

CHEMICAL AND ISOTOPIC CHARACTERISTICS OF BRINES FROM THREE
OIL- AND GAS-PRODUCING SANDSTONES IN EASTERN OHIO, WITH
APPLICATIONS TO THE GEOCHEMICAL TRACING OF BRINE SOURCES

By Kevin J. Breen, Clifford G. Angelo,
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CONVERSION FACTORS

Factors for converting inch-pound units used in this report to International System of units (SI) are listed below:

<u>Multiply inch-pound unit</u>	<u>By</u>	<u>To obtain SI units</u>
foot (ft)	0.3048	meter (m)
barrel (bbl), petroleum (1 bbl=42 gallons)	0.1590	cubic meter (m ³)

Conversions from units of millimoles per kilogram of brine to milligrams per kilogram of brine are made by multiplying mmol/kg units by the gram formula weight of the element of interest.

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ABSTRACT

Chemical and isotopic characteristics of selected inorganic constituents are reported for brines from the Berea Sandstone of Mississippian age, the "Clinton" sandstone (drillers term) in the Albion Sandstone of Silurian age, and the Rose Run sandstone (informal term) in the equivalent of the Knox Dolomite of Cambrian and Ordovician age in 24 counties in eastern Ohio.

Ionic concentrations of dissolved constituents in brine from the three sandstones generally fall in the following ranges: (in millimoles per kilogram of brine): Na, Cl \geq 1,000; $100 \geq$ Ca, Mg $<$ 1,000; $1 \geq$ K, Br, Sr, Li, Fe, SO₄ $<$ 100; Mn, Zn, Al, I, HCO₃, SiO₂ $<$ 1. Mean ionic concentrations of Ca, Mg, Na, Cl, K, SO₄, and Br, and mean values of density and dissolved solids are significantly different at the 95-percent confidence level in each sandstone. Only potassium has a unique concentration range in each sandstone (millimoles per kilogram): 0.3 - 12 (Berea), 13 - 57 ("Clinton"), and 81 - 92 (Rose Run).

For applications involving brine contamination, selected concentration ratios are identified as potential indicators for geochemical tracing of brines having some history of dilution. The K:Na ratios work best for identifying the source sandstone of an unidentified brine. These ranges are K:Na, 0.0002 - 0.0185 (Berea); 0.0073 - 0.0238 ("Clinton"); 0.0230 - 0.0462 (Rose Run). Other constituent ratios may prove useful for differentiating one brine from the other two. "Clinton" and Rose Run brines have no statistical difference in mean values for Ca:Mg, Na:Ca, Na:Cl, Mg:K, Ca:K, Cl:Ca, Mg:Br, and Na:Br. These ratios, in combination with K:Br and Cl:Br, may be used to identify Berea brines.

With respect to isotopic characteristics of hydrogen, oxygen, and sulfate sulfur, a moderate range of δ D (-48.0 to -13.5 permil) and $\delta^{18}\text{O}$ (-5.45 to -1.25 permil) indicate a meteoric water origin for the water matrix in Ohio brines. δ D and $\delta^{18}\text{O}$ values are not useful for differentiating brines from the three formations. The $\delta^{34}\text{S}$ (SO₄²⁻) values for Ohio brines range between +4.6 to +28.4 permil. The heaviest sulfate sulfur is in brine from the Cambrian and Ordovician Rose Run sandstone. A single Berea brine sample was determined to have the lightest $\delta^{34}\text{S}$ (SO₄²⁻) value. "Clinton" brines have $\delta^{34}\text{S}$ (SO₄²⁻) intermediate between those of the Rose Run and Berea sandstones. Sulfur isotopes may have utility for differentiating the isotopically heavy sulfate found in brines from the isotopically light sulfate found in oxidizing ground water.

INTRODUCTION

Background

The Paleozoic sedimentary rock succession that underlies Ohio includes several important oil- and gas-bearing units. Most of the currently productive petroleum reservoirs are located in the eastern half of the State (fig. 1).

Brines are commonly associated with oil and gas accumulation in sedimentary basins, and they constitute an unwanted byproduct in oil and gas recovery. Although the brines typically lie far below the zone of potable water, drilling for oil and gas creates the potential for contamination of aquifers both by upward leakage of brines due to improperly cased wells and by improper disposal methods.

Ohio's daily brine production has been estimated to be more than 38,000 barrels per day (Templeton, 1980). About one-fourth of this amount is returned to the subsurface by means of disposal wells, annular disposal, and by use in secondary recovery. Disposal of nearly 30,000 barrels per day is by "unknown" means, much of which is attributed to road spreading, illicit dumping, and evaporation ponding.

Knowledge of the inorganic constituents that characterize these brines is important for understanding their origin and evolution, for identifying the source formation during drilling, for investigating incidents of pollution by brines, and for developing disposal strategies. In many cases, the absolute variation of individual chemical constituents from one formation to another may be all that is required. However, for studies of aquifer and surface-water contamination by brines, which typically involves dilution and mixing of the brine with other waters, ratios of chemical constituents are more useful for brine identification.

Purpose and Scope

The purpose of this report is to characterize the inorganic chemical constituents in brines from three oil- and gas-producing sandstones in eastern Ohio: the Berea Sandstone of Mississippian age; the "Clinton" sandstone (driller's term) in the Albion Sandstone of Silurian age, and the Rose Run sandstone (informal term) at the top of the equivalent of the Knox Dolomite of Cambrian and Ordovician age. Emphasis is placed on identification of chemical constituents and constituent ratios that may be used as source-formation indicators or geochemical tracers in production or pollution problems. Stable-isotope geochemistry is incorporated to determine the origin of the water in oilfield and gasfield brines and to evaluate the feasibility of using selected stable-isotope ratios as geochemical tracers. It is beyond the scope of this report to discuss in detail the local and regional geologic and mineralogic variations within each formation, or how these variations operate to impart observed differences in brine geochemistry.

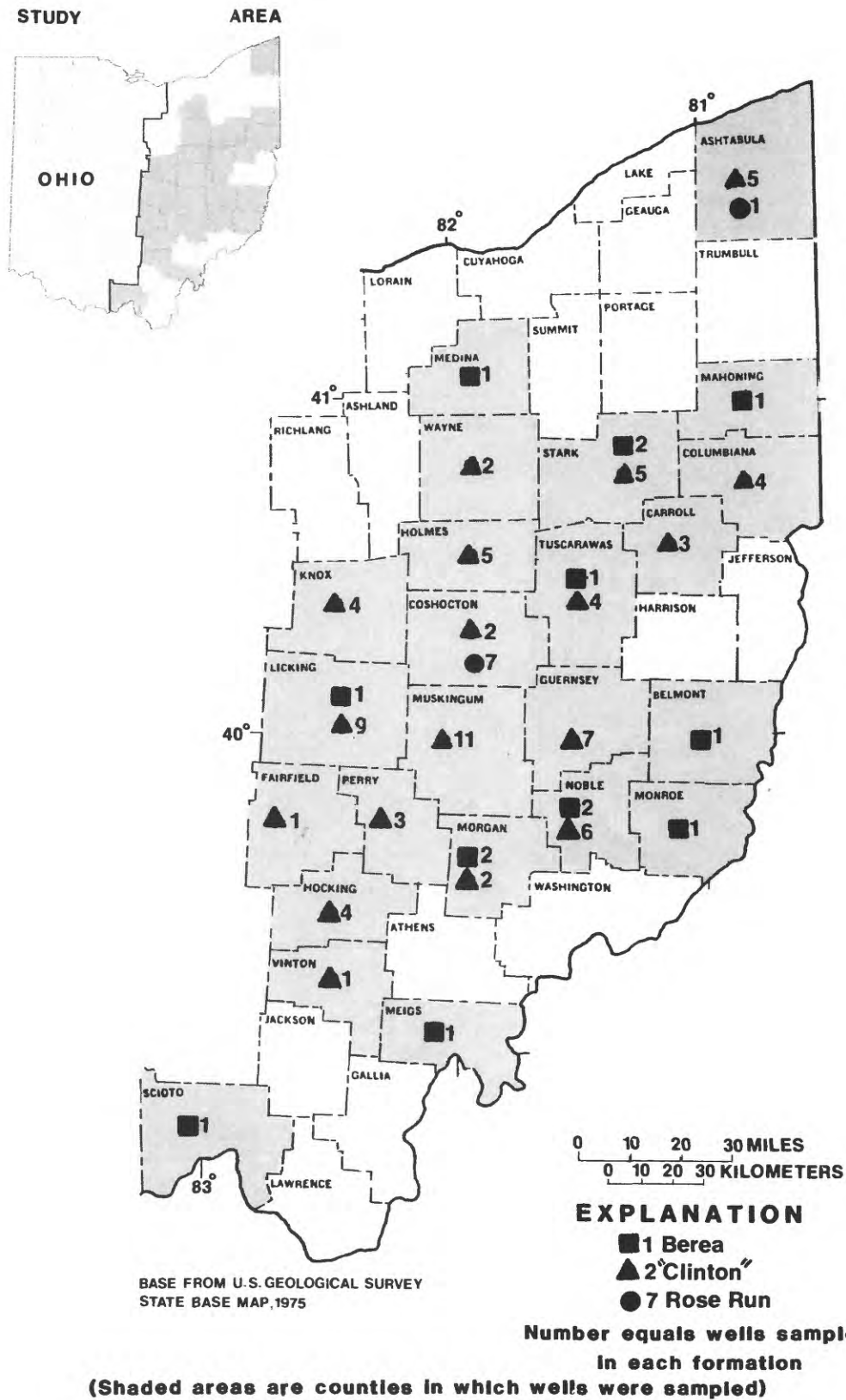


Figure 1.--Location of oil- and gas- producing area of eastern Ohio and distribution of wells sampled.

In this report "brine" is defined as natural water having a dissolved solids content of 35,000 milligrams per liter (mg/L) or more; in Ohio, such natural waters are associated with, though not limited to, oil and gas reservoirs.

Data on the Berea Sandstone compiled by Stout and others (1932) and "Clinton" analyses reported by Stith (1979) were supplemented by analyses of 10 samples of Berea and "Clinton" brines collected for this study. Eight additional samples were collected from wells producing from the Rose Run sandstone. The Rose Run data are the first chemical analyses to be reported since Lamborn (1952) for brine in oil- and gas-producing strata of Cambrian and Ordovician age in Ohio.

Location of Study Area

The study area encompasses approximately the eastern third of Ohio (fig. 1), and is based on regional boundaries established by the Ohio Department of Natural Resources, Division of Oil and Gas. Wells completed in the study area account for 99 percent of Ohio's oil and gas production.

Overview of Stratigraphy and Geology of the Sandstones Studied

The generalized stratigraphic chart for eastern Ohio (fig. 2) is based largely on usage of the Ohio Department of Natural Resources, Division of Geological Survey. Included are some of the names commonly used by oil and gas drillers in Ohio.

Where applicable, equivalent units recognized by the U.S. Geological Survey's Geologic Names Committee are shown in figure 2; thus, the rock units discussed in this report could be appropriately designated the Berea Sandstone, the Albion Sandstone, and the Knox equivalent. For the purposes of this report, however, driller's and informal nomenclature will be used for the latter two units, the "Clinton" sandstone (driller's term) and Rose Run sandstone (informal term), as these names are more compatible with most of the literature on these units.

The shallowest oil wells and gas wells sampled produce from the Berea Sandstone of Early Mississippian age. From central Ohio northward, the Berea yields sufficient quantities of potable water for domestic and small municipal systems. As the Berea is followed downdip to the southeast, its waters become more saline and oil and gas are produced in places.

The Berea Sandstone is characterized petrologically by quartz, although small percentages of chert, rock fragments, unaltered feldspar, and heavy minerals are present. Pettijohn and others (1972, p. 189, 215) refer to the Berea as a protoquartzite. Pepper and others (1954, p. 94) believe that much of the Berea is composed of sediments that have passed through one or more sedimentary cycles.

Sys-tem	Group	Formation or principal lithology of Ohio Geological Survey	Driller's terms (partial list)	Designation by U.S. Geological Survey
Per-mian	Dunkard	Sandstone Shale		Dunkard Group (includes Pennsylvanian)
Penn-sylvan-ian		Limestone Coals Clays		Undifferentiated
Missis-sippian		Maxville Ls Logan Fm Cuyahoga Fm Sunbury Sh Berea Ss Bedford Sh Cussewago Ss	Big Injun 1st Berea 2nd Berea	Maxville Ls Logan Fm Cuyahoga Fm Sunbury Sh Berea Ss Bedford Sh Cussewago Ss
Devon-ian		Shale Limestone Oriskany Ss	1st water	Oriskany Ss
Silurian	Bass Islands	Dolomite	Big Lime	Bass Islands Dol
	Salina	Dolomite		Salina Fm
	Lockport	Dolomite		Lockport equivalent
		Shale, lime-stone, dolomite		Clinton Fm
		Thorold Ss		Stray "Clinton"
		Grimsby Ss		Red or 1st "Clinton"
	Albion	Cabot Head Sh		White or 2nd "Clinton"
		Whirlpool Ss		Albion Ss
Ordovician		Queenston Sh Reedsville Sh	Red Medina	Queenston Sh
		Trenton Ls		Trenton Ls
	Black River	Limestone, dolomite		Black River Fm
	Chazy			Chazy equivalent
	Knox	Chepultepec Dol Copper Ridge Dol	Rose Run	Knox equivalent
Cambrian		Conasauga Sh Rome Fm Shady Dol Mount Simon Ss		Conasauga equivalent Rome equivalent Shady equivalent Mount Simon Ss
Pre-cam-brian		Igneous and metamorphic	Granite	

Modified from Calvert (1963) and Janssens (1973)

Figure 2.--Generalized stratigraphic chart for eastern Ohio (Dol, dolomite; Fm, formation; Ls, limestone; Sh, shale; SS, sandstone)

By far the most economically significant oil- and gas-producing unit in Ohio is the "Clinton" sandstone of Early Silurian age. In 1982, more than 3,000 wells (approximately 72 percent of all new wells in Ohio) were completed in the "Clinton" (Patchen and others, 1983, p. 1582). The name "Clinton" was first applied to a sandstone encountered while drilling in Fairfield County, Ohio; the name has been used by drillers ever since, and it has become well entrenched in the literature.

Typically, the driller's "Clinton" is composed of three sandstones more or less separated by intercalations of clay. These sandstones in descending order are the "Stray Clinton," the "Red (or First) Clinton," and the "White (or Second) Clinton" (fig. 2). Thin-section studies of the "Clinton" show it to be largely a fine-grained protoquartzite, although variations to subgraywacke and lithic graywacke and intercalations of shale have been described (Overby and Henniger, 1971, p. 187-94).

The oldest and deepest geologic unit sampled was the Rose Run sandstone, an informal unit of the Knox Dolomite (as described by Janssens, 1973). Because of the Knox unconformity, a regional erosional break, the age of the Rose Run is given as Cambrian and Ordovician because the boundary between the two systems cannot be placed precisely. The Rose Run became a target for exploration after a Holmes County gas well was completed in the unit in 1965. The Rose Run consists of mature sedimentary rock dominated by stable minerals. It is regarded as quartz arenite to subarkose (Atha, 1980).

Sampling Procedures for Chemical and Isotopic Analysis

Samples were collected from the bleeder valve on the wellhead whenever possible. Brine samples were impossible to obtain from the wellhead bleeder valve on wells that produce practically all oil; for such wells, brine samples were collected from the storage tank. Tank samples were collected only from storage tanks that received at least one barrel of brine per day. Of the 18 samples collected and analyzed in this study, 10 were bleeder-valve samples and 8 were from storage tanks.

Collection of samples from the wellhead and storage tanks ensured a sample that had not been diluted by rainfall or concentrated by open-air evaporation. Sampling from storage tanks does have a disadvantage in that certain physical properties and chemical constituents (pH, $\text{CO}_2(\text{aq})$, $\text{H}_2\text{S}(\text{aq})$, and others) may change significantly during storage, primarily due to the temperature and pressure differences between the storage tank and the host rock formation (J. R. Hatch, U.S. Geological Survey, written commun., 1984).

Brine was separated from the oil, filtered through Whatman No. 1 paper¹, then filtered through a 0.45-micrometer membrane to remove remaining traces of immiscible oil. All filtering was done by means of a U.S. Geological Survey modified filtration unit and compressed air. All samples for chemical and isotopic analyses were treated and preserved in compliance with established procedures and methods (Federal Interagency Work Groups, 1977).

All chemical analyses for dissolved constituents were performed at the U.S. Geological Survey's central laboratory at Doraville, Ga. Samples for hydrogen and oxygen isotopes were analyzed in the Survey's Isotope Fractionation Unit, Reston, Va. Analyses for the sulfur isotopes were done by private laboratories under the supervision of the Survey's central laboratory in Denver, Colo.

