansas, was found to have a δD value of -52.3 per mil and $\delta^{18}O$ value of -7.38 per mil (SMOW). The δD and $\delta^{18}O$ isotopic

values of the Tuttle Creek reservoir water lie on the composition line of all meteoric waters verifying their meteoric nature. As δD and $\delta^{18}O$ values are dependent on the temperature of precipitation, the isotopic composition of meteoric waters show a negative correlation with both latitude and altitude (Dansgaard, 1961; Friedman et al., 1964). A review of the position of Kansas throughout the Phanerozoic reveals that the latitudinal position of Kansas never has been higher than it is at the present time and at several times has been lower than presently (Dott and Batten, 1971). Any shift of the position of Kansas toward the equator, would cause and enrichment of D and ^{18}O in the local meteoric water. Assuming there has been negligible change in the latitudinal position of Kansas, the isotopic composition of the present-day meteoric waters may be similar to those of the meteoric waters that formed in Kansas throughout most of the Phanerozoic. Therefore, the isotopic values of the present-day water could serve as a reasonable basis for the values of local meteoric water in the past. The stable isotopic values of the meteoric water from the vicinity of Bindley field are not known. As the latitudinal position of the Tuttle Creek Reservoir and Bindley field are relatively similar, the isotopic values of water from the Tuttle Creek Reservoir may be used to characterize the values of meteoric water from Bindley field. When compared to the local meteoric water, the oil-field brines are clearly more depleted in both D and ^{18}O. The brines are not simply meteoric in origin. The brines must have obtained their isotopic values through processes which generated more depleted

isotopic values than those of seawater and local meteoric water.

Isotopic compositions of oil-field waters can be influenced by varied diagenetic reactions in the subsurface. These reactions can make the identification of the source(s) of the water difficult. Despite these inherent difficulties, (Clayton et al., 1966) was able to recognize that reactions with carbonate minerals, or possibly with clay minerals, by meteoric water can account for the O and H isotopic compositions of waters from several sedimentary basins.

An 'oxygen-isotope shift' to the right of the meteoric water values, displayed by geothermal water (Craig, 1961) and by formation water (Clayton et al., 1966), was attributed to isotopic exchange of O between local meteoric water and carbonate rocks. As carbonate rocks have essentially no hydrogen and large amounts of oxygen, as compared to water, isotopic exchange between the meteoric water and carbonate minerals causes substantial changes in the O isotopic composition but not the H isotopic composition of the water. The range of the average $\delta^{18}O$ values for Paleozioic marine carbonate rocks is +18.0 to +28.0 per mil (SMOW). Thus, isotopic exchange between meteoric water and marine carbonate rocks would cause the $\delta^{18}O$ values of the water to become more enriched than they were originally. The oil-field brines from Bindley field are depleted in ^{18}O with respect to the local meteoric water, so the brines could not have developed through isotopic exchange between local meteoric water and the Mississippian carbonate rocks of Bindley field reservoir.

The importance of the clay mineral-water interactions as a

viable factor influencing the isotopic composition of subsurface water was not fully realized until the work of Savin and Epstein (1970), who reported that the hydroxyls in the clay-mineral structures are enriched in ^{18}O by about 26 per mil and depleted in D by 30 to 70 per mil relative to the ambient waters with which they are in equilibrium at surface temperatures. Although Savin and Epstein (1970) noted very little isotopic exchange between the clay minerals and the seawater, O'Neil and Kharaka (1976) found that extensive H isotopic exchange and negligible O isotopic exchange between clay minerals and water can occur at temperatures as low as 100^{o} C. The isotopic exchange is enhanced by small particle size and high temperatures.

Any attempt to explain the isotopic composition of the brines from Bindley field as a result of isotopic exchange between clay minerals and water requires some assumptions concerning the origin of clay minerals. Let the first assumption be that Upper Paleozoic rocks in central Kansas contained detrital clay minerals that had formed in higher latitudes at distances as far as 1000 km away from Bindley field. The clay minerals formed under weathering conditions in equilibrium with meteoric water at this high latitude would have δD's as low as -150 per mil but $\delta^{18}O$'s of about -1 per mil (SMOW). Now reactions of the meteoric water (δD = -52.3 per mil, $\delta^{18}O$ = -7.38 per mil) in the vicinity of Bindley field with these detrital clays, at least qualitatively, can explain the observed δD values (-70.1 to -80.2 per mil) but not the $\delta^{18}O$ values (-8.38 to -8.91 per mil) of the

brines from Bindley field. For lack of agreement with the O isotopic data, controlling factors other than exchange reactions between clay minerals and water must be sought.