Acknowledgments

The authors are indebted to the Ohio Department of Natural Resources, Division of Oil and Gas, for their help in obtaining oilwell logs (to identify the producing formations), locating wells, and assisting in brine-sample collection. D. A. Stith (Ohio Division of Geological Survey) and J. R. Hatch (U.S. Geological Survey, Branch of Oil and Gas Resources) supplied information on sampling and analysis techniques for brines from the "Clinton." The authors also thank the oil and gas companies and landowners involved for their cooperation.

CHEMICAL CHARACTERISTICS

Concentrations of Dissolved Ionic Constituents

Two definitions of the term "brine" currently are being used in the literature: (1) An aqueous solution having a total dissolved solids concentration of 35,000 milligrams per liter (mg/L) or more, and (2) an aqueous solution having a total dissolved solids concentration of 100,000 mg/L or more. A number of samples included in this study were below 100,000 mg/L; thus, the 35,000-mg/L limit is adopted in this report as the concentration defining a brine. Because of the magnitude of these dissolved-solids concentrations and the corresponding increases in the density of the solutions, a weight basis for reporting concentrations of dissolved constituents is used in this report. Concentrations of dissolved ionic constituents are reported as millimoles per kilogram of brine (mmol/kg) instead of in the more common volumetric units of milligrams per liter and micrograms per liter. Concentrations listed in this report have been rounded to conform to the U.S. Geological Survey standards for significant figures.

¹Use of the trade name in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

The concentrations of dissolved ionic constituents present in oilfield and gasfield brines from the Berea, "Clinton", and Rose Run sandstones are generally categorized in the following table:

Descriptive term	Constituent	Concentration range (mmol/kg)
Dominant	Na, Cl	$\geq 1,000$
Major	Ca, Mg	≥ 100 to $< 1,000$
Minor	K, Br, Sr, Li ¹ , Fe, SO ₄	≥ 1 to < 100
Trace	Mn, Zn, Al, I, HCO ₃ , SiO ₂	< 1

¹ Based only on samples of "Clinton" brines.

Brines in the Berea Sandstone

Wells were sampled that produced oil and gas from the Berea Sandstone at depths ranging from 339 to 2,160 feet below land-surface datum. Tables 1 and 2 represent a compilation of chemical data for Berea brines collected by Stout and others (1932) and data collected for this study. The constituents selected for analysis represent the alkali metals (Li⁺, Na⁺, K⁺), alkaline earth metals (Mg²⁺, Ca²⁺, Sr²⁺), group III elements (Al³⁺), halide anions (Cl⁻, Br⁻, I⁻), sulfur and carbon anions (SO₄²⁻, HCO₃⁻), transition metals (Fe, Mn, Zn), silica (SiO₂), and hydrogen ion (pH). The aluminum, zinc, manganese, iron, and pH determinations are the first to be reported for brines in the Berea Sandstone. Strontium also has not previously been determined in Berea brines except for five analyses reported by Sunwall and Pushkar (1979).

The density and total dissolved-solids concentration for Berea brines are summarized in table 1 as well. The median density of the 14 Berea samples is 1.078 grams per milliliter (g/ml at 20°C). The concentration of total dissolved solids ranges from 57,500 to 144,000 milligrams per kilogram of brine (mg/kg) with a median value of 93,400 mg/kg. The dissolved-solids values correlate very poorly (14 percent) with sample depth. Oilfield brines are known to have increasing salinity with increasing depth (Dickey, 1969), however, this relationship cannot be established within the Berea Sandstone on the basis of available data.

The pH of Berea brines ranged from 5.9 to 6.7 based on three field determinations on samples collected for this study.

Table 1.--Description of oilfield and gasfield wells sampled in the Berea Sandstone,
and pH, density, and total dissolved-solids concentrations of brines

[A dash (--) indicates not determined]

County	Latitude	Longitude	Local number	Identification number used by Stout and others (1932)	Depth of sample (feet) ¹	Depth of well (feet) ¹	pH	Density (grams per milliliter at 20°C) ²	Dissolved solids, total (milligrams per kilogram of brine) ³
Belmont	--	--	9BBEL	211	1,740	1,740	--	1.080	108,000
Licking	400721	0821435	3BLIC	--	735	760	6.7	1.044	57,580
Mahoning	--	--	13BMAH	17	620	620	--	1.064	109,000
Medina	--	--	14BMED	33	460	463	--	1.063	80,300
Meigs	--	--	5BMEI	41	1,816	1,822	--	1.115	135,000
Monroe	--	--	8BMON	209	2,162	2,162	--	1.060	84,800
Morgan	393851	0815330	1BMOR	--	1,422	1,470	6.0	1.100	145,000
	393642	0815753	2BMOR	--	1,560	1,625	5.9	1.094	137,000
Noble	--	--	6BNOB	215	1,760	--	--	--	49,500
	--	--	7BNOB	214	1,592	--	--	--	59,000
Scioto	--	--	4BSCI	20	315	339	--	1.078	102,000
Stark	--	--	11BSTA	217	920	930	--	--	78,500
	--	--	12BSTA	218	835	840	--	--	82,800
Tuscarawas	--	--	10BTUS	222	880	886	--	1.073	105,000

¹ Below land surface

² Stout and others (1932) report density at 15°C.

³ Solids residue on evaporation at 180°C. Stout and others (1932) do not report temperature of the dissolved-solids determination.

Table 2.--Concentrations of selected dissolved constituents in brines from the Berea Sandstone

[All concentrations in millimoles per kilogram of brine. A dash (--) indicates not determined; nd indicates not detected]

County	Local number	Hydrogen sulfide	Calcium	Magnesium	Sodium	Potassium	Bicarbonate	Sulfate	Chloride	Bromide	Iodide	Silica, as SiO ₂	Aluminum	Iron (total)	Lithium	Manganese	Strontium	Zinc
Belmont	9BBEL*	--	210	80	1,300	--	.3	nd	1,900	--	--	1.2	--	--	--	--	--	--
Licking	3BLIC	nd	86	43	1,000	.3	2.0	.15	1,200	1.3	.04	.01	.01	.50	--	.01	1.6	.01
Mahoning	13BMAH*	--	210	100	1,300	.7	1.2	.6	1,900	5.5	--	.5	--	--	--	--	--	--
Medina	14BMED*	--	110	58	1,100	5	.3	.3	1,400	3.7	--	.1	--	--	--	--	nd	--
Meigs	5BMEI*	--	220	120	1,700	3	nd	nd	2,400	5.0	--	.2	--	--	--	--	nd	--
Monroe	8BMON*	--	170	46	1,100	--	.9	nd	1,500	--	--	--	--	--	--	--	--	--
Morgan	1BMOR	.04	270	120	2,100	.5	1.8	.06	2,800	20	.05	.15	.02	1.6	--	.01	4.1	.24
	2BMOR	.05	250	110	1,800	2.3	2.1	1.8	2,600	12	.04	.26	2.7	9.5	--	.35	4.1	.02
Noble	6BNOB* ⁺	--	65	33	650	12	5.6	nd	840	--	--	3.4	--	--	--	--	--	--
	7BNOB* ⁺	--	65	38	790	12	.8	nd	1,000	--	--	2.2	--	--	--	--	--	--
Scioto	4BSCI*	--	280	110	1,000	5	.3	.53	1,800	6.0	--	.3	--	--	--	--	--	--
Stark	11BSTA* ⁺	--	110	60	1,000	--	.9	.15	1,300	4.8	.05	.15	--	--	--	--	--	--
	12BSTA* ⁺	--	120	60	1,100	2.1	1.1	.09	1,200	2.0	.13	.2	--	.09	--	--	--	--
Tuscarawas	10BTUS*	--	180	100	1,300	--	--	--	1,800	3.1	.10	.3	--	--	--	--	--	--

* Brine analysis reported by Stout and others (1932)

⁺ Concentrations computed on a weight basis assuming density = 1.078g/mL.

Sodium and chloride are the dominant ions contributing to the observed levels of total dissolved solids. Sodium and chloride in Berea brines have median concentrations of 1,000 and 1,600 mmol/kg, respectively. However, chloride concentration has a range nearly twice that of sodium. The Na:Cl ratios are consistently less than 1.0 and have a median value of 0.74. Average sea water has a Na:Cl value close to 0.5 (Nordstrom and others, 1979).

Calcium and magnesium are major constituents of Berea brines, and make a combined contribution of nearly 10 percent of the total dissolved solids. The median Ca:Mg ratio equals 2.0, and is more than six times the value for average seawater (0.3).

Potassium, bromide, and iron are relatively abundant minor constituents that have concentrations in the range of 0.3 to 12 mmol/kg. Sulfate, bicarbonate, and iodide anions and the remaining cationic constituents occur in minor to trace amounts in brines from the Berea.

Brines in the "Clinton" Sandstone

Brines from the "Clinton" sandstone have been analyzed to a greater extent than brines from either the Berea or Rose Run sandstones due to the relative abundance of "Clinton" wells drilled in eastern Ohio. Brine analyses are reported for wells that produce from the "Clinton" at depths ranging from 2,500 to 5,885 feet below land-surface datum.

Seventy-eight analyses of "Clinton" brine, which are listed by county, appear in tables 3 and 4. These tables combine the data of Stith (1979) and data collected for this study. Thompson (1973) has reported analyses of 20 "Clinton" brines from Perry County, Ohio; those analyses include common constituents and the nickel, cadmium, cobalt, copper, lead, and mercury ions. Thompson's data are not included in this report because no density information was given to allow conversion from milligrams per liter to weight-based concentrations. Sunwall and Pushkar (1979) report analyses for strontium in eight "Clinton" brines from southeastern Ohio.

The density of "Clinton" brine ranges from 1.085 to 1.260 g/ml and has a median value of 1.180. The corresponding median concentration of total dissolved solids is 232,000 mg/kg. Ninety-five percent of the total dissolved solids are accounted for in the density values. The concentration of total dissolved solids correlates poorly (-31 percent) with sample depth as measured from a land-surface datum. Using Stith's (1979) data set referenced to a sea level datum, Parsons (1982) has also indicated an inverse relationship exists between total dissolved solids and sample depth within the "Clinton" sandstone. The tendency for increasing concentrations of total dissolved solids with increasing depth may only be justified for static systems (B. F. Jones, U.S. Geological Survey, written commun., 1984). The results for the "Clinton" may indicate a non-static hydrodynamic environment.

Table 3.--Description of oilfield and gasfield wells sampled in the "Clinton" sandstone, and pH, density, and total dissolved-solids concentrations of brines

[A dash (--) indicates not determined]

County	Latitude	Longitude	Local number	Field identification number used by Stith (1979)	Depth of sample (feet) ¹	Depth of well (feet) ¹	pH	Density (grams per milliliter at 20°C)	Dissolved solids, total (milligrams per kilogram of brine) ²
Ashtabula	413212	0804418	4CASH	--	3,845	3,996	6.0	1.167	221,000
	413642	0804640	5CASH	--	3,655	3,750	6.1	1.217	279,000
	414014	0805002	78CASH	97	3,124	3,462	--	1.137	177,000
	414136	0804404	43CASH	41	3,534	3,605	6.1 ^a	1.204	257,900
	414120	0804911	44CASH	42	3,337	3,420	4.7 ^a	1.195	244,200
Carroll	403845	0811537	29CCAR	27	5,268	5,360	5.6 ^a	1.196	249,000
	403744	0811445	30CCAR	28	5,363	5,451	6.2 ^a	1.188	239,000
	403517	0811431	31CCAR	29	5,470	5,561	5.7 ^a	1.195	247,000
Columbiana	405224	0810308	63CCOL	77	3,294	5,450	--	1.242	283,000
	405308	0810318	64CCOL	78	5,223	5,321	--	1.166	293,000
	404934	0810341	65CCOL	79	5,306	5,403	--	1.182	231,000
	405143	0810357	66CCOL	80	5,315	5,428	--	1.187	233,000
Coshocton	402554	0820858	39CCOS	37	3,370	3,395	4.8 ^a	1.232	279,000
	402438	0820947	40CCOS	38	3,260	3,288	5.3 ^a	1.229	282,000
Fairfield	394442	0822721	27CFAR	20	2,385	2,418	5.8 ^a	1.138	186,000

Table 3.--Description of oilfield and gasfield wells sampled in the "Clinton" sandstone,
and pH, density, and total dissolved-solids concentrations of brines--Continued

County	Latitude	Longitude	Local number	Field identification number used by Stith (1979)	Depth of sample (feet) ¹	Depth of well (feet) ¹	pH	Density (grams per milliliter at 20°C)	Dissolved solids, total (milligrams per kilogram of brine) ²
Guernsey	400529	0812331	3CGUR	--	5,700	5,879	5.3	1.166	217,000
	400534	0813801	61CGUR	62	4,974	4,999	--	1.130	176,700
	395238	0813608	45CGUR	46	5,400	5,482	5.6 ^a	1.183	236,000
	400342	0813353	46CGUR	47	4,965	5,052	6.2 ^a	1.172	221,000
	400351	0813438	47CGUR	48	4,938	5,125	6.5 ^a	1.122	161,000
	400335	0813750	48CGUR	49	4,942	5,029	6.1 ^a	1.167	215,000
	400540	0813824	49CGUR	50	4,889	4,980	6.2 ^a	1.085	118,000
Hocking	393406	0822711	21CHOC	14	2,545	2,551	4.9 ^a	1.132	180,000
	393138	0822326	22CHOC	15	2,650	2,665	4.3 ^a	1.222	279,000
	393205	0822144	23CHOC	16	2,780	2,788	4.9 ^a	1.222	272,000
	392950	0822024	7CHOC	--	2,860	2,866	5.1 ^a	1.218	278,000
Holmes	402929	0815545	6CHOL	--	3,758	3,826	6.1	1.198	256,000
	403522	0815832	35CHOL	33	3,435	3,446	4.9 ^a	1.143	191,000
	403348	0815835	36CHOL	34	3,453	3,462	4.5 ^a	1.123	167,000
	403925	0814059	41CHOL	39	4,144	4,158	5.2 ^a	1.184	239,000
	403028	0820048	42CHOL	40	3,318	3,321	4.9 ^a	1.157	204,000
Knox	402503	0821236	11CKNX	4	2,966	3,010	5.4 ^a	1.209	263,000
	402345	0821339	12CKNX	5	3,080	3,094	5.6 ^a	1.221	276,000
	402353	0821216	13CKNX	6	3,235	3,246	5.7 ^a	1.228	277,000
	402537	0821118	38CKNX	36	2,898	2,919	5.2 ^a	1.228	281,000

Table 3.--Description of oilfield and gasfield wells sampled in the "Clinton" sandstone and pH, density, and total dissolved-solids concentrations of brines--Continued

County	Latitude	Longitude	Local number	Field identification number used by Stith (1979)	Depth of sample (feet) ¹	Depth of well (feet) ¹	pH	Density (grams per milliliter at 20°C)	Dissolved solids, total (milligrams per kilogram of brine) ²
Licking	400650	0821752	2CLIC	--	2,825	2,825	4.9 ^a	1.220	275,000
	400618	0821646	8CLIC	1	2,678	2,736	4.8 ^a	1.230	279,000
	400535	0821400	9CLIC	2	2,945	2,996	5.8 ^a	1.177	223,000
	401327	0821648	10CLIC	3	2,862	2,862	5.5 ^a	1.221	274,000
	395851	0821217	14CLIC	7	3,160	3,258	5.7 ^a	1.167	214,000
	395650	0821559	15CLIC	8	2,942	3,008	5.5 ^a	1.187	237,000
	395618	0821554	16CLIC	9	2,947	2,995	5.7 ^a	1.154	198,000
	400131	0821747	17CLIC	10	2,750	2,834	6.0 ^a	1.229	282,000
	400135	0821656	18CLIC	11	2,800	2,836	5.0 ^a	1.212	266,000
	394050	0815843	1CMOR	--	4,200	4,338	5.4	1.209	269,000
Morgan	394413	0813836	76CMOR	90	5,364	5,885	--	1.122	161,000
	400409	0814321	50CMUS	51	4,690	4,823	6.8 ^a	1.114	155,000
Muskingum	400451	0814408	51CMUS	52	4,580	4,741	2.8 ^a	1.174	223,000
	400451	0814339	52CMUS	53	4,600	4,748	2.9 ^a	1.172	219,000
	395651	0815431	53CMUS	54	4,030	4,150	4.5 ^a	1.151	195,000
	395650	0815515	54CMUS	55	4,060	4,152	5.7 ^a	1.144	189,000
	395648	0815457	55CMUS	56	4,070	4,188	6.3 ^a	1.185	242,000
	395712	0815451	56CMUS	57	4,000	4,145	6.4 ^a	1.137	181,000
	400229	0814518	57CMUS	58	4,636	4,646	--	1.187	241,000
	400343	0814650	58CMUS	59	4,370	4,449	--	1.172	221,000
	400828	0815248	59CMUS	60	4,129	4,246	--	1.203 1.143	255,000
	395853	0820238	60CMUS	61	3,641	3,678	--	1.182	188,100

Table 3.--Description of oilfield and gasfield wells sampled in the "Clinton" sandstone and pH, density, and total dissolved-solids concentrations of brines--Continued

County	Latitude	Longitude	Local number	Field identification number used by Stith (1979)	Depth of sample (feet) ¹	Depth of well (feet) ¹	pH	Density (grams per milliliter at 20°C)	Dissolved solids, total (milligrams per kilogram of brine) ²
Noble	394502	0813708	71CNOB	85	5,432	5,553	--	1.136	227,300
	394801	0813829	72CNOB	86	5,360	5,560	--	3.178	176,000
	394930	0813407	73CNOB	87	5,370	5,483	--	1.174	222,000
	394658	0813650	74CNOB	88	5,287	5,450	--	1.162	221,000
	394516	0814014	75CNOB	89	5,161	5,200	--	1.099	208,000
	394825	0813322	77CNOB	91	5,488	5,627	--	1.129	130,000
Perry	393849	0820852	24CPER	17	3,679	3,698	5.6 ^a	1.129	172,000
	393816	0821702	25CPER	18	3,180	3,203	5.0 ^a	1.229	278,500
	393738	0821719	26CPER	19	3,240	3,257	5.9 ^a	1.151	198,700
Stark	403938	0811721	28CSTA	26	5,012	5,054	5.5 ^a	1.207	261,000
	404732	0811708	67CSTA	81	4,860	4,899	--	1.260	242,000
	404603	0811817	68CSTA	82	4,810	4,856	--	1.230	243,000
	404723	0811717	69CSTA	83	4,884	4,938	--	1.209	260,000
	404403	0811612	70CSTA	84	5,020	5,128	--	1.210	256,000
Tuscarawas	402327	0813358	62CTUS	63	4,878	4,926	--	1.163	215,400
	401717	0812714	32CTUS	30	5,210	5,402	5.2 ^a	1.155	200,000
	401740	0812730	33CTUS	31	5,288	5,425	4.5 ^a	1.141	181,000
	401742	0812805	34CTUS	32	5,130	5,358	6.1 ^a	1.133	178,000
Vinton	392322	0822618	20CVIN	13	?	?	5.1 ^a	1.167	215,000
Wayne	400151	0821548	19CWAY	12	2,842	2,849	5.8 ^a	1.213	262,000
	404019	0820021	37CWAY	35	3,203	3,203	5.6 ^a	1.136	180,000

¹ Below land surface

² Density at 20°C.

³ Solids residue on evaporation at 180°C

^a Lab determination, others are field determinations

Table 4.--Concentrations of selected dissolved constituents in brines from the "Clinton" sandstone

[All concentrations in millimoles per kilogram of brine. A dash (--) indicates not determined; nd indicates not detected]

County	Local number	Hydrogen sulfide	Calcium	Magnesium	Sodium	Potassium	Bicarbonate	Sulfate	Chloride	Bromide	Iodide	Silica, as SiO ₂	Aluminum	Iron (total)	Lithium	Manganese	Strontium	Zinc
Ashtabula	4CASH	nd	560	95	2,800	31	.35	1.4	3,600	7.8	.04	.07	.02	3.1	--	.73	7.4	.02
	5CASH	nd	760	150	3,400	29	.34	1.7	4,600	62	.11	.04	.02	4.0	--	1.2	nd	.02
	78CASH*	--	560	76	1,900	17	--	1.8	3,000	14	.1	--	--	--	4.4	1.0	6.8	.03
	43CASH*	--	730	130	2,700	24	.6	3.4	4,400	21	.1	--	--	3.0	6.6	.83	10.6	.02
	44CASH*	--	710	120	2,500	18	.1	3.5	4,200	20	.1	--	--	2.4	6.0	.84	9.6	.02
Carroll	29CCAR*	--	660	120	2,800	28	.3	4.3	4,200	21	.1	--	--	2.8	10	.79	11.1	.04
	30CCAR*	--	610	100	2,600	28	.7	4.6	4,000	21	.07	--	--	2.7	11	.79	10.8	.04
	31CCAR*	--	610	100	2,800	30	.3	5.9	4,200	21	.08	--	--	2.6	12	.81	11.0	.03
Columbiana	63CCOL*	--	1,100	220	2,100	25	--	3.8	4,900	25	.02	--	--	--	7.5	.15	13.6	.01
	64CCOL*	--	590	110	2,100	25	--	5.6	3,500	19	.03	--	--	--	6.1	.86	13.0	.01
	65CCOL*	--	550	97	2,800	24	--	8.2	3,900	20	.01	--	--	--	6.1	.69	10.3	.01
	66CCOL*	--	620	120	2,400	27	--	5.6	4,000	22	.04	--	--	--	7.3	.84	11.7	.01
Coshocton	39CCOS*	--	1,100	250	2,500	31	.1	3.6	4,700	23	.03	--	--	--	4.1	.60	13.3	.01
	40CCOS*	--	1,100	260	2,500	31	.3	4.5	4,700	24	.02	--	--	--	3.8	.62	13.0	.01
Fairfield	27CFAR*	--	510	120	1,800	22	.9	4.7	3,000	15	.06	--	nd	2.0	2.7	.35	6.3	.03
Quernsey	3CGUR	.04	510	92	2,400	57	1.4	5.6	5,800	36	.20	.11	.13	8.0	--	.97	6.6	.16
	61CGUR*	--	460	87	1,900	27	--	5.0	3,000	14	.1	--	--	--	5.7	.72	--	.03
	45CGUR*	--	590	90	2,700	30	.1	8.8	4,000	32	.05	--	--	--	12	.92	9.4	.05
	46CGUR*	--	610	88	2,500	26	.9	10	3,700	31	.06	--	--	--	9.8	.85	9.3	.1
	47CGUR*	--	440	61	1,800	17	.3	8.5	2,700	23	.04	--	--	--	8.3	.66	6.9	.08
	48CGUR*	--	600	88	2,300	26	.8	12	3,600	31	.04	--	--	--	9.3	1.0	9.2	.03
	49CGUR*	--	290	51	1,300	16	.6	12	1,900	15	.1	--	--	--	5.0	.50	4.3	.01

Table 4.--Concentrations of selected dissolved constituents in brines from the "Clinton" sandstone--Continued

County	Local number	Hy- dro- gen sul- fide	Cal- cium	Mag- ne- sium	Sod- ium	Potas- sium	Bi- car- bon- ate	Sul- fate	Chlo- ride	Bro- mide	Io- dide	Sili- ca, as SiO ₂	Alu- mi- num	Iron (to- tal)	Lith- ium	Man- ga- nese	Stron- tium	Zinc
Hocking	21CHOC*	--	610	150	1,400	13	1.2	2.4	2,900	13	.09	--	nd	2.7	1.6	.32	7.8	.11
	22CHOC*	--	1,100	230	2,520	23	nd	5.4	5,000	24	.08	--	nd	4.0	2.2	.62	13.1	.02
	23CHOC*	--	1,100	210	2,300	20	.2	4.2	4,600	22	.06	--	nd	1.4	2.5	.77	12.4	.28
	7CHOC	nd	900	290	2,800	48	.27	1.5	4,600	57	.08	.08	.02	3.1	--	.28	8.2	.12
Holmes	6CHOL	nd	790	210	2,700	38	1.3	2.8	4,200	8.1	.09	.06	.02	5.7	--	.97	nd	.22
	35CHOL*	--	660	140	1,800	21	.2	7.1	3,200	17	.01	--	--	--	3.2	.56	8.9	.15
	36CHOL*	--	550	110	1,600	20	nd	9.3	2,700	15	.04	--	--	--	3.1	.46	7.0	.14
	41CHOL*	--	800	140	2,400	28	.2	4.3	4,000	23	.04	--	--	--	5.0	.84	10.8	.1
	42CHOL*	--	750	150	1,800	21	.00	3.3	3,400	19	.02	--	--	--	3.2	.65	9.5	.08
Knox	11CKNX*	--	900	220	2,300	27	.2	3.1	4,300	21	.23	.23	nd	3.1	2.7	.51	11.7	.02
	12CKNX*	--	890	240	2,400	25	.4	4.8	4,700	15	.2	.26	nd	3.1	3.0	.45	12.1	.02
	13CKNX*	--	900	240	2,400	27	.2	3.6	4,600	21	.16	.2	nd	2.0	2.9	.50	11.7	.01
	38CKNX*	--	1,000	240	2,400	33	.3	2.8	4,700	23	.02	--	--	--	3.9	.58	13.0	.01
Licking	2CLIC	nd	920	310	2,000	42	.32	--	6,200	42	.13	.08	.12	2.6	--	.28	8.6	.03
	8CLIC*	--	1,000	260	2,400	25	.08	2.8	4,600	23	.2	.26	nd	3.8	2.9	.43	12.0	.01
	9CLIC*	--	790	180	1,900	20	.3	4.6	3,700	18	.2	.25	nd	3.3	2.7	.51	9.7	.02
	10CLIC*	--	1,000	250	2,400	24	.4	3.1	4,600	23	.2	.2	nd	4.2	3.0	.49	11.9	.02
	14CLIC*	--	720	140	2,000	24	.4	5.1	3,600	17	.18	.26	nd	2.3	2.8	.51	10.2	.01
	15CLIC*	--	770	220	2,200	30	.4	2.5	4,100	18	.15	.22	nd	1.5	3.5	.18	9.3	.01
	16CLIC*	--	670	140	1,900	23	.4	6.6	3,400	16	.11	.2	nd	3.1	2.9	.39	9.5	.01
	17CLIC*	--	1,000	240	2,400	29	.6	2.6	4,800	23	.15	.2	nd	7.7	3.0	.44	12.0	.01
	18CLIC*	--	940	220	2,300	28	.1	2.6	4,600	22	.13	.2	nd	2.6	3.2	.45	12.7	.01

Table 4.--Concentrations of selected dissolved constituents in brines from the "Clinton" sandstone--Continued

County	Local number	Hydrogen sulfide	Calcium	Magnesium	Sodium	Potassium	Bicarbonate	Sulfate	Chloride	Bromide	Iodide	Silica, as SiO ₂	Aluminum	Iron (total)	Lithium	Manganese	Strontium	Zinc
Morgan	1CMOR	nd	780	180	3,000	42	.87	--	5,600	29	.23	.08	.03	3.8	--	.69	8.7	.04
	76CMOR*	--	370	40	1,900	30	--	3.7	2,700	14	.11	--	--	--	7.0	.54	6.3	.01
Muskingum	50CMUS*	--	430	66	1,600	34	.6	7.8	2,500	21	.05	--	--	--	5.4	.54	6.7	.01
	51CMUS*	--	700	120	2,200	39	nd	9.1	3,800	19	.03	--	--	--	5.5	1.0	12.0	.05
	52CMUS*	--	700	140	2,100	40	nd	8.2	3,700	19	.03	--	--	--	5.5	1.0	11.6	.05
	53CMUS*	--	540	110	2,100	22	nd	9.3	3,300	17	.02	--	--	--	5.0	.87	9.2	.05
	54CMUS*	--	520	110	2,000	29	.5	10	3,200	20	.01	--	--	--	4.4	.71	8.4	.08
	55CMUS*	--	440	170	2,900	52	1.3	7.6	4,100	16	.02	--	--	--	11	.05	5.8	.03
	56CMUS*	--	530	67	1,800	27	.7	7.4	3,000	15	.03	--	--	--	4.4	.72	8.7	.01
	57CMUS*	--	750	130	2,200	37	--	9.0	4,000	21	.06	--	--	--	5.5	1.4	12.8	.09
	58CMUS*	--	650	100	2,000	37	--	7.4	3,700	18	.04	--	--	--	5.5	.62	11.3	.10
	59CMUS*	--	810	160	2,200	32	--	7.4	4,200	22	.07	--	--	--	3.0	1.2	13.6	.10
	60CMUS*	--	580	130	1,700	27	--	10	3,100	16	.02	--	--	--	3.2	.96	9.1	.05
Noble	71CNOB*	--	580	97	2,700	37	--	2.6	3,900	17	.18	--	--	--	13	.55	11.7	.03
	72CNOB*	--	420	54	2,100	27	--	3.4	3,000	13	.1	--	--	--	7.2	.54	7.5	.03
	73CNOB*	--	640	80	2,600	35	--	3.1	3,800	17	.17	--	--	--	9.8	.54	9.7	.03
	74CNOB*	--	570	70	2,600	33	--	3.2	3,700	18	.14	--	--	--	9.0	.76	9.7	.04
	75CNOB*	--	500	57	2,500	33	--	4.8	3,500	17	.16	--	--	--	8.0	.52	7.4	.04
	77CNOB*	--	230	30	1,600	20	--	4.3	2,100	11	.11	--	--	--	6.0	.81	5.2	.03

Table 4.--Concentrations of selected dissolved constituents in brines from the "Clinton" sandstone--Continued

County	Local number	Hydrogen sulfide	Calcium	Magnesium	Sodium	Potassium	Bicarbonate	Sulfate	Chloride	Bromide	Iodide	Silica, as SiO ₂	Aluminum	Iron (total)	Lithium	Manganese	Strontium	Zinc
Perry	24CPER*	--	540	91	1,700	20	2.7	7.8	2,800	14	.08	--	nd	2.8	2.8	.44	6.9	.02
	25CPER*	--	1,000	300	2,300	23	.14	4.5	4,700	22	.06	--	nd	2.4	2.9	.27	9.5	.1
	26CPER*	--	630	150	1,700	21	.6	6.1	3,200	15	.06	--	nd	2.0	2.5	.38	8.3	.07
Stark	28CSTA*	--	720	130	2,900	32	.5	10	4,400	22	.2	--	--	3.0	11	1.0	13.8	.06
	67CSTA*	--	680	150	2,500	32	--	9.9	4,200	23	.03	--	--	--	6.3	.72	11.6	.05
	68CSTA*	--	680	140	2,400	33	--	4.9	4,300	22	.02	--	--	--	6.4	.74	11.7	.06
	69CSTA*	--	710	160	2,600	34	--	6.6	4,300	24	.03	--	--	--	6.6	.75	12.4	.01
	70CSTA*	--	690	130	2,600	32	--	6.8	4,400	24	.04	--	--	--	7.1	.90	11.8	.05
Tuscarawas	62CTUS*	--	560	94	2,300	31	--	11	3,500	18	.04	--	--	--	5.0	.94	9.8	.14
	32CTUS*	--	480	98	2,300	30	.6	6.2	3,400	16	.05	--	--	2.7	8.9	.80	8.5	.12
	33CTUS*	--	440	94	2,000	21	nd	4.9	3,100	15	.1	--	nd	6.5	7.7	.59	8.3	.03
	34CTUS*	--	490	61	2,000	25	1.0	6.1	3,000	15	.1	--	--	4.4	7.8	.61	7.3	.04
Vinton	20CVIN*	--	680	150	2,000	23	.2	5.3	3,600	18	.06	--	nd	2.7	2.6	.51	8.8	.07
Wayne	19CWAY*	--	920	210	2,300	27	.7	3.0	4,600	22	.18	.2	nd	3.2	3.1	.46	14.1	.02
	37CWAY*	--	630	170	1,400	27	.4	4.0	3,100	14	.02	--	--	--	5.3	.34	8.0	.04

* Analyses reported by Stith (1979). Samples taken during 1972-73 by Ohio Division of Geological Survey.

The hydrogen ion activity ($10^{-\text{pH}}$) varied over four orders of magnitude for "Clinton" brines. Corresponding pH values ranged from 2.8 to 6.8. It is peculiar that this range of pH would exist, especially because it was observed in two wells located near one another in Muskingum County. Given this range of pH values, the question must be raised whether the low values represent a remnant of acidification during well development or stimulation.

Measurements of pH were performed at the field site on the samples collected for this study. The pH data of Stith (1979) are laboratory determinations. Although no major differences were noted between pH values measured in the field versus those measured in the laboratory, field values generally appear to be higher for wells in Holmes and Hocking Counties.

Sodium and chloride are dominant constituents in "Clinton" brines and have median ionic concentrations of 2,300 and 4,100 mmol/kg, respectively. The Na:Cl ratios are all less than 1.0, and have a median value of 0.6. Concentrations of these constituents range widely throughout the study area; however, concentrations are similar in well samples from the same county or from wells in close proximity. The range in chloride concentrations is more than twice the range of the sodium concentrations (that is, the standard deviation from the mean concentration for chloride is double that for sodium).

Calcium and magnesium are major components; their concentrations range from 230 to 1,100 mmol/kg and from 30 to 310 mmol/kg, respectively. The median concentration ratio equals 5.0.

Potassium and bromide are present as relatively concentrated minor components in "Clinton" brines. Eighty-seven percent of the potassium concentrations are in the 20 to 40 mmol/kg range. The minimum potassium concentration (13 mmol/kg) was from a well in Hocking County and the maximum potassium concentration (57 mmol/kg) was from a well in Guernsey County. Bromide concentrations are more variable, even within an individual county. The minimum (7.8 mmol/kg) and maximum (62 mmol/kg) bromide concentrations were in wells from Ashtabula County. The majority of the strontium, lithium, iron, and sulfate concentrations range between 1 and 10 mmol/kg. Aluminum, iodide, silica, and zinc are trace constituents.