Fractionation of H and O isotopes during filtration through clay-shale membranes can also account for isotopic variations in formation water (Coplen and Hanshaw, 1973). The fractionation during the filtration is greater for the H isotopes than for the O isotopes, thus the filtered water is depleted in both D and ^{18}O. The oil-field brines from Bindley field have δD and $\delta^{18}O$ values that are depleted relative to local meteoric water. If Bindley field brines were primarily meteoric in origin, then membrane filtration could have produced the observed stable isotopic values. However, this process of isotopic modification of the local meteoric water cannot explain the chemical composition and the salinity of the brines. Even the ultrafiltration of seawater or any mixture of seawater and local meteoric water will not account for the chemical data and the salinities of the waters, although a process is capable of generating the observed isotopic values. A plausible mechanism by which the observed stable isotopic data and the chemical data may be explained, would be mixing of two waters, one of which was membrane-filtered water, local meteoric or mixed in origin, and the other a membrane-concentrated water, possibly marine in origin.

Although it has been pointed out that the very high negative δD values of the brines from Bindley field could have been generated both by reactions with clay minerals and fractionation associated

with clay-shale membraned filtration, other processes can also account for lowered δD values in brines. The interlayer water of clay minerals is highly organized and thought to have an ice-like structure. O'Neil (1968) reported that ice has a δD value that is approximately 20 per mil higher than that of the water from which it forms. Therefore, neoformation of clay minerals with interlayer water having an ice-like structure could cause some measurable differences in the isotopic composition of the associated water. The difference would be appreciable only when the volume of the pore fluid is small and is comparable to the amount of water in the interlayer structure. Hence, the pore water freed from a highly compacted rock that contained the newly formed clay minerals could be depleted in D.

The depletion of D in the brines may be related to a process that probably had no effect on the O isotopic composition of the brines, as suggested by the poor correlation between the δD and $\delta^{18}O$ values (Fig. 20). Hitchon and Friedman (1969) suggested that the exchange of D between water and methane could account for changes in δD values. Methane derived from organic material is likely to be highly depleted in D, thus, exchange with methane would lower the δD values of the brines but would not affect the $\delta^{18}O$ values. Exchange with hydrogen sulfide may also cause a depletion of D in brines (Hitchon and Friedman, 1969). For lack of experimental data on the extent of fractionation of H between water and methane and between water and hydrogen sulfide, the precise role of these processes as a cause of depletion of D in the brines from Bindley field cannot be

fully evaluated.

In summary, the O and H isotopic composition of the oil-field brines from Bindley field can be accounted for plausibly by mixing of waters, one component of which had a meteoric origin and was membrane-filtered, and the other component a membrane-concentrated water possibly of seawater origin. Either or both of the waters may have had their stable isotopic compositions modified by isotopic exchange with clay minerals, neoformation of clay minerals, or even perhaps by methane or hydrogen sulfide reactions.

Strontium Isotopic Composition

Because seawater has often been considered as a source of salinity for the oil-field brines, Sr isotopic data could be useful in testing the role of seawater in the chemical evolution of these oil-field brines. The Sr isotopic ratios in seawater fluctuated within 0.7068 and 0.7090 throughout Phanerozoic time (Peterman et al., 1970; Burke et al., 1982). Because the brines from Bindley field have Sr isotopic ratios between 0.7231 and 0.7254, which are significantly greater than the marine isotopic values, marine waters cannot be the sole Sr component in the brines. If the original water was a seawater, the higher $^{87}Sr/^{86}Sr$ ratios of the brines indicate that the original water must have received Sr from a source that was enriched in ^{87}Sr. An evaporated seawater could achieve the observed salinities but not the enriched $^{87}Sr/^{86}Sr$ values, because evaporation does not affect the Sr isotopic ratios of waters.

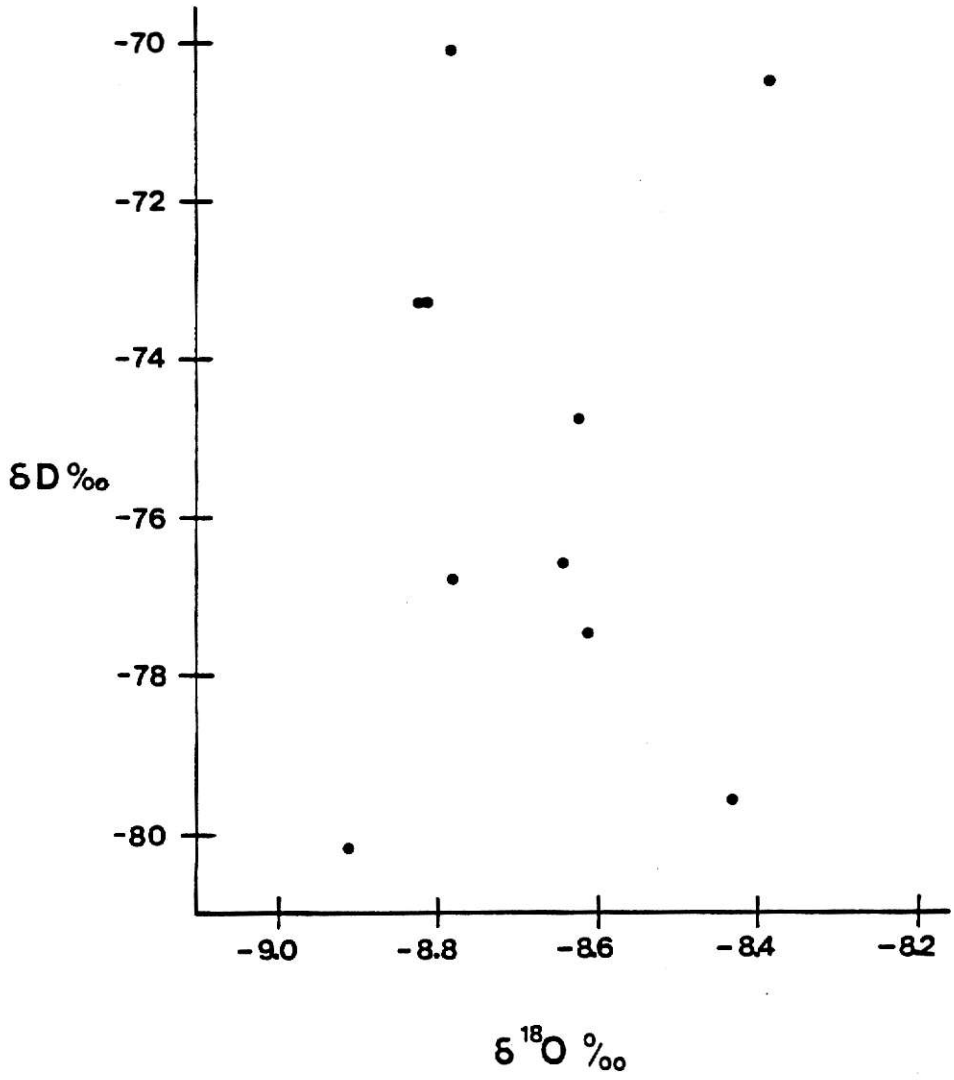

Figure 20. Scatter-plot of $\delta^{18}O$ versus δD of oil-field brines from Bindley field, Hodgeman County, Kansas.

Minerals that form by precipitation from seawater, such as carbonates, sulfates and halite, will inherit the Sr isotopic composition of the seawater at the time of their formation. The dissolution of evaporite minerals causes the release of Sr having marine $^{87}Sr/^{86}Sr$ values into the waters, hence the Sr isotopic ratios of waters of Bindley field could not have been derived primarily from the dissolution of the marine evaporite deposits.

The present Mississippian reservoir rocks are largely dolomitic carbonate rocks. The original calcium carbonate reef in Bindley field presumably was dolomitized during a pervasive migration of water. Had the present reservoir water been the dolomitizing fluid, the water would have developed an isotopic composition similar to that of the marine carbonate rocks. The reservoir water has much higher Sr isotopic ratios than that of marine carbonate rocks, which have the same isotopic composition as seawater.

Filtration by clay-shale membranes and exchange with clay minerals are intimately related processes that can affect the chemical characters of the oil-field brines. As water passes through clay-shale membranes, exchange of Sr between the water and clay mineral occurs and may change the isotopic composition of Sr in the water. The Warsaw Limestone of Bindley field contains beds of shale that are composed essentially of illite, in which Rb can be present as an interlayer cation. The decay of ^{87}Rb to ^{87}Sr will cause a rise in the $^{87}Sr/^{86}Sr$ ratios of the clay minerals in the interbedded shales. The $^{87}Sr/^{86}Sr$ ratio determined for clay minerals from a

shale sample from the Warsaw Limestone is 0.7950. Exchange between a low $^{87}Sr/^{86}Sr$ marine water and the high $^{87}Sr/^{86}Sr$-bearing clay minerals, such as those in the shale of the Warsaw Limestone, could account for the Sr isotopic composition of the oil-field brines.

Dissolution of potash feldspar, which has high $^{87}Sr/^{86}Sr$ ratios, by a water with low $^{87}Sr/^{86}Sr$ ratios, such as seawater, can also generate the observed isotopic values of the oil-field brines. The dissolution of feldspar will cause a rise not only in the Sr isotopic values but also a rise in the K content of the water. As Bindley field brines are depleted in K relative to seawater the dissolution of feldspar cannot be the source of the high $^{87}Sr/^{86}Sr$ ratios of the brines. Feldspars are known to selectively lose radiogenetic Sr when they come into contact with water. This selective leaching may account for the high $^{87}Sr/^{86}Sr$ ratios but again not the observed K depletion of the oil-field brines.

Infiltration of meteoric water into the carbonate reservoir that already contained water, essentially marine in origin, could also account for the Sr isotopic composition of the oil-field brines. Continental or meteoric water is often associated with silicate rocks and minerals that have high $^{87}Sr/^{86}Sr$ ratios. The meteoric water, therefore, has higher $^{87}Sr/^{86}Sr$ ratios than the marine water. If one of these meteoric waters infiltrated Bindley field carbonate reservoir, the mixing of the meteoric water with entrapped marine water could explain the high $^{87}Sr/^{86}Sr$ ratios of the oil-field brines. As will be shown later, this concept of a two-component mixing of Sr

isotopic composition between seawater and meteoric water alone is unlikely to explain the range in the isotopic compositions of the brines from Bindley field.