Brines in the Rose Run Sandstone

The results of the chemical analyses of brines in the Rose Run sandstone appear in tables 5 and 6. Seven of the eight samples collected in this study are from a rather limited geographic area in Coshocton County. One sample of Rose Run brine was collected in Ashtabula County. Rose Run samples were collected from wells producing at depths ranging from 6,140 to 6,640 feet below land-surface datum.

Table 5.--Description of oilfield and gasfield wells sampled in the Rose Run Sandstone, and pH, density, and total dissolved-solids concentrations of brines

County	Latitude	Longitude	Local number	Depth of sample (feet) ¹	Depth of sample (feet) ¹	pH	Density (grams per millimeter at 20°C)	Dissolved solids, total (milligrams per kilogram of brine) ²
Ashtabula	413648	0804658	5RASH	6,360	7,136	6.1	1.166	220,000
Coshocton	402205	0814852	1RCOS	6,225	6,409	5.4	1.226	281,000
	402054	0814621	2RCOS	6,620	6,626	5.3	1.224	286,000
	401824	0814644	3RCOS	6,550	6,600	5.3	1.227	288,000
	401802	0814852	4RCOS	6,140	6,251	5.7	1.218	271,000
	401733	0814854	6RCOS	6,145	6,150	5.5	1.228	265,000
	401430	0815115	7RCOS	6,155	6,175	5.7	1.224	278,000
	401541	0814708	8RCOS	6,490	6,494	4.9	1.222	274,000

¹Below land surface

²Residue on evaporation at 180°C

Table 6.--Concentrations of selected dissolved constituents in brines from the Rose Run sandstone

[All concentrations in millimoles per kilogram of brine; a dash (--) indicates not determined;
nd indicates not detected]

County	Local number	Hy- dro- gen sul- fide	Cal- cium	Mag- ne- sium	So- dium	Potas- sium	Bi- car- bon- ate	Sul- fate	Chlo- ride	Bro- mide	Io- dide	Silica as SiO ₂	Alu- mi- num	Iron (to- tal)	Lith- ium	Man- gane- se	Zinc	Stron- tium
Ashtabula	5RASH	nd	540	100	3,000	81	1.1	1.6	3,400	42	0.05	0.08	0.02	5.1	--	0.25	0.05	9.0
Coshocton	1RCOS	nd	980	270	2,000	90	0.86	4.6	7,400	41	.15	nd	.03	0.76	--	.01	.03	3.4
	2RCOS	0.02	880	260	2,000	92	1.7	--	5,500	40	.19	.06	.12	.70	--	.08	.04	3.4
	3RCOS	nd	900	260	2,100	88	.80	--	6,200	37	.13	.08	--	.44	--	.07	.03	8.2
	4RCOS	nd	920	220	2,800	88	1.6	1.2	4,400	62	.12	.04	.03	.59	--	.10	.10	7.5
	6RCOS	nd	1,000	210	2,800	81	.96	1.2	4,800	63	.12	.05	.01	.55	--	.07	.01	0.9
	7RCOS	.01	940	190	3,000	84	2.1	1.5	4,800	66	.03	.10	.02	3.5	--	.16	.08	7.5
	8RCOS	.01	940	280	3,600	82	.19	8.5	4,600	22	.14	.02	.16	11	--	.25	.01	nd

Although no lithium determinations were made on any of the brines collected and analyzed for this study, the Rose Run data set is relatively complete compared to those for the Berea and "Clinton" sandstones.

The density of Rose Run brines in Coshocton County ranges from 1.218 to 1.228 g/ml and has a median value of 1.224 g/ml. The median concentration of total dissolved solids in the Rose Run brines from Coshocton County is 278,000 mg/kg. The Rose Run sample from Ashtabula County has a density of 1.166 and total dissolved-solids concentration of 220,000 mg/kg. The Ashtabula County values are 26 and 21 percent lower, respectively, than the median values for density and total dissolved solids in the Coshocton County samples.

The pH of Rose Run brine ranges from 4.9 to 5.7 in Coshocton County. A pH of 6.1 was determined for the sample from Ashtabula County.

Sodium and chloride are dominant chemical constituents in Rose Run brines. Sodium has a mean ionic concentration of $2,600 \pm 600$ mmol/kg (1 standard deviation), whereas the mean ionic concentration for chloride is $5,100 \pm 1,200$ mmol/kg. The Na:Cl ratios are all less than 1.0. The range in chloride concentrations is 2.5 times the range for sodium.

Calcium and magnesium are major components of the Rose Run brines, and have mean ionic concentrations of 880 ± 150 mmol/kg and 220 ± 60 mmol/kg, respectively. The mean Ca:Mg ratio equals 4.0.

Potassium concentrations are relatively high for a minor constituent, and fall within the narrow range of 81-92 mmol/kg. Bromide, strontium, and iron are also minor constituents. The mean bromide concentration is 47 mmol/kg. Strontium and iron are less concentrated; mean values are 5.7 mmol/kg for strontium, and 2.8 mmol/kg for iron. Iodide, bicarbonate, silica, manganese, aluminum, and zinc are trace constituents in Rose Run brines.

Concentrations of Dissolved Gases

Table 7 presents concentrations of dissolved hydrogen sulfide and carbon dioxide gas as determined in the 18 samples collected for this study. A qualitative positive correlation exists between H_2S (aq) and CO_2 (aq). Samples that have H_2S also appear to have higher concentrations of dissolved CO_2 than samples without H_2S . Due to the limited number of analyses and the unstable nature of these constituents, any apparent relationships are to be viewed with caution.

Table 7.--Concentrations of hydrogen sulfide and carbon dioxide in selected samples of Ohio brines.

[nd, not detected]

Sandstone	Local well number	Concentration of constituent (in mmol/kg of brine)	
		Hydrogen sulfide (aq.)	Carbon dioxide (aq.)
Berea	3BLIC	nd	0.92
	1BMOR	0.04	3.95
	2BMOR	.05	5.86
"Clinton"	4CASH	nd	.78
	5CASH	nd	1.87
	3CGUR	.04	15.6
	7CHOC	nd	4.74
	6CHOL	nd	2.22
	2CLIC	nd	9.00
	1CMOR	nd	7.67
Rose Run	5RASH	nd	1.89
	1RCOS	nd	7.57
	2RCOS	.02	19.3
	3RCOS	nd	8.9
	4RCOS	nd	7.15
	6RCOS	nd	6.74
	7RCOS	.01	9.49
	8RCOS	.01	5.24

Chemical Types

Equivalent concentrations of the principal ionic constituents in the 18 brines sampled for this study are used to illustrate the types of brine found in the Berea, "Clinton", and Rose Run sandstones. Stiff diagrams are used to graphically illustrate the principal ionic constituents (Stiff, 1951). Also, a brine classification scheme proposed by Sulin is adopted to categorize Berea, "Clinton," and Rose Run brines by their dissolved inorganic constituents. A detailed discussion of chemical typing of oilfield and gasfield waters including computation of equivalent concentration, application of Stiff diagrams, and the Sulin classification procedure, is given by Collins (1975a, p. 258).

Brines in the Berea Sandstone

Stiff diagrams were constructed for the three Berea brines samples collected for this study (fig. 3). The horizontal scale is expanded to the left side of each diagram to compensate for the less abundant equivalent concentrations of potassium and magnesium. Figure 3 illustrates the predominance of sodium, calcium, and chloride in these brines. Magnesium happens to be in a location between calcium and potassium such that the upper left wing of the diagram forms a right triangle. Diagrams A and B are very similar in shape and represent two wells located within Morgan County. Diagram C has noticeably smaller triangles (indicating the brine is less concentrated) and represents a sample from a well in Licking County that is producing at a considerably shallower depth (735 feet) than the two Morgan County wells (1,422 and 1,520 feet.)

The ratio of sodium to chloride is consistently less than 1.0 in all Berea samples except in the Licking County sample illustrated in diagram C. The fact that $(\text{Cl}-\text{Na}):\text{Mg}$ is greater than 1.0 places 13 of the 14 Berea samples in Sulin's chloride-calcium type class for oilfield waters.

Brines in the "Clinton" Sandstone

Seven Stiff diagrams representing the "Clinton" brines appear in figure 4. As was the case for the Berea samples, the left-side scale is expanded. The predominance of sodium, chloride, and calcium is readily apparent. The upper left wing of the diagrams is four sided, and the 5:1 ratio of $\text{Ca}:\text{Mg}$ accounts for this feature. The lower left wing of the diagrams has an elongated appearance that contrasts the extreme difference in sodium and potassium concentrations (potassium plots very near zero). The equivalent concentrations of calcium and magnesium are two times their ionic concentrations; this accounts for the enlargement of the calcium wing relative to the sodium wing even though the mean ionic concentration ratio of $\text{Na}:\text{Ca}$ equals 3.5:1. The chloride point plots such that the right side of the diagrams closely approximate an equilateral triangle. All 78 of the "Clinton" samples fall into Sulin's chloride-calcium type of oilfield water.

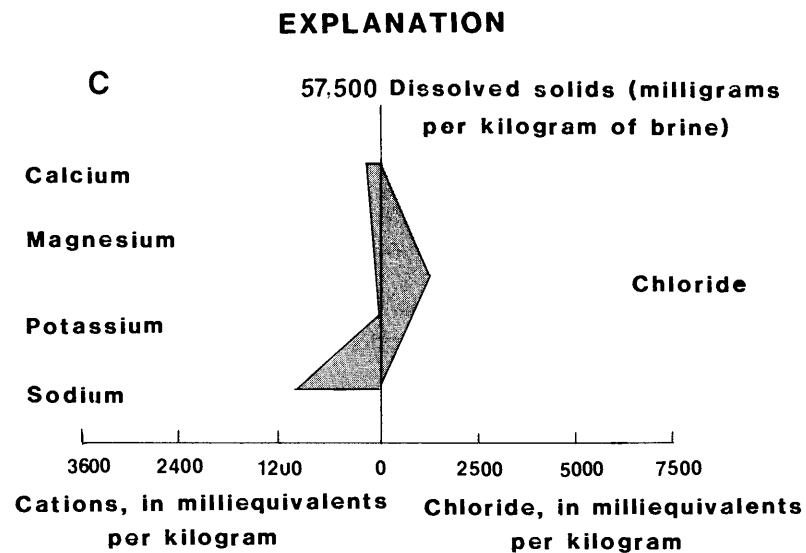
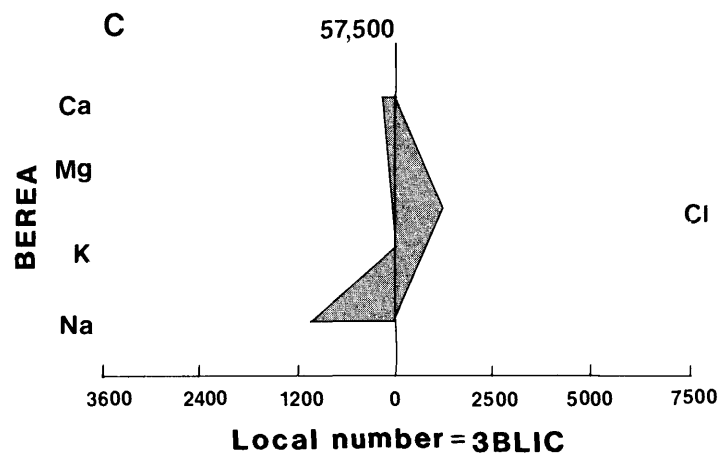
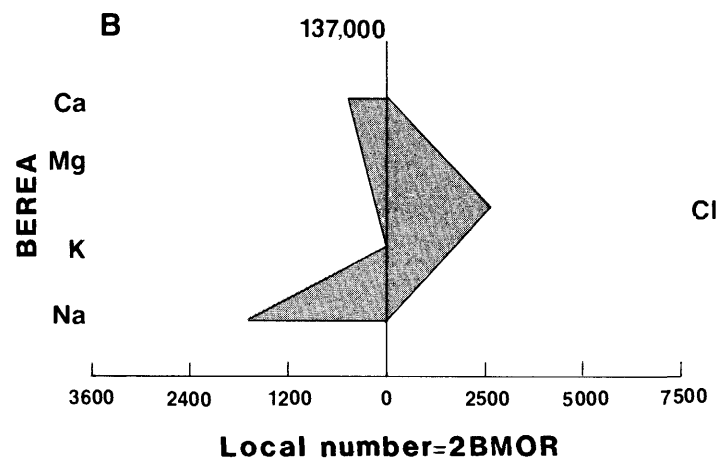
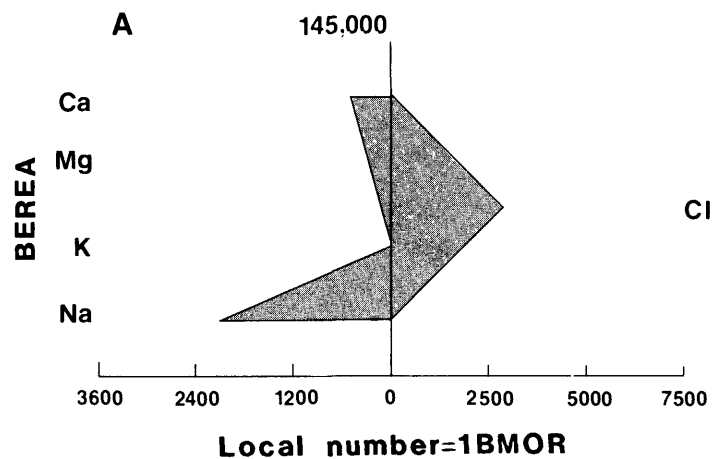


Figure 3.--Stiff diagrams illustrating the predominant chemical constituents of brines in the Berea Sandstone.