The similarity of the $^{87}Sr/^{86}Sr$ ratios of brines produced from one field cannot unambiguously establish a hydrologic continuity among the reservoirs of the field. However, dissimilarities of the Sr isotopic composition of brines reveals that a hydrologic discontinuity must exist among the reservoirs of those brines. An example of a discontinuity would be the one that exists between the reservoirs of the Everton 1 and Everton 2 wells. The brine from the adjacent Everton 1 and Everton 2 wells (Fig. 21) are produced from similar stratigraphic intervals and have $^{87}Sr/^{86}Sr$ ratios of 0.7253 and 0.7232, respectively. Although the reservoirs of these brines are spatially close, the dissimilarity of the isotopic values indicates that a hydrologic continuity does not exist between the two reservoirs. The $^{87}Sr/^{86}Sr$ ratios of the brines from Bindley field range from 0.7231 to 0.7254. The dissimilarities of the isotopic ratios indicate that several hydrologic discontinuities exist in Bindley field. An obvious correlation does not exist between the depth of the intervals from which the brines are produced and the $^{87}Sr/^{86}Sr$ ratios of the brines.

When the Sr isotopic ratios of the brines are compared to the location of the wells on a paleotopographic-structural map of the top of the Mississippian (Fig. 22), a relationship appears between the Sr isotopic values and their distribution within the bryozoan-mound

facies. The wells on the central portion of the bryozoan-mound facies of the Warsaw Limestone have similar $^{87}Sr/^{86}Sr$ ratios. The other wells, from which the brines having the lowest and highest $^{87}Sr/^{86}Sr$ ratios were produced, occur along the flanks of the mound or in separate extensions of the mound. The full meaning of this relationship between the Sr isotopic values of the brines and their distribution within the bryozoan-mound facies is not determined.

What is the cause of the variation of the Sr isotopic ratios among the brines of Bindley field? A mixing of Sr from two or more sources, each with differenct Sr isotopic compositions, can yield the observed values of the oil-field brines. Mixing of various Sr sources can be tested by comparing the $^{87}Sr/^{86}Sr$ ratios either to the Sr content or to the Cl content of the waters. A straight line plot of the $^{87}Sr/^{86}Sr$ versus 1/Sr will indicate that a two-component mixing of Sr sources has occurred (Faure, 1977). The comparison of these data from the waters of Bindley field (Fig. 23) form a scatter-plot that can be interpreted to mean that more than two sources of Sr have generated the Sr isotopic character of the brines.

A comparison of two parameters that are least affected by reactions in diagenetic environments could be used to test a hypothesis of mixing of waters from two chemically and isotopically different sources. Strontium isotopic ratios and Cl contents are two parameters that are not affected by mineral precipitation, unless the water salinity becomes so high as to cause precipitation of halite and thus reduce the Cl content. Hence, these two parameters of $^{87}Sr/^{86}Sr$ ratios and Cl

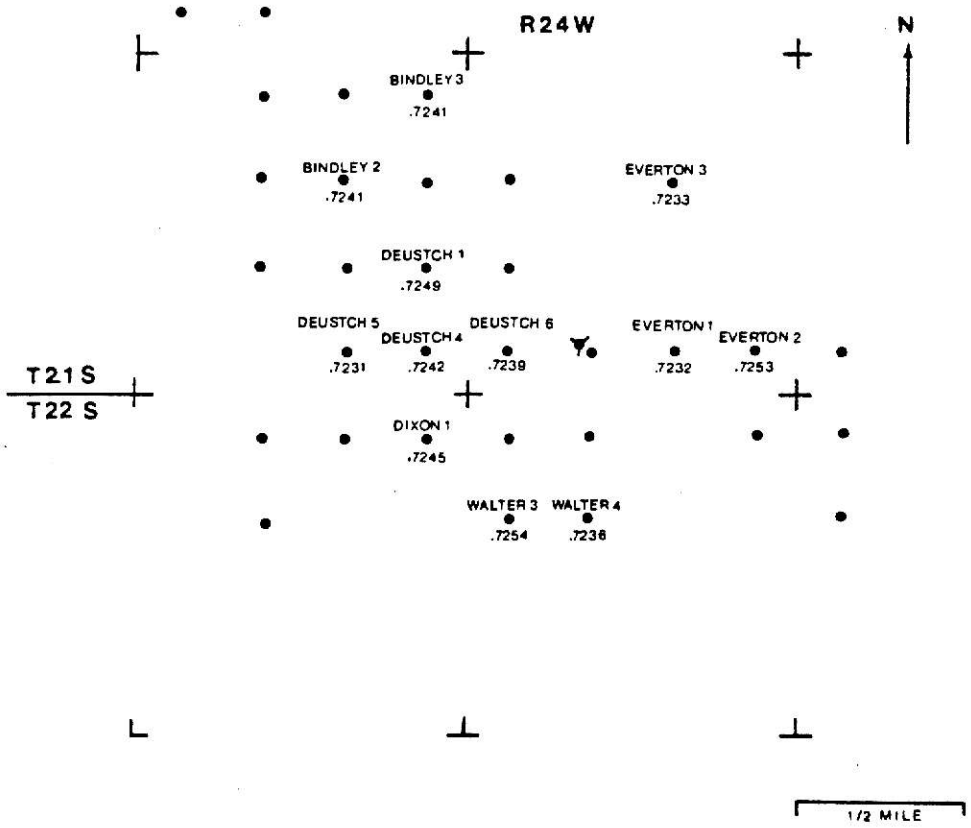

Figure 21. $^{87}Sr/^{86}Sr$ ratios of the oil-field brines collected from wells in Bindley field, Hodgeman County, Kansas.

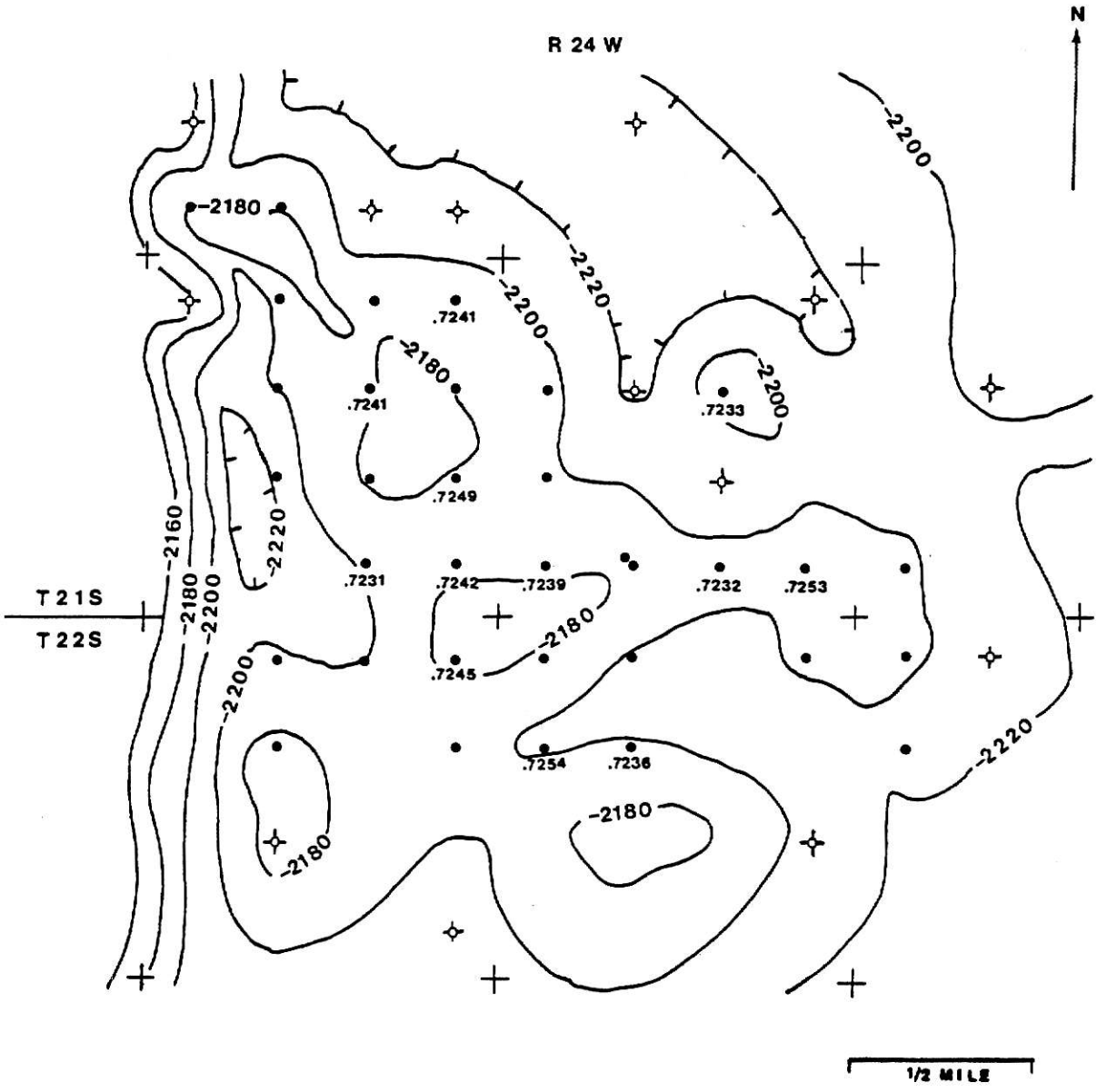

Figure 22. Paleotopographic-structural map of top of the Mississippian comparing the $^{87}Sr/^{86}Sr$ ratios of the oil-field brines to the location of wells in Bindley field, Hodgeman County, Kansas. Datum sea level. Contour interval 20 feet (contouring by Ebanks et al., 1977, p. 311).

content may serve as a means of testing the mixing between seawater and meteroric water. Meteoric waters have high $^{87}Sr/^{86}Sr$ ratios and low Cl values, whereas seawater has high Cl contents and low $^{87}Sr/^{86}Sr$ ratios. A mixture of these two waters would produce a negative slope between the two parameters. The comparison of $^{87}Sr/^{86}Sr$ versus Cl data from the oil-field brines of Bindley field (Fig. 24) results in a scatter plot, which indicates again that a simple mixing between meteoric water and seawater has not occurred.