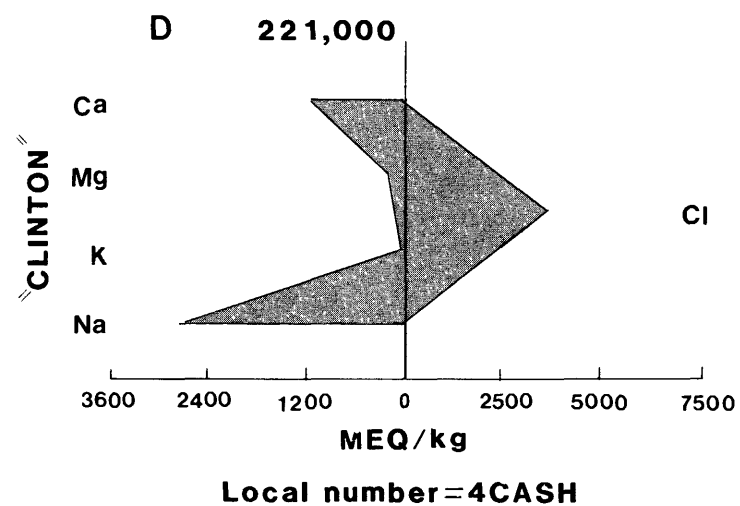
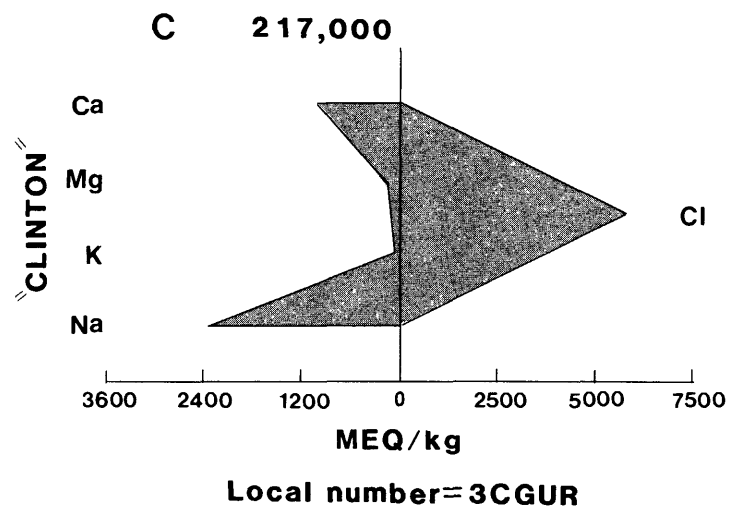
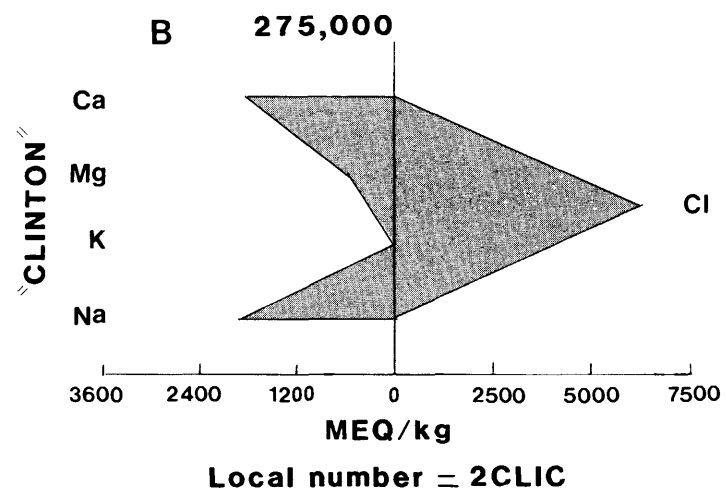
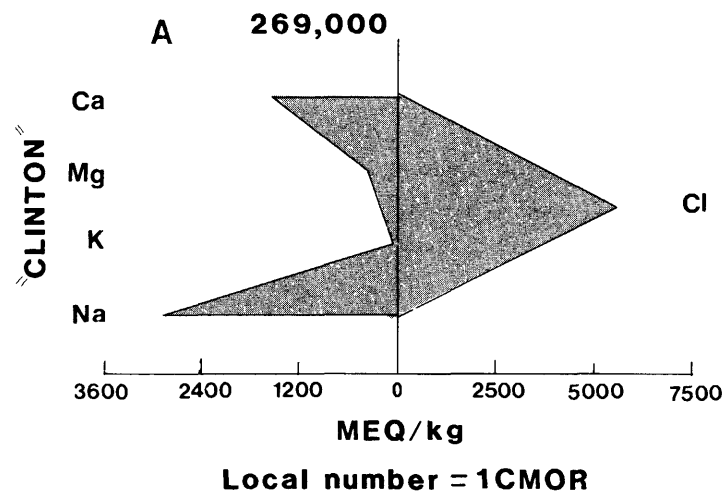
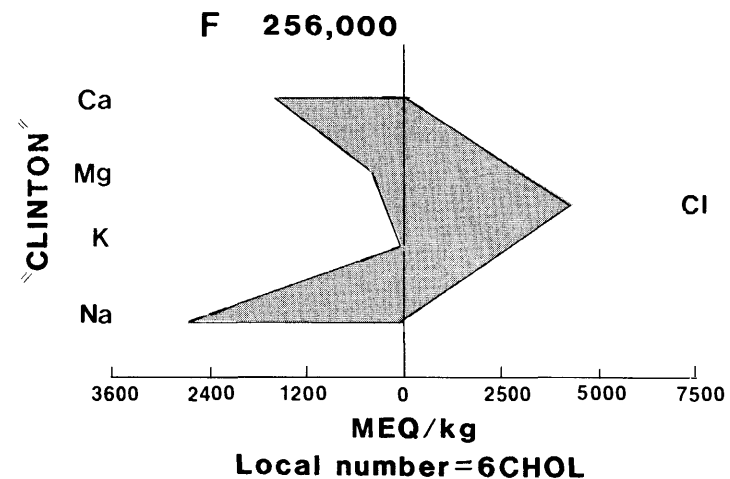
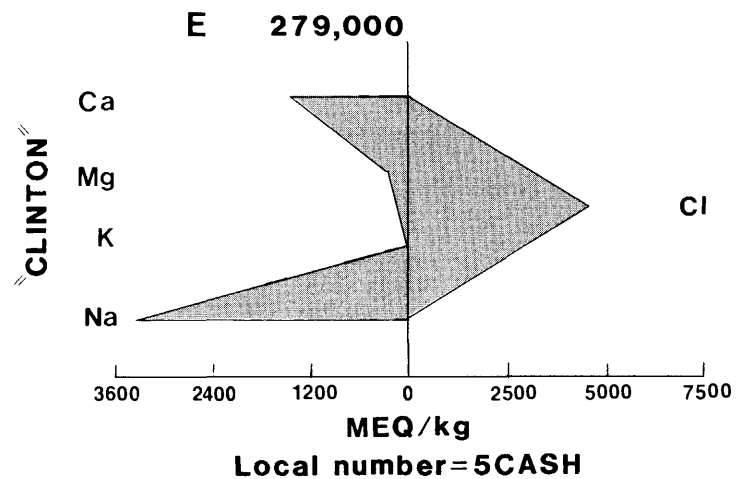


Figure 4.--Stiff diagrams illustrating the predominant chemical constituents of brines in the "Clinton" sandstone.



EXPLANATION

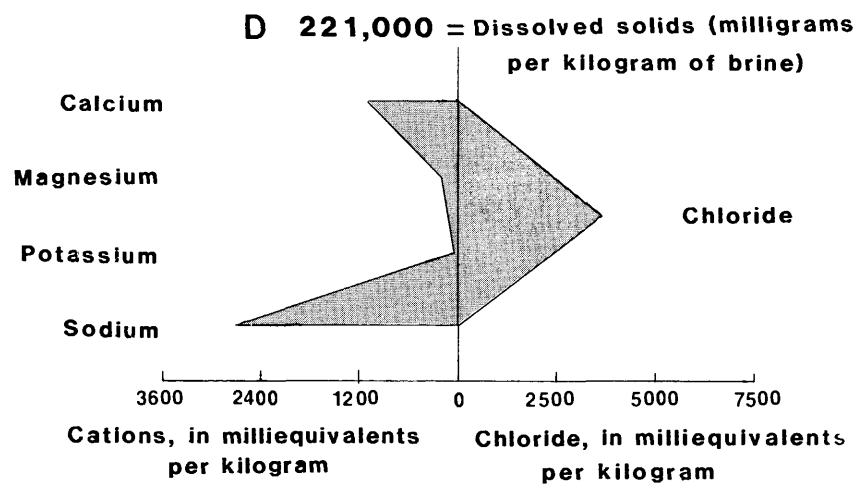
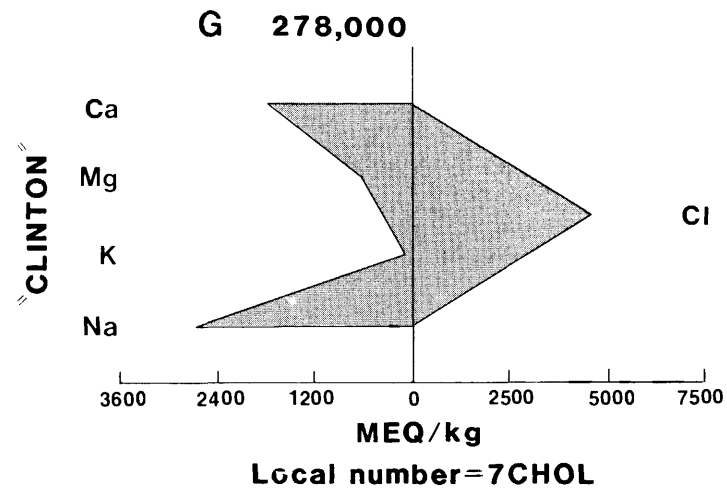


Figure 4.--Stiff diagrams illustrating the predominant chemical constituents of brines in the "Clinton" sandstone--continued.

Brines in the Rose Run Sandstone

Stiff diagrams for the seven Rose Run samples from Coshocton County and the one sample from Ashtabula County appear in figure 5. All diagrams have a characteristic four-sided wing at the upper left. The distinctive feature of the Rose Run brines is the potassium concentration, which now plots away from the center origin at nearly 100 milliequivalents per kilogram of brine. The sodium wing (lower left) is elongated. In diagrams A, B, and C, the calcium and sodium wings are nearly equidimensional, whereas sodium is more pronounced relative to calcium in the other five diagrams. Diagram E represents the Ashtabula County sample, which is noticeably less concentrated in calcium, magnesium, and chloride, and has a sodium concentration similar to the Coshocton County samples.

The Na:Cl ratio combined with the (Cl-Na):Mg ratio places the Rose Run brines into Sulin's chloride-calcium type of oilfield water.

Interformational Differences in Brine Chemistry

Emphasis in this section is placed on identifying interformational differences in brine chemistry as opposed to local and regional mineralogic variations within each sandstone that may be operating to impart the observed differences. Brine samples within a given sandstone were taken from a wide geographic area and from wells producing at different depths within the same sandstone. These factors are important and may influence the observed chemistry. The range of sample depths or production-zone depths is unique for each of the three sandstones.

Sample depth was used as a variable to aid in illustrating the variations of the dominant constituents (sodium and chloride), the major constituents (calcium and magnesium), and selected minor and trace constituents for which enough data are available to make interformational comparisons. The data were first compared graphically and were then tested statistically to determine the significance of differences in mean concentrations of constituents between the sandstones.

Figures 6 through 9 are plots of chemical-constituent concentrations for the three sandstones versus sample depth (in feet relative to a wellsite land-surface datum). Sample depth serves to group the samples by formation, but the spread of points in the Y-axis direction is qualitative (that is, depths are not reported relative to a common reference elevation, such as sea level.) The variation or spread of data in relation to concentration of the chemical constituent (X-axis direction) is most important in this study. Samples collected for this investigation are plotted as solid data symbols and those from Stout and others (1932) and Stith (1979) are plotted as open symbols.

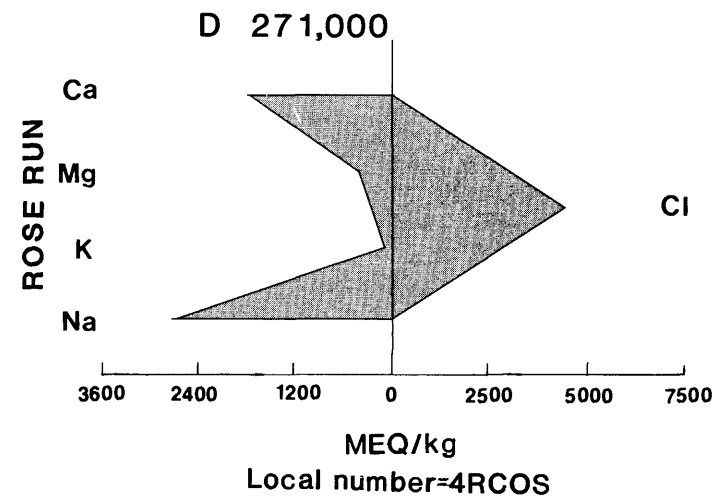
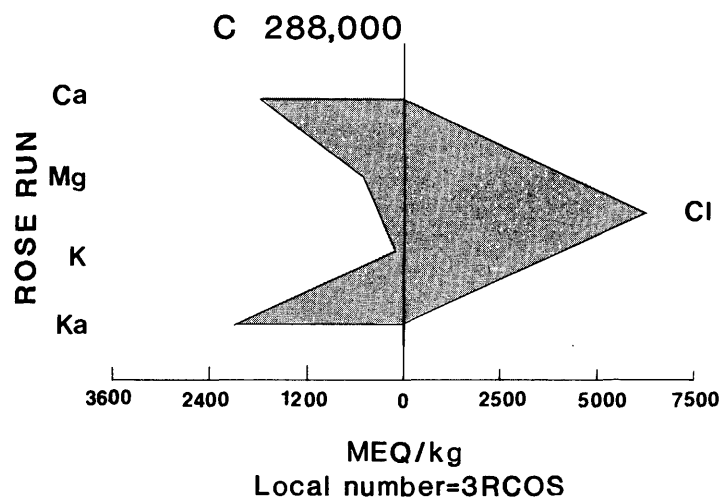
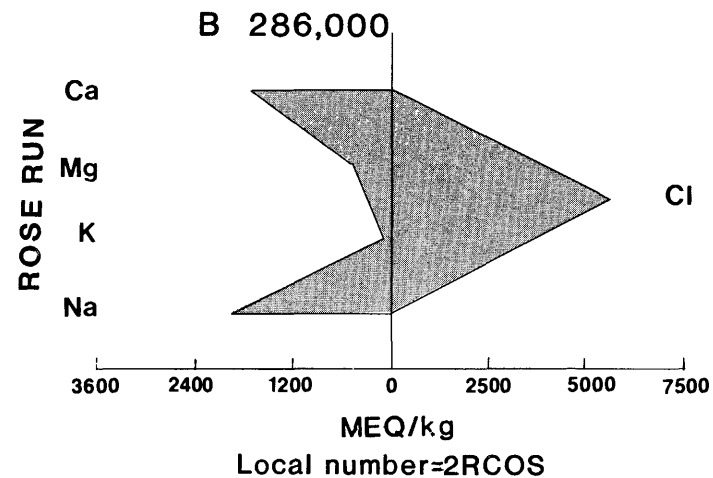
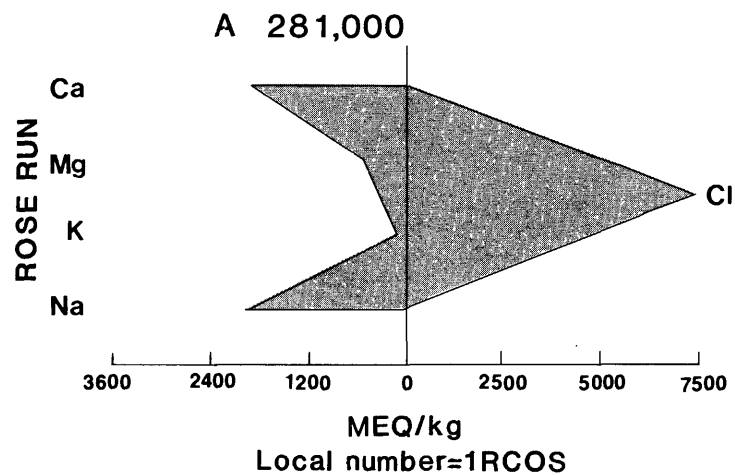


Figure 5.--Stiff diagrams illustrating the predominant chemical constituents of brines in the Rose Run sandstone.

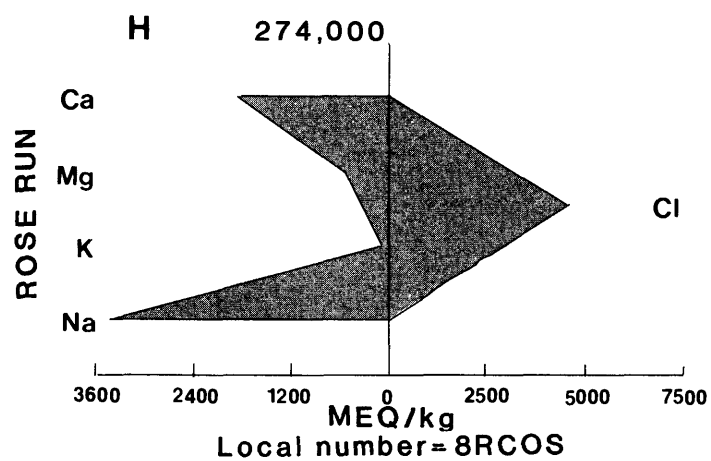
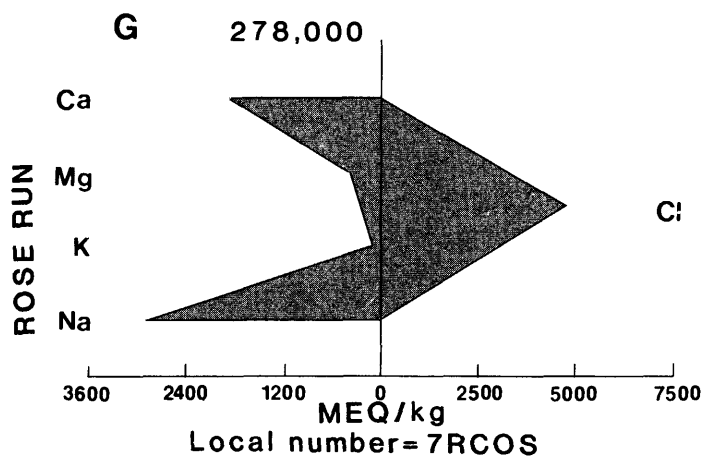
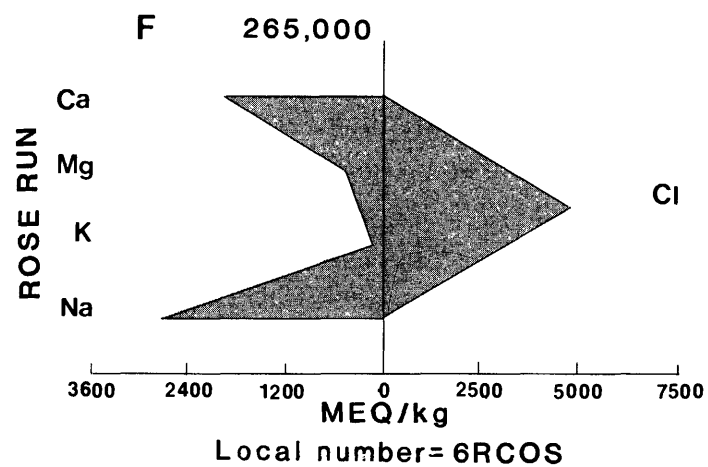
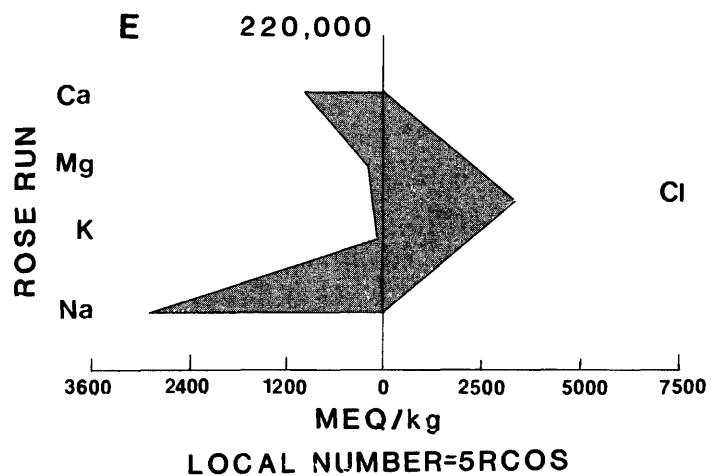