Because a two-component mixing model is inadequate to explain the observed chemical and isotopic compositions of the oil-field brines, a simple mixing of three components may result in the observed values. An assumption will be made that when any water enters the Warsaw Limestone reservoir of Bindley field, the water will have a uniform Sr isotopic composition, as well as uniform Sr and Cl contents.

The three components that possibly mix within the reservoir need to be identified. In the first explanation to be considered, the infiltrating water retains its uniform composition until it mixes with waters in separate zones that have different $^{87}Sr/^{86}Sr$ ratios and Sr and Cl contents. As a carbonate unit does not have a uniform Sr isotopic composition (Ramakrishnan, 1983), separated waters within a reservoir may develop differenct $^{87}Sr/^{86}Sr$ ratios and Sr contents during local exchange between the waters and carbonate rocks. Also, the Sr and Cl contents of the waters in separate zones may be different because of various exchange of evaporation within each zone.

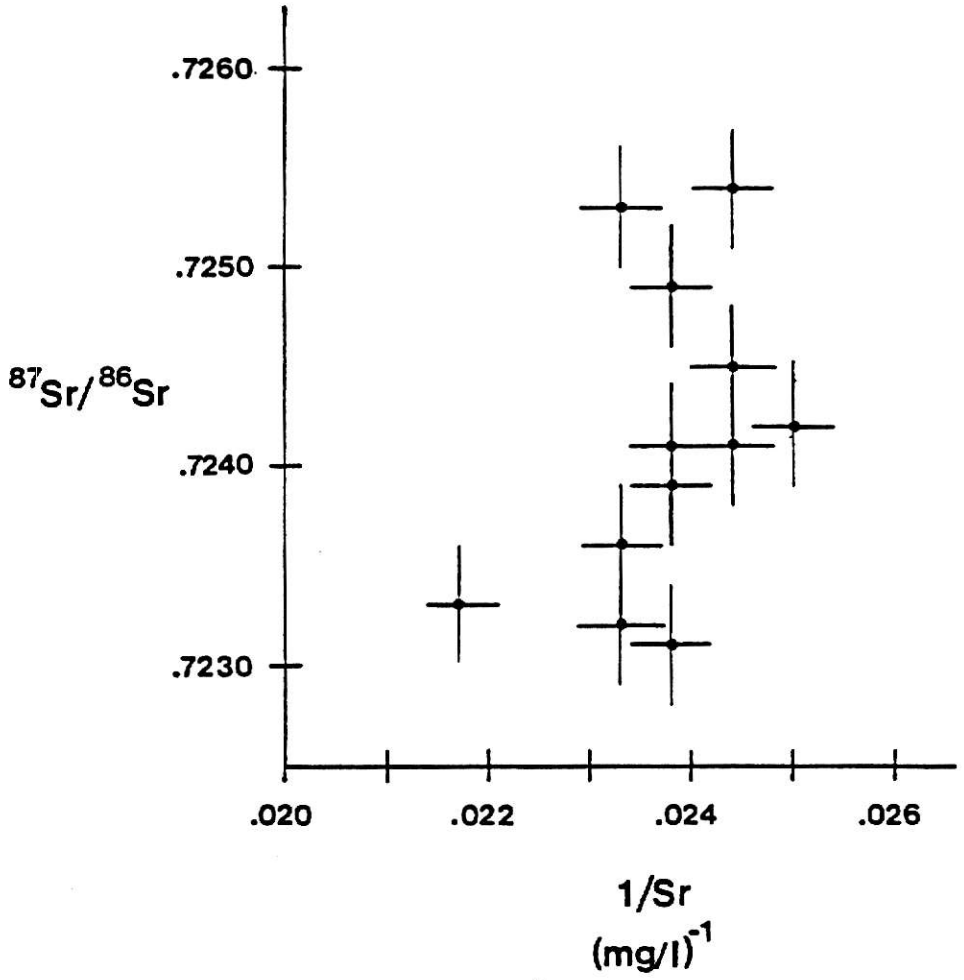

Figure 23. Scatter-plot of $^{87}Sr/^{86}Sr$ versus 1/Sr of oil-field brines from Bindley field, Hodgeman County, Kansas.