Figure 5—Stiff diagrams illustrating the predominant chemical constituents of brines in the Rose Run sandstone.—Continued

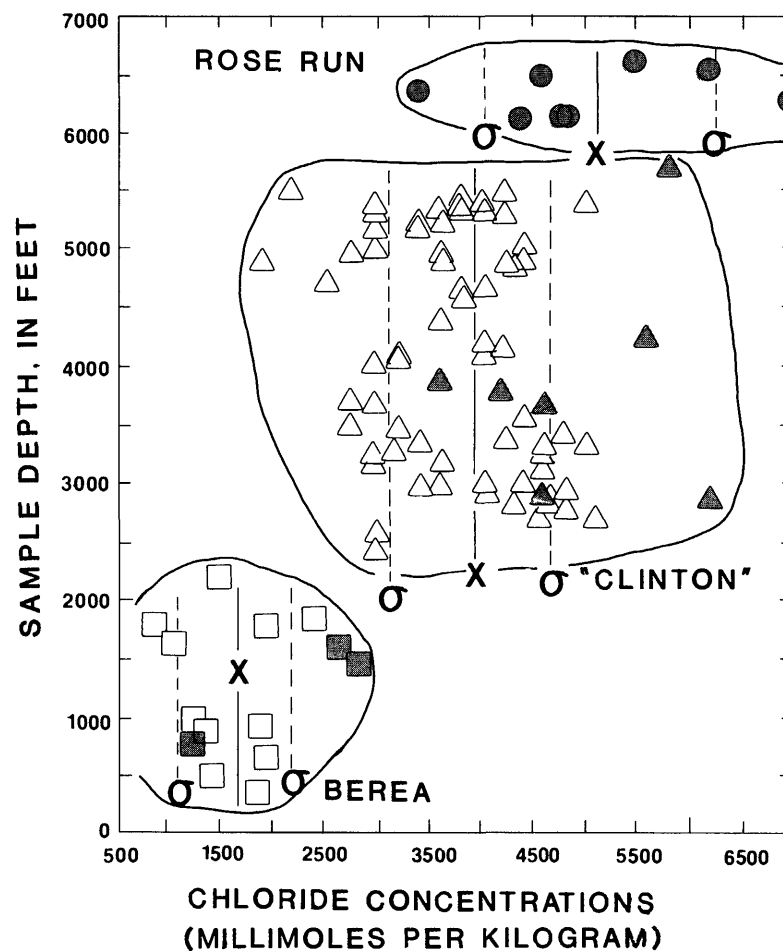
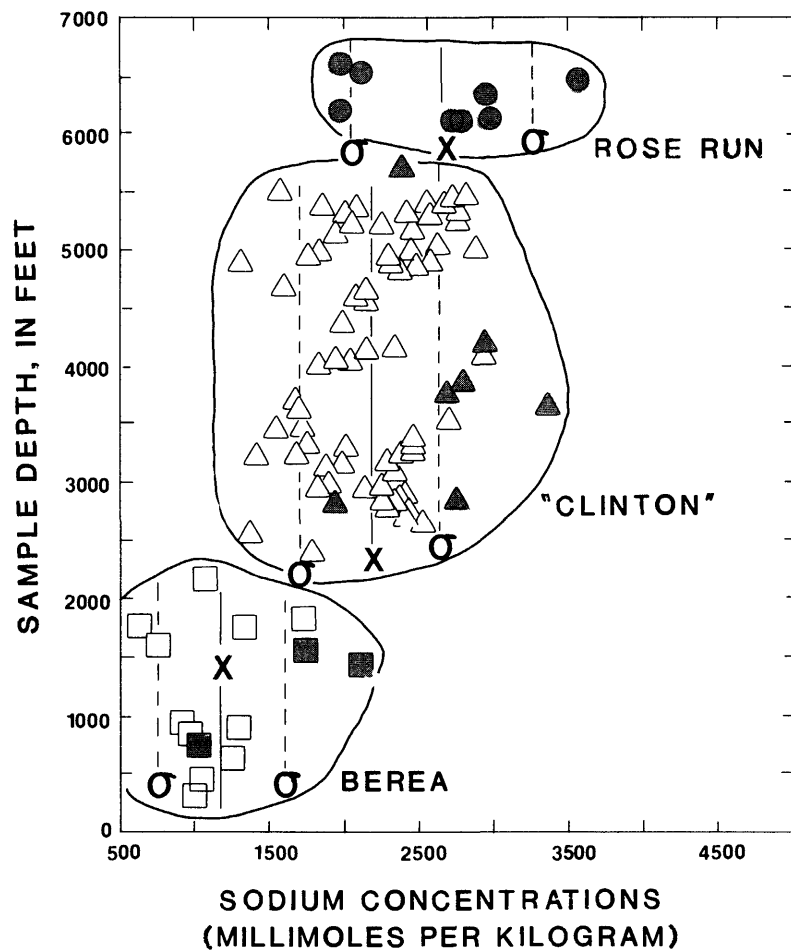


Figure 6.—Concentrations of sodium and chloride versus sample depth for Berea, "Clinton," and Rose Run brines (solid data symbols represent samples collected for this study; open symbols are data from Stout and others, 1932, and Stith, 1979).

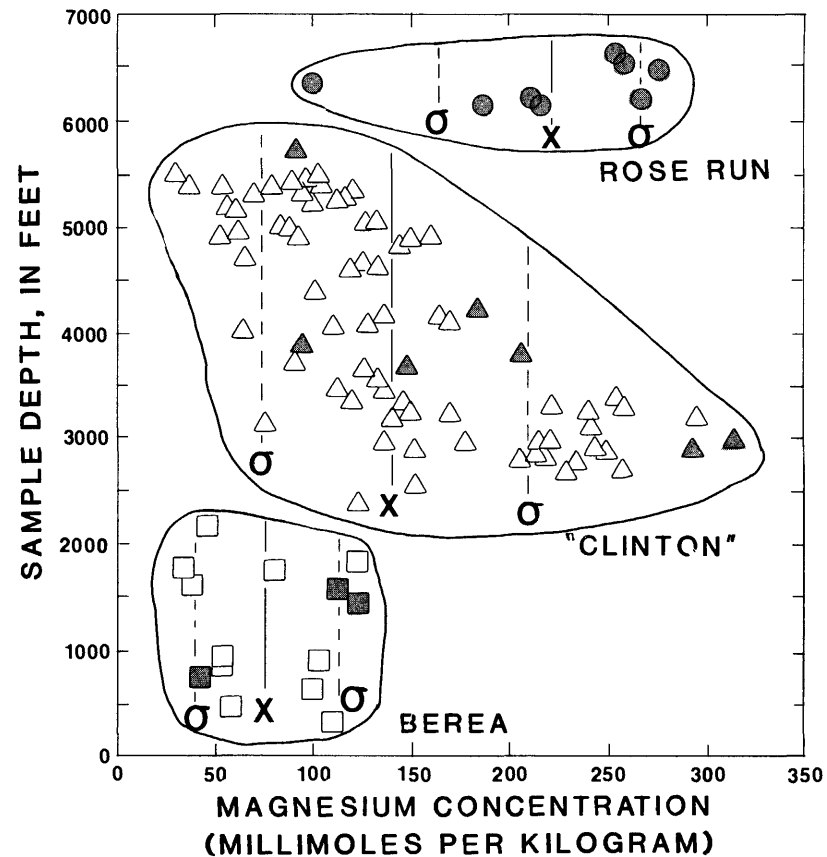
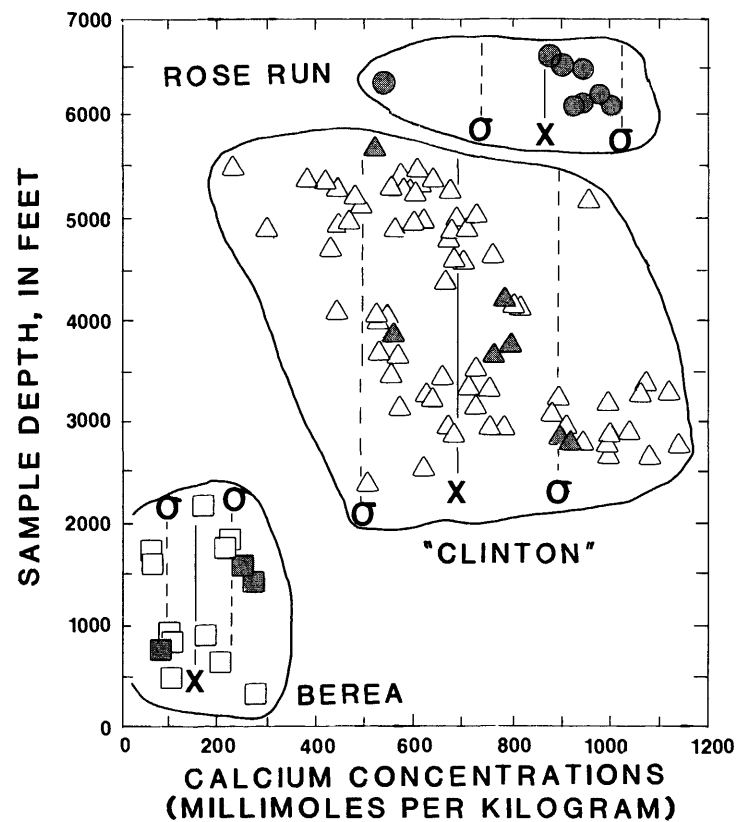


Figure 7.--Concentrations of calcium and magnesium versus sample depth for Berea, "Clinton," and Rose Run brines (solid data symbols represent samples collected for this study; open symbols are data from Stout and others, 1932, and Stith, 1979).

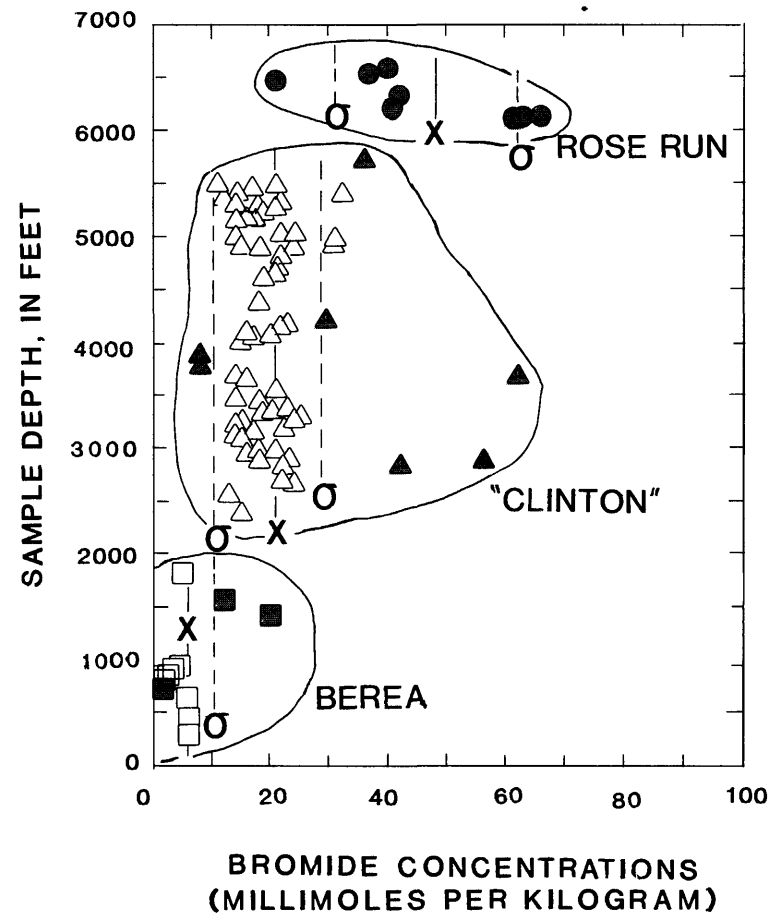
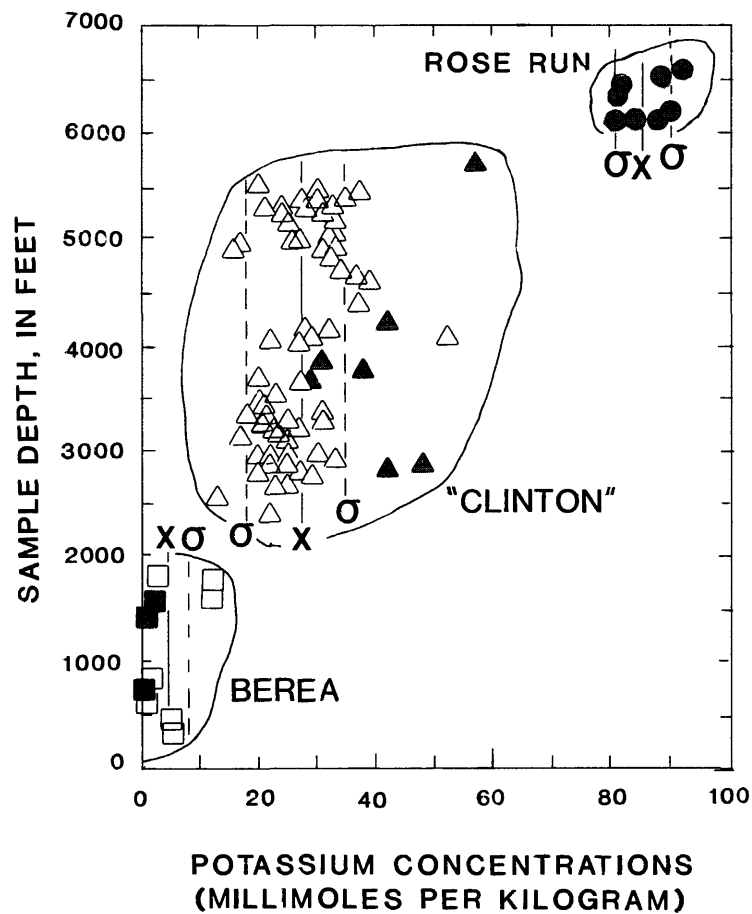


Figure 8.—Concentrations of potassium and bromide versus sample depth for Berea, "Clinton," and Rose Run brines (solid data symbols represent samples collected for this study; open symbols are data from Stout and others, 1932, and Stith, 1979).

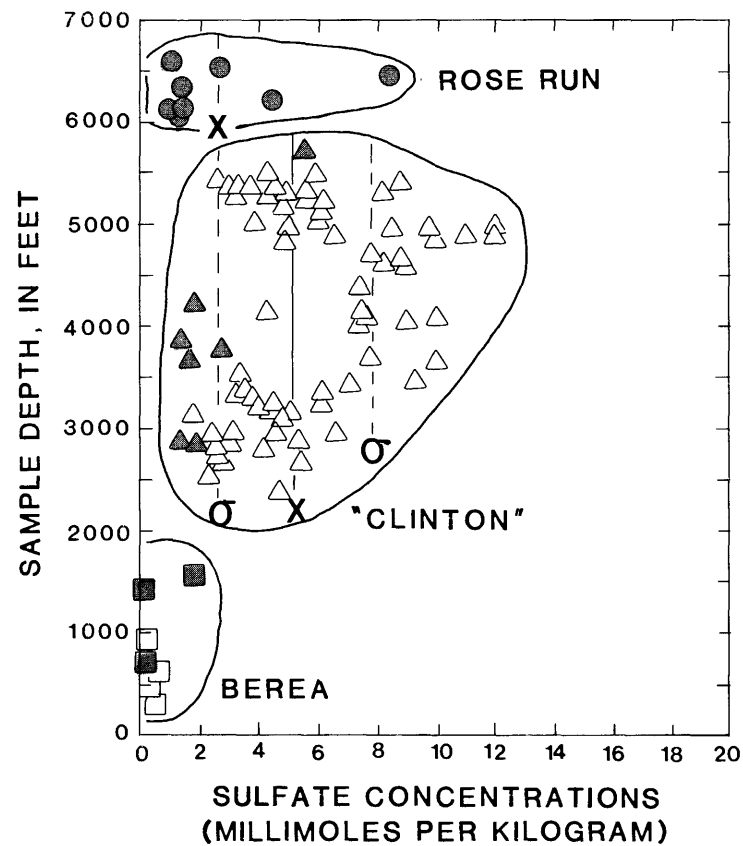
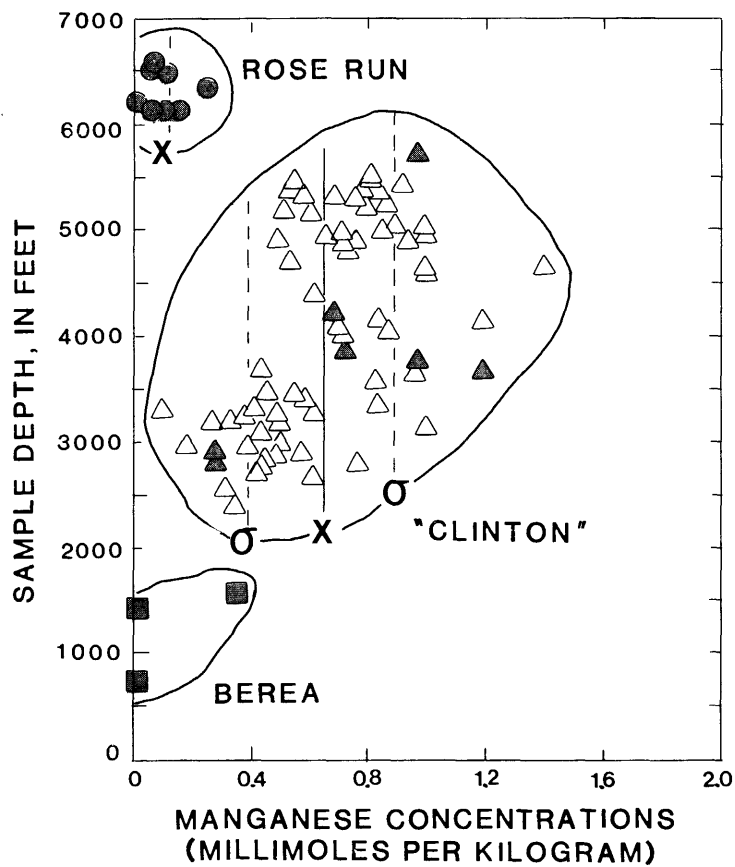


Figure 9.--Concentrations of manganese and sulfate versus sample depth for Berea, "Clinton", and Rose Run brines (solid data symbols represent samples collected for this study; open symbols are data from Stout and others, 1932, and Stith, 1979).