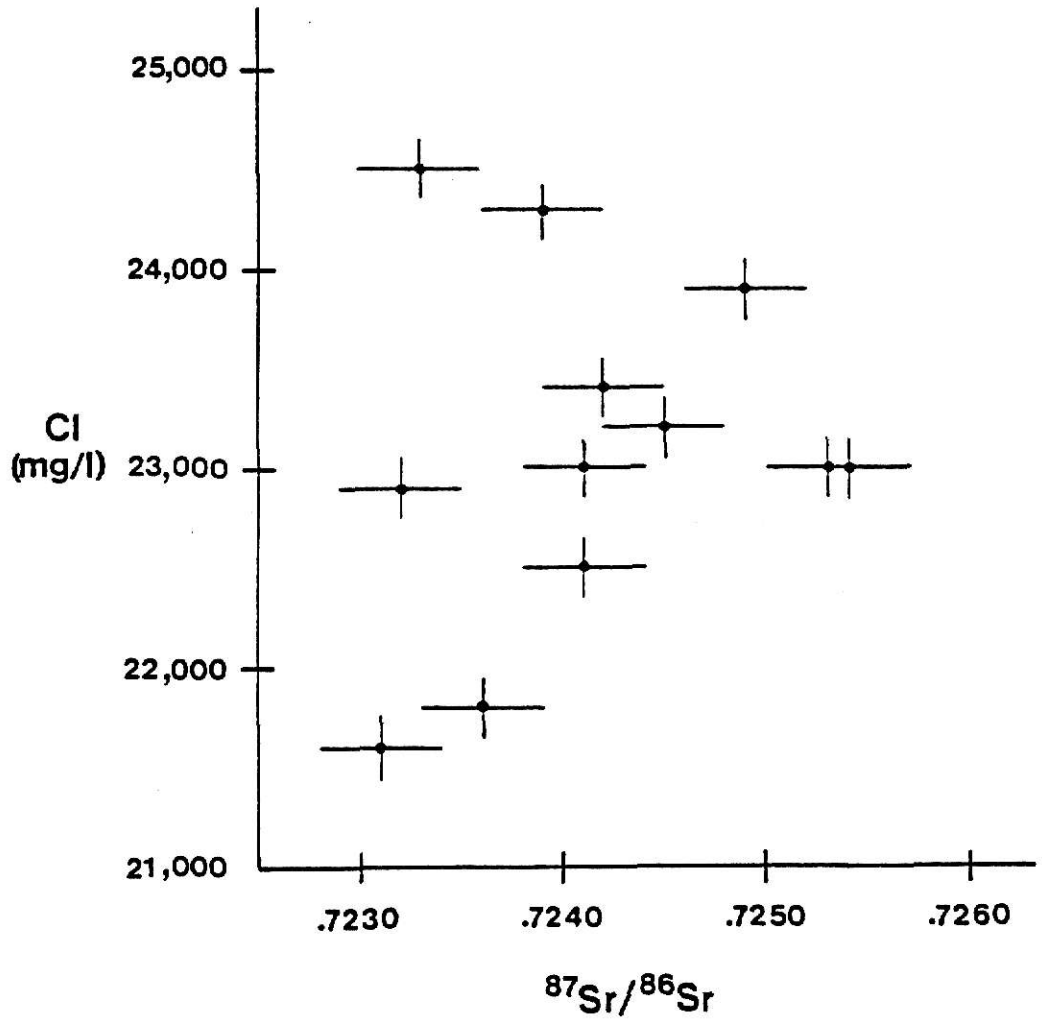

Figure 24. Scatter-plot of $^{87}Sr/^{86}Sr$ versus Cl of oil-field brines from Bindley field, Hodgeman County, Kansas.

In the second explanation, the reservoir water will have a uniform $^{87}Sr/^{86}Sr$ ratio and Sr and Cl compositions. The infiltrating water will develop different $^{87}Sr/^{86}Sr$ ratios and Sr contents as the water migrates along different paths through the carbonate reservoir before it mixes with the reservoir water.

Because both the $^{87}Sr/^{86}Sr$ versus 1/Sr and $^{87}Sr/^{86}Sr$ versus Cl data of Bindley field brines form scatter plots, a multiple-component mixing of Cl has occurred together with a multiple-component mixing of Sr. Although the Sr and $^{87}Sr/^{86}Sr$ compositions of the infiltrating water change through reactions with the carbonate reservoir rocks, the Cl content of the infiltrating water essentially remains unchanged. Thus the second interpretation involves a two-component mixing of Cl that is contrary to the $^{87}Sr/^{86}Sr$ versus Cl relationship. The first alternative, where the reservoir waters had different compositions prior to mixing with the infiltrating water, therefore best describes the condition that existed in Bindley field reservoir.

In summary, the Sr isotopic ratios of the oil-field brines can be explained by: (1) mixing of seawater with meteoric water followed by local interactions with the reservoir carbonate rocks, (2) seawater interacting with clay minerals followed by local interactions with the reservoir carbonate rocks or (3) meteoric water, possibly a diagenetically modified meteoric water, interacting with clay minerals followed by local interactions with the reservoir carbonate rocks.

SUMMARY

The 13 oil-field brine samples from the Mississippian carbonate reservoir of Bindley field are similar in chemical and stable isotopic compositions. Compared to evaporated seawater the brines are depleted in Mg, K, Br, and SO_4, are enriched in Ca, Sr, Rb, and Li and are similar in Na. The brines are identified as chloride-calcium waters. The brines, whose δD ranges from -70.1 to -80.2 per mil and $\delta^{18}O$ from -8.38 to -8.91 per mil (SMOW), are depleted in D and ^{18}O relative to local meteoric water. The $^{87}Sr/^{86}Sr$ ratios of the brines range from 0.7231 to 0.7254. The differences in these brine ratios are sufficient to suggest that hydrologic discontinuities exist between several pools within Bindley field.

The evaluation of chemical and isotopic data reveals that different processes can account for the observed compositions of the brines. The development of the TDS and Br contents have involved a mixing of seawater (or concentrated seawater) and meteoric water and the dissoluiton of halite. Ca, Sr, and Mg contents may have developed from dolomitization or filtration of seawater through clay-shale membranes. Membrane filtration of seawater can also account for the K and Rb contents of the brines as do extensive reactions with silicates by meteoric water, seawater or mixed waters. The Li content of the waters was not solely generated by membrane filtration of seawater. An additional source is needed to account for the enrichment of Li relative to other alkali elements. Ion

exchange with clay minerals, decomposition of Li-bearing silicates, or both, may have provided the excess Li. Any of the known processes, such as the evaporation of seawater, dissolution of halite crystals or beds, dissolution of Na-bearing silicates, neoformation of clay minerals, ion exchange with clay minerals, and mixing of meteoric water, may explain the Na contents of the brines from Bindley field. The only process that could have caused the depletion of SO_4 is the reduction of SO_4 by bacterial action. Membrane filtration and the precipitation of SO_4 minerals may have operated to modify further the SO_4 content.

The O and H isotopic compositions of the oil-field brines are best explained by the mixing of a membrane-filtered meteoric water with a membrane-concentrated marine water. The isotopic values of either, or both, of the waters may have been modified by isotopic exchange with clay minerals, neoformation of clay minerals, or reactions with methane or hydrogen sulfide. The processes involved in the development of Sr isotopic ratios are interactions between seawater, meteoric water, clay minerals, and the host carbonate rocks.

The overall chemistry of the brines has been influenced strongly by membrane filtration, mixing of meteoric and marine waters, and clay mineral reactions. Reactions between the carbonate reservoir rock and the brines had minimal influence on the composition of the brines.

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STRONTIUM ISOTOPIC GEOCHEMISTRY OF OIL-FIELD BRINES BINDLEY FIELD, HODGEMAN COUNTY, KANSAS

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Strontium, oxygen, and hydrogen isotopic determinations and chemical analyses were made on 13 oil-field brine samples that were produced from the Mississippian Warsaw Limestone in Bindley field in Hodgeman County, Kansas. The high TDS contents of the brines, which average 42,800 mg/l, result from the abundance of Na and Cl, which average 13,600 mg/l and 23,000 mg/l, respectively. The brines have an average Mg content of 430 mg/l, Ca of 1,520 mg/l, and Sr of 42 mg/l. The average alkali abundance are K = 325 mg/l, Rb = 0.9 mg/l, and Li = 12 mg/l. The SO_4, HCO_3, and Br contents of the brines average 2,290 mg/l, 58 mg/l, and 33 mg/l, respectively. In comparison to evaporated seawater, the oil-field brines are depleted in K, Mg, Br, and SO_4, are enriched in Ca, Sr, Rb, and Li, and are similar in Na. These brines are identified as chloride-calcium waters. The brines, whose δD ranges from -70.1 to -80.2 per mil and $\delta^{18}O$ from -8.38 to -8.91 per mil (SMOW), are depleted in D and ^{18}O relative to local meteoric water (δD = -52.3 per mil and $\delta^{18}O$ = -7.38 per mil, SMOW). The $^{87}Sr/^{86}Sr$ ratios of the brines range from 0.7231 to 0.7254. The differences in these ratios are sufficient to suggest the presence of hydrologic discontinuities among several pools within Bindley field.

The chemical and isotopic characters of the oil-field brines are attributable to the combined effects of physical and chemical processes. The evaluation of chemical and isotopic data helps eliminate the processes that are unimportant in the chemical and isotopic evolution of the brines. Dolomitization, evaporation of seawater,

and reactions with minerals of evaporite deposits (such as gypsum, halite, and anhydrite) are not considered to be the major processes governing the chemical and isotopic evolution of the brines. The carbonate reservoir rocks have had a minimal influence on the isotopic and chemical characters of the brines. The predominant processes that explain the chemical and isotopic compositions of the oil-field brines are the mixing of seawater and meteoric water, the interactions of the waters with clay minerals, and the filtration of the waters through clay-shale membranes. Bacterial activity may also have been an additional process involved in the depletion of SO_4 in the brines from the Bindley field.