Envelopes have been drawn around the data from a given sandstone to illustrate the range of concentrations found for brines in each sandstone. The means and standard deviations of the concentrations are plotted for each sandstone.

In figure 6, the mean concentrations of sodium and chloride increase as sample depth increases. Even though the concentration scale is expanded for sodium relative to chloride, the fact that the chloride concentrations vary over twice the range for sodium is apparent. The sodium concentrations are tightly grouped within the individual sandstones as well as interformationally. The mean and standard deviation markers are useful for seeing overlapping concentration ranges between the sandstones. The "Clinton" and Rose Run sandstones overlap within one standard deviation of the mean sodium and chloride concentrations. In both cases, the Berea samples plot independently of the "Clinton" and Rose Run with respect to standard deviation, although some data points overlap.

Figure 7 shows plots for calcium and magnesium, which are classified as major constituents in Ohio oilfield and gasfield brines. The mean concentrations of calcium and magnesium increase as sample depth increases. Calcium concentrations are grouped well for the Berea and Rose Run sandstones. The Rose Run has one sample plotting to the far left of the grouping of the seven other samples. This less concentrated sample represents the Rose Run in Ashtabula County and the other points represent Coshocton County. The "Clinton" data cover a fairly wide concentration range for both calcium and magnesium.

An excellent separation exists between calcium concentration for the Berea and Rose Run brines. Magnesium concentrations separate for Berea brines and the samples of Rose Run brine collected in Coshocton County. The standard deviation markers for calcium overlap between the "Clinton" and Rose Run brines. The standard deviations about the means for magnesium overlap for all three sandstones.

The concentrations of three minor constituents (potassium, bromide, and sulfate) and one trace constituent (manganese) appear in figures 8 and 9. The minor constituents have notably less variation in concentration (smaller standard deviations) than the major constituents. The mean concentrations of potassium and bromide (fig. 8) follow the trend of increasing with sample depth, however, the mean concentrations of sulfate and manganese (fig. 9) do not. The Rose Run brines are depleted in both sulfate and manganese relative to the "Clinton" brines.

Potassium has perhaps the most distinct interformational groupings of any of the constituents examined. Mean potassium concentrations are well separated; there is no overlap even within two standard deviations of each mean value. Bromide concentrations are also tightly grouped for the "Clinton" brines but the interformational differences in bromide are not as pronounced as those for potassium. Bromide is known to be conservative in a

geochemical sense, therefore, bromide may prove useful as a tracer constituent for brines in Ohio. Potassium may participate in ion-exchange and adsorption reactions with clay minerals, thus it is not as conservative geochemically as bromide. The well-defined differences in potassium concentration between the sandstones, however, should prove ideal for use in the geochemical tracing of brines.

Duncan's multiple range test and Tukey's studentized range test were performed to evaluate whether differences exist between mean values of chemical concentration from samples of N observations. In this study, the three sample groups are the Berea, the "Clinton", and the Rose Run. These data are unbalanced because they do not have the same number of observations in each sample group. The chemical data from each sandstone were found to follow normal probability distributions. Standard F tests showed that significant differences existed between the sandstones. The Duncan and Tukey mean separation tests were used to specifically determine which brines were different. Both tests were done because Duncan's test is more prone to rejecting the null hypothesis that all brines are the same, when indeed they may be the same (Type I statistical errors). A 95-percent confidence interval was chosen for the tests.

The results of Tukey's and Duncan's tests are presented in table 8. The mean concentration and the corresponding number of samples are listed for each sandstone by chemical constituent. Significantly different sample means are denoted by different letters (A, B, or C). These results show that the dominant (sodium, chloride), major (calcium, magnesium), and three of the minor constituents (potassium, bromide, and sulfate) all have interformational means that are statistically different at the 95-percent confidence limit. The mean concentrations of manganese and strontium are not different in each sandstone, but have combinations of similarities and differences. Strontium concentrations are restricted to a rather narrow range (4.3-14.1 mmol/kg) in "Clinton" brines. This fact should be useful for identifying "Clinton" brines, and should be tested further as more data for the Berea and Rose Run are collected. Mean concentrations of iron and iodide are statistically equivalent in all three sandstones.

Density and dissolved-solids data also are compared in table 3. The mean values of density and total dissolved solids are statistically different at the 95-percent confidence limit for brines from all three sandstones.

The statistical analysis has shown that the mean concentrations of all constituents, except iron, strontium, and the trace constituents, have statistically significant differences. This information, when used in conjunction with plots of the actual range of concentrations that exist for each sandstone (figs. 6-9) help to identify the constituents that will aid in differentiating between brines from the Berea, "Clinton," and Rose Run sandstones.

Table 8.--Results of Tukey's studentized range test and Duncan's multiple range test for statistical differences in the concentration of chemical constituents in Ohio brines

[T, Tukeys test; D, Duncan's test; X, mean concentration in mmol/kg of brine, except where specified otherwise; N, number of samples. Means with the same letter are not significantly different at the 0.05 level]

	Property or constituent																			
	Density (grams per milliliter)				Dissolved solids, total (mg/kg)				Calcium				Magnesium				Sodium			
Sandstone	T	D	X	N	T	D	X	N	T	D	X	N	T	D	X	N	T	D	X	N
Berea	A	A	1.078	10	A	A	95,100	14	A	A	170	14	A	A	77	14	A	A	1,200	14
"Clinton"	B	B	1.179	78	B	B	227,000	78	B	B	690	78	B	B	140	78	B	B	2,200	78
Rose Run	C	C	1.217	8	C	C	270,000	8	C	C	880	8	C	C	220	8	C	C	2,600	8
	Chloride				Potassium				Sulfate				Bromide				Iodide			
	T	D	X	N	T	D	X	N	T	D	X	N	T	D	X	N	T	D	X	N
Berea	A	A	1,700	14	A	A	4.3	10	A	A	0.5	8	A	A	6.3	10	A	A	0.07	6
"Clinton"	B	B	3,900	78	B	B	28	76	B	B	5.4	78	B	B	21	78	A	A	0.09	78
Rose Run	C	C	5,100	8	C	C	86	8	C	C	2.8	8	C	C	47	8	A	A	0.12	8
	Iron				Manganese				Strontium											
	T	D	X	N	T	D	X	N	T	D	X	N								
Berea	A	A	2.9	4	A	A	0.12	3	A	A	3.3	3								
"Clinton"	A	A	3.3	36	B	B	0.66	78	B	B	9.9	76								
Rose Run	A	A	2.8	8	A	A	0.11	8	A,B	A,B	5.7	7								

A point to note in figures 6 through 9 is that several of the solid data points (samples collected for this study) plot outside of the one-standard-deviation bounds in concentration for the Berea and "Clinton" brines. The shifts in concentration data away from those reported by Stith (1979) and Stout and others (1932) do not appear related to sample geography, and may be temporal in nature. Stith's samples were analyzed from 1972 through 1974, and samples for this report were analyzed in 1982. On a geologic time scale, this period is very short, and an additional 8 to 10 years of subsurface water-rock interaction would be unlikely to cause concentration shifts of the magnitude that are observed. An example is the shift of 20-40 mmol/kg in potassium concentration between the 1972-74 and the 1982 analyses for "Clinton" wells in Licking and Hocking Counties. Another possible explanation for the apparent differences in concentration may be the use of different and (or) more or less sensitive analytical techniques. Sample handling and preparation are also possible causes of differences in concentration.

Table 9 shows a comparison of the methods used for sample collection, sample preservation/preparation, and chemical analysis between this study and the studies by Stith (1979) and Stout and others (1932). The most obvious differences between studies are (1) method of sample collection, and (2) the analytical methods for sulfate, chloride, and iodide. Stith's data are based almost entirely on samples collected from brine storage tanks. In contrast, more than 50 percent of the samples collected for this study were taken from the wellhead bleeder valve. The "Clinton" data in figures 6 through 9 that appear as solid symbols plot at higher concentrations than the upper one-standard-deviation boundary for chloride, sodium, magnesium, manganese, bromide, and potassium. "Clinton" data (solid symbols) for sulfate concentration plot below the lower one-standard-deviation boundary. Calcium data for the "Clinton" are generally conformable between studies.

For the "Clinton" data in figures 6 through 9, 20 solid data points plot at concentrations higher than the upper one-standard-deviation boundaries. Of the 20 anomalous analyses, 15 represent samples taken from the wellhead bleeder valve. All of the anomalous solid data points for sodium and chloride are wellhead samples. These results suggest that chemical transformations may be taking place within the brine storage tank. The lower concentrations of dissolved constituents in Stith's study may have resulted from precipitation of mineral phases from a saturated brine. Saturation conditions found in the host rock formation may change significantly as the brine is stored at land-surface temperatures and pressures. Wellhead samples have not been subjected to the storage-tank environment and may, therefore, be a better representation of the formation waters.

Alternatively, because 25 percent of the high concentration samples in this study were from storage tanks, evaporative concentration of the samples is possible during filtration, sample preservation, or in laboratory storage.

Table 9.--Comparison of sample-collection, preparation, and chemical analysis procedures for brine samples

[AAS, Atomic Absorption Spectrometry]

Sample-collection method	This study	Stith (1979)	Stout and others (1932)
	Number of samples		
Brine storage tank-----	8	59	(Samples were collected between 1888 and 1931 by the U.S. Geological Survey and Ohio Geological Survey. Procedures for sample collection, preparation, and chemical analysis are not known. Comments reported with the analyses indicate filtration was not done, and results may represent total instead of dissolved concentrations.)
Wellhead bleeder valve----	10	0	
Separator unit-----	--	6	
Unknown-----	--	6	
Sample preparation method	Constituents		
Filtration through 0.45µ membrane-----	Ca, Mg, Na, K, Mn, Sr, Fe, Zn, Al, SiO ₂ , SO ₄ , Cl, Br, I	All constituents	
HNO ₃ acidification----	Ca, Mg, Na, K, Mn, Fe, Sr, Zn, Al	All constituents	
Chemical constituent	Analytical method		
pH-----	Field determination	Laboratory determination	
Calcium-----	AAS - direct	AAS - direct	
Magnesium-----	AAS - direct	AAS - direct	
Sodium-----	AAS - direct	AAS - direct	
Potassium-----	AAS - direct	AAS - direct	
Lithium-----	--	AAS - direct	
Manganese-----	AAS - direct	AAS - direct	
Strontium-----	AAS - direct	AAS - direct	
Iron-----	AAS - direct	--	
Zinc-----	AAS - direct	AAS - direct	
Aluminum-----	AAS - direct	--	
Silica-----	Colorimetric, molybdate blue	--	
Sulfate-----	Methyl - thymol blue, Colorimetric, Complexometric	Gravimetric	
Chloride-----	Ferric thiocyanate, Colorimetric	Titrimetric, Mohr	
Bromide-----	Titrimetric, hypochlorite oxidation	Titrimetric, hypochlorite oxidation	
Iodide-----	Colorimetric, ceric arsenious oxidation	Titrimetric (oxidation?)	

Variations between analytical techniques cannot be discounted to explain differing concentrations, especially with the results for sulfate. The colorimetric analyses performed for this study may be less sensitive or have a poorer recovery than the gravimetric (BaSO_4 precipitation) method employed by Stith (1979). However, BaSO_4 gravimetric procedures are prone to coprecipitation problems, especially in solutions containing iron. Coprecipitation of iron with the barium sulfate would cause high results for sulfate.

The lack of documentation available on the techniques used by Stout and others (1932) preclude comparison to the current investigation. From the comments included with Stout's analyses that refer to particulate matter in the samples, it can only be inferred that filtration was not done. The data of Stout and others (1932) may be total concentrations rather than dissolved concentrations.

This comparison of methods and techniques illustrates that analytical results may be affected by many factors. Combining data from different sources may lead to confusion unless care is taken to ensure consistency in the sampling, sample handling, and analytical techniques employed. The adoption of consistent techniques for sample handling, preparation, and analysis is warranted in future studies of this type.

In summary, interformational differences in concentrations of sodium, chloride, calcium, magnesium, potassium, bromide, and sulfate could be discriminated in all three sandstones. Iron, strontium, and the trace constituents iodide and manganese have mean concentrations that could not be discriminated for all three sandstones.

Chemical variability within the "Clinton" brines is most pronounced. This variability makes it difficult to differentiate "Clinton" brines from Berea and Rose Run brines by means of sodium, magnesium, chloride, and calcium concentrations. Berea and Rose Run brines, on the other hand, may be distinguished relatively easily due to their different mean concentrations of sodium, magnesium, chloride, and calcium, and ranges of concentrations that do not overlap.

Potassium and bromide appear to be the most useful inorganic chemical indicators for brine identification because their concentration ranges are narrow within each sandstone. Bromide has unique concentration ranges for the Berea and Rose Run brines. "Clinton" brines have sufficient overlap in bromide concentration to make discrimination from Rose Run and Berea brine difficult. The means of potassium concentration are displaced so that no overlap exists in the potassium data for all three brines. Berea, "Clinton," and Rose Run brines are most easily identified by potassium concentrations.

Concentration Ratios as Geochemical Tracers

Ratios of the concentrations of selected constituents are a practical means of geochemically tracing the source of a brine that has been diluted by mixing with ground or surface waters. Once a brine has been diluted, individual constituent concentrations lose their utility as a method for differentiating brines from different formations. Assuming that all constituents in a brine are diluted by the same amount, concentration ratios present in the original brine should remain the same in a diluted sample. This "equal-dilution" assumption may be an oversimplification in light of the many geochemical reactions that may alter ion concentrations in the ground- and surface-water environments. Nevertheless, concentration ratios of selected constituents are useful for determining the source formation of a brine that has a history of mixing and dilution with surface and (or) other subsurface waters.

Concentration ratios were calculated for possible permutations of chloride, calcium, magnesium, sodium, potassium, and bromide concentrations for each of the three sandstones.¹ The mean ratio values for each sandstone were compared by Duncan's multiple range test and Tukey's studentized range test for statistical significance. A 95-percent confidence limit again was chosen for the tests.

The results of the statistical tests appear in table 10. The usefulness of the various mean ratios to differentiate between formations is apparent. The K:Na ratio is the only one to pass both Tukey's and Duncan's tests for statistical differences in the mean ratio values of all three sandstones. The K:Br and Cl:Br values are significantly different for all three sandstones in Duncan's test, but the "Clinton" and Rose Run brines could not be differentiated by K:Br and Cl:Br in the Tukey test. The "Clinton" and Rose Run brines have no statistical differences in mean values for Ca:Mg, Na:Ca, Na:Cl, Mg:K, Ca:K, Cl:Ca, Mg:Br and Na:Br. The Berea and "Clinton" brines could not be differentiated by mean K:Cl and Ca:Br values. The Na:Mg and Cl:Mg ratios are not statistically different for any of the sandstones.

Figure 10 is used to illustrate the utility of K:Na and Cl:Br concentration ratios determined by the statistical analysis. There is a break in the K:Na ratio at 0.0060 between all "Clinton" brine samples and all Berea brine samples, except for the Berea samples from Noble County (which are plotted at Cl/Br = 0 because data are lacking for Br⁻). A second break at K:Na = 0.024 corresponds to change from "Clinton" brine samples to Rose Run brine samples. The Cl:Br values appear to be more continuous from sandstone to sandstone, and no characteristic interformational breaks are apparent.

¹Ratios were not computed using aluminum, iron, iodide, lithium, manganese, strontium, or zinc because of limited data for Berea brines.

Table 10.--Results of Tukey's studentized range test and Duncan's multiple range test for statistical differences in mean concentration ratios of chemical constituents in Ohio brines

[T, Tukeys test; D, Duncan's test; X, mean of individual concentration ratios; N, number of samples. Means with the same letter are not significantly different at the 0.05 level]

	Property or constituent																			
Sandstone	Calcium/Magnesium				Sodium/Calcium				Sodium/Magnesium				Sodium/Chloride				Potassium/Chloride			
	T	D	X	N	T	D	X	N	T	D	X	N	T	D	X	N	T	D	X	N
Berea	A	A	2.2	14	A	A	8.1	14	A	A	17	14	A	A	0.81	14	A	A	.0058	10
"Clinton"	B	B	4.1	78	B	B	3.5	78	A	A	19	78	B	B	0.58	78	A	A	.0074	78
Rose Run	B	B	5.4	8	B	B	3.1	8	A	A	13	8	B	B	0.56	8	B	B	.0174	8
	Potassium/Sodium				Magnesium/Potassium				Chloride/Bromide				Potassium/Bromide				Calcium/Potassium			
	T	D	X	N	T	D	X	N	T	D	X	N	T	D	X	N	T	D	X	N
Berea	A	A	.005	10	A	A	72	10	A	A	410	10	A	A	0.46	8	A	A	151	10
"Clinton"	B	B	.013	78	B	B	5.3	78	B	B	203	78	B	B	1.5	78	B	B	26	78
Rose Run	C	C	.034	8	B	B	2.6	8	B	C	126	8	B	C	2.1	8	B	B	10	8
	Calcium/Bromide				Chloride/Magnesium				Chloride/Calcium				Magnesium/Bromide				Sodium/Bromide			
	T	D	X	N	T	D	X	N	T	D	X	N	T	D	X	N	T	D	X	N
Berea	A	A	38	10	A	A	22	14	A	A	10	14	A	A	19	10	A	A	304	10
"Clinton"	A	A	36	78	A	A	32	78	B	B	5.9	78	B	B	7.4	78	B	B	118	78
Rose Run	B	B	22	8	A	A	24	8	B	B	5.8	8	B	B	5.6	8	B	B	66	8

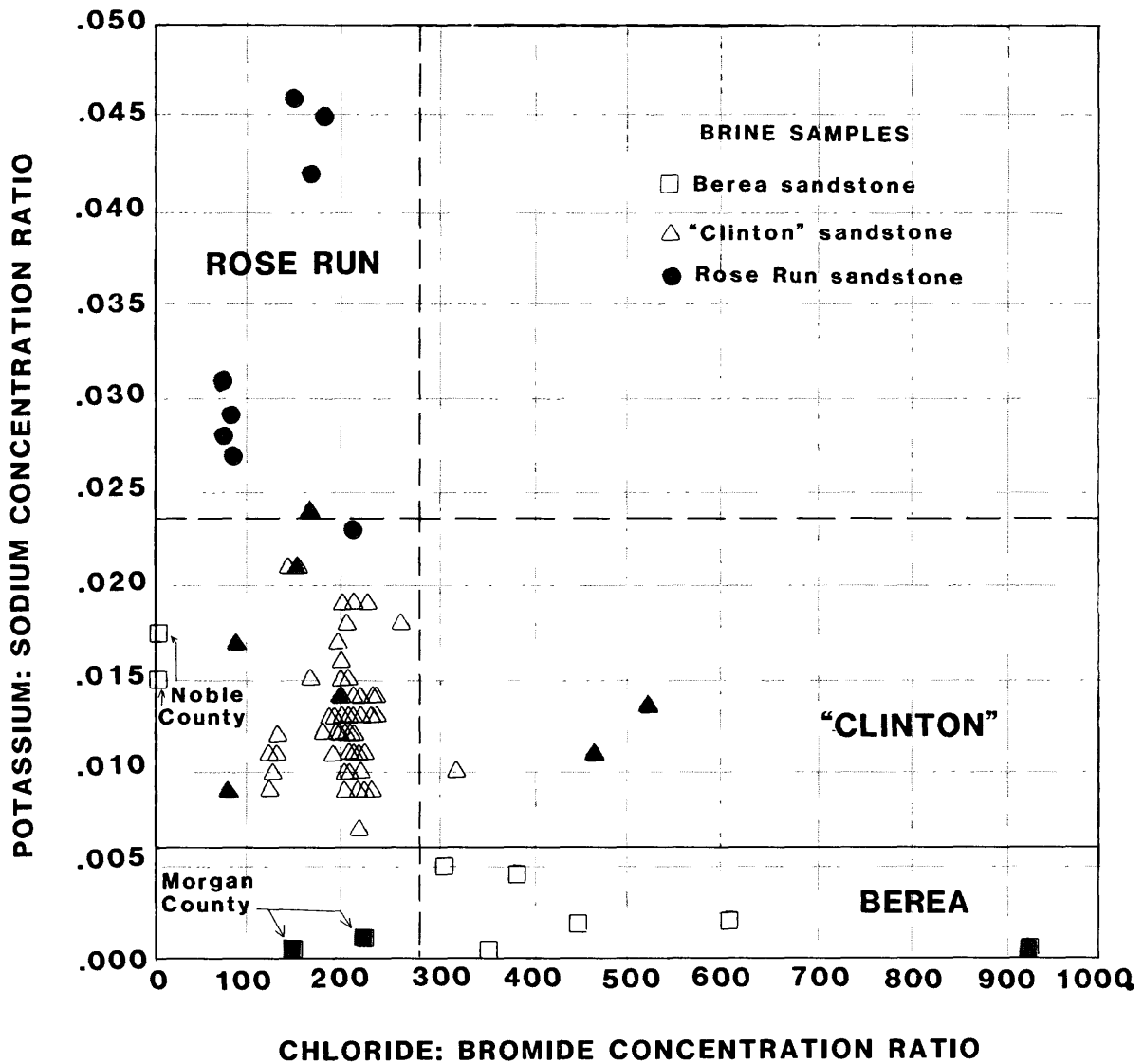


Figure 10.--Potassium: sodium concentration ratios as a function of chloride:bromide concentration ratios of brine samples. Solid data symbols represent samples collected for this study; open symbols are data from Stout and others, 1932, and Stith, 1979.

K:Na is plotted versus Ca:Mg in figure 11, and the interformational breaks in the K:Na values are easy to distinguish. The statistical testing determined that Ca:Mg could be used to differentiate the Berea from the Rose Run and "Clinton," but that the "Clinton" and Rose Run could not be differentiated using Ca:Mg. The vertical line plotted at Ca:Mg = 3 demonstrates this relationship.

The reason for the distinct separations or breaks between formations for K:Na is related to the way the amount of potassium and sodium in solution varies individually within the three sandstones. Sodium is a dominant constituent that has a narrow interformational range of concentration. Sodium effectively acts to normalize potassium and permits the naturally occurring variations in potassium concentration to be used for geochemical tracing that involves dilution.

There is poor agreement between Berea samples from Noble County and Morgan County with other Berea samples. This emphasizes that only a limited number of samples are available for the Berea and Rose Run brines. Conclusions based on 8 Rose Run samples and 14 Berea samples are obviously preliminary.

However, concentration ratios do provide a geochemical tool to help identify brines and their source formation. Characteristic concentration ratios appear to exist for brines from limited geographic areas (that is, within counties). Harrison (1983) has recently described a hydrogeologic model for evaluating ground and surface-water contamination from gas-well brines in northwestern Pennsylvania. Harrison stressed the proper identification of the flow system involved in a particular contamination study. Flow systems were classified as regional, intermediate, and local. This general type of classification also may be useful when interpreting chemical data.

Establishing the flow system and eliminating unlikely sources of brine contamination is important in geochemical tracing of brines. For example, a domestic water well in Coshocton County will unlikely be contaminated by Rose Run brine from Ashtabula County. Therefore, for this example, a knowledge of wells in the vicinity of the contamination would be useful. If wells in the vicinity are producing from the "Clinton" or Rose Run, then chemical data should first be compared that relates specifically to the Rose Run and "Clinton" in Coshocton or adjoining counties. In this case, K:Na is 0.0124 for "Clinton" brines and K:Na ranges from 0.0230 to 0.0462 for Rose Run brines in Coshocton County. Ideally, a difference of this magnitude would be detectable and would provide evidence for the source formation of the brine contamination. A more extensive data base (including multiple samples from oilfields and gasfields) would be helpful to support geochemical studies for tracing brine contamination.

In summary, the ratio of potassium to sodium offers the best general means of chemically differentiating brines from the Berea, the "Clinton," and the Rose Run sandstones. Other ratios may have specific applications depending on the problem involved.

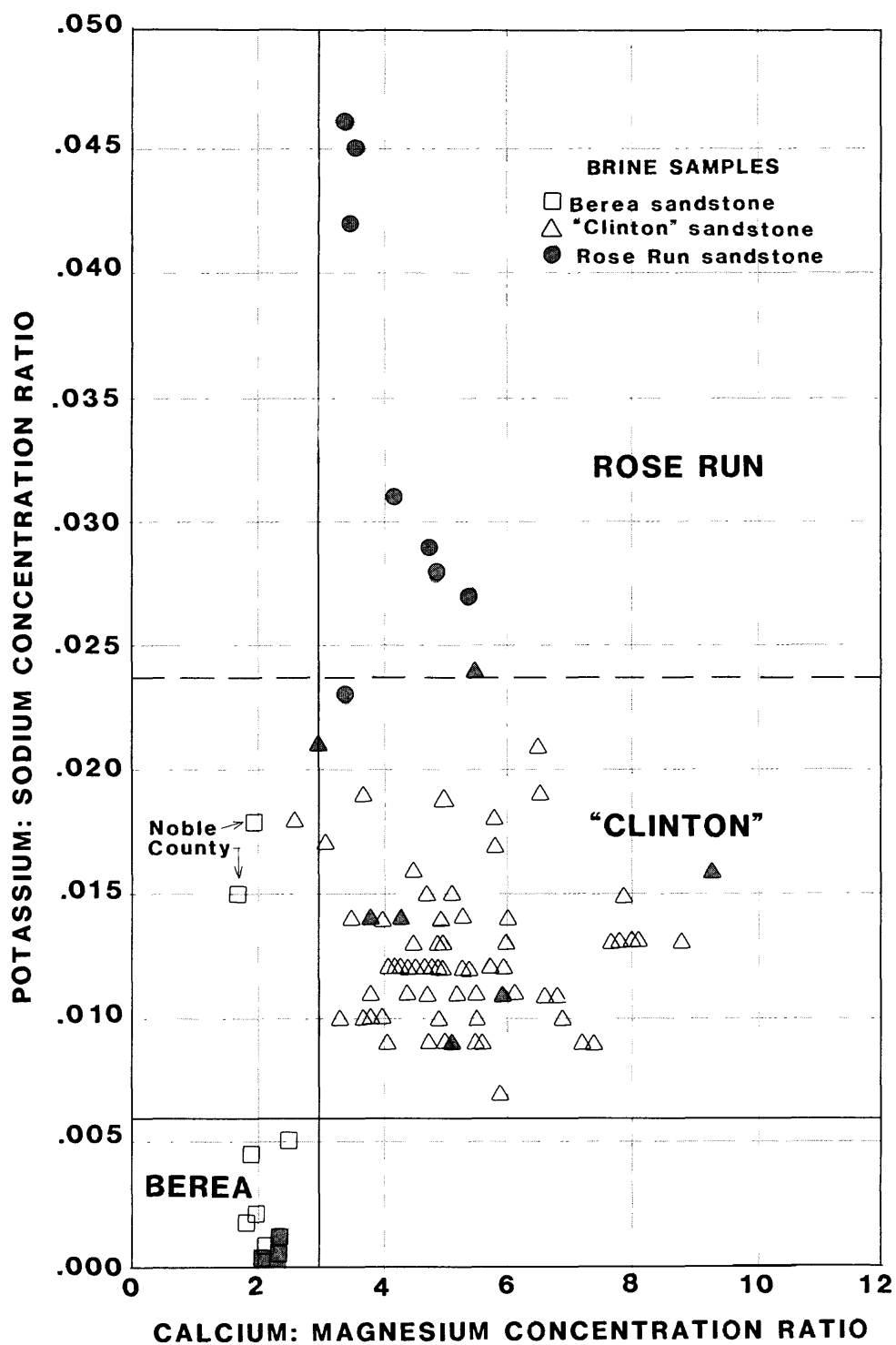


Figure 11.--Potassium: sodium concentration ratios as a function of calcium: magnesium concentration ratios of brine samples. Solid data symbols represent samples collected for this study; open symbols are data from Stout and others, 1932, and Stith, 1979.

ISOTOPIC CHARACTERISTICS

Hydrogen- and Oxygen-Isotope Geochemistry

The stable-isotope geochemistry of hydrogen and oxygen can be utilized to determine the origin of the water molecules in aqueous samples and minerals. Water is the dominant component of Ohio's oilfield and gasfield brines. The complex chemical characteristics of these subsurface brines may be better understood if the origin of the water in the brine can be determined by isotopic techniques.

Subsurface brines in the mid-continent region of the United States and Canada may have originated as (1) seawater (connate water) present at the time the host rock units were deposited, which has been retained, evaporated and reacted within the host rock; or as (2) meteoric water (atmospheric precipitation) that has migrated into the host rocks as recharge water and dissolved, exchanged, or precipitated chemical and mineral components with the rocks along its path.

Clayton and others (1966) and Hitchon and Friedman (1969) have demonstrated that the oxygen and hydrogen stable-isotopic composition of water in oilfield brines from several sedimentary basins in North America reflects the origin of the water. Their isotopic studies were not successful, however, in distinguishing brines from individual stratigraphic units within a given sedimentary basin. Nevertheless, stable isotopes may provide useful insight on brine evolution in Ohio as evidenced in brine studies in the nearby states of Michigan and Illinois (Clayton and others, 1966). The stratigraphy of the brine-bearing rocks of Michigan and Illinois are generally similar to those found along the flanks of the Appalachian basin in eastern Ohio.

Hydrogen (D/H) and oxygen ($^{18}O/^{16}O$) stable isotope ratios are reported as δD or $\delta^{18}O$ values in units of parts per thousand (permil) relative to the standard, SMOW (Standard Mean Ocean Water). Analytical precision is ± 2.0 permil for hydrogen and ± 0.20 permil for oxygen.

The hydrogen and oxygen isotopic compositions of Ohio oilfield brines appear in table 11. Figure 12 shows the δD and $\delta^{18}O$ values of Ohio brine plotted against the salinity (total dissolved-solids concentration) of the brine. The δD values show no relationship to salinity. The $\delta^{18}O$ values have a poorly correlated, positive relationship with salinity.

Figure 13 shows the relationship between δD and $\delta^{18}O$ for Ohio brines, brines from the Illinois and Michigan basins (Clayton and others, 1966), and for meteoric water. The Ohio brines all plot below the global meteoric water line and form a linear trend with a slope of about 2, which can be extrapolated to intersect the meteoric water line at a composition of $\delta D = -45.0$ permil and $\delta^{18}O = -7.0$ permil.

Table 11--Hydrogen, oxygen, and sulfate sulfur isotopic compositions of Ohio brines

Sandstone and sample number	Isotopic ratios, in permil		
	^a Deuterium: hydrogen	^a Oxygen 18: oxygen 16	^b Sulfur 34: sulfur 32
<u>Berea</u>			
1BMOR	-13.5	-2.2	--
2BMOR	-35.0	-2.9	+4.6
3BLIC	-34.5	-5.5	--
<u>"Clinton"</u>			
1CMOR	-33.5	-1.7	+16.9
2CLIC	-34.5	-1.9	+26.5
3CGUR	-38.0	-3.1	+21.8
4CASH	-48.0	-4.8	+18.6
5CASH	-37.5	-4.1	+21.7
6CHOL	-32.0	-1.5	+27.9
7CHOC	-35.0	-2.2	+18.1
<u>Rose Run</u>			
1RCOS	-33.0	-1.6	+27.6
2RCOS	-33.0	-1.4	+28.3
3RCOS	-32.5	-1.3	+26.9
4RCOS	-32.5	-1.5	+27.8
5RASH	-40.5	-4.2	+10.6
6RCOS	-30.0	-1.3	+28.4
7RCOS	-31.0	-3.7	+24.1
8RCOS	-33.0	-1.8	+25.4

^aRelative to Standard Mean Ocean Water (SMOW)

^bRelative to Cañon Diablo Troilite (CDT)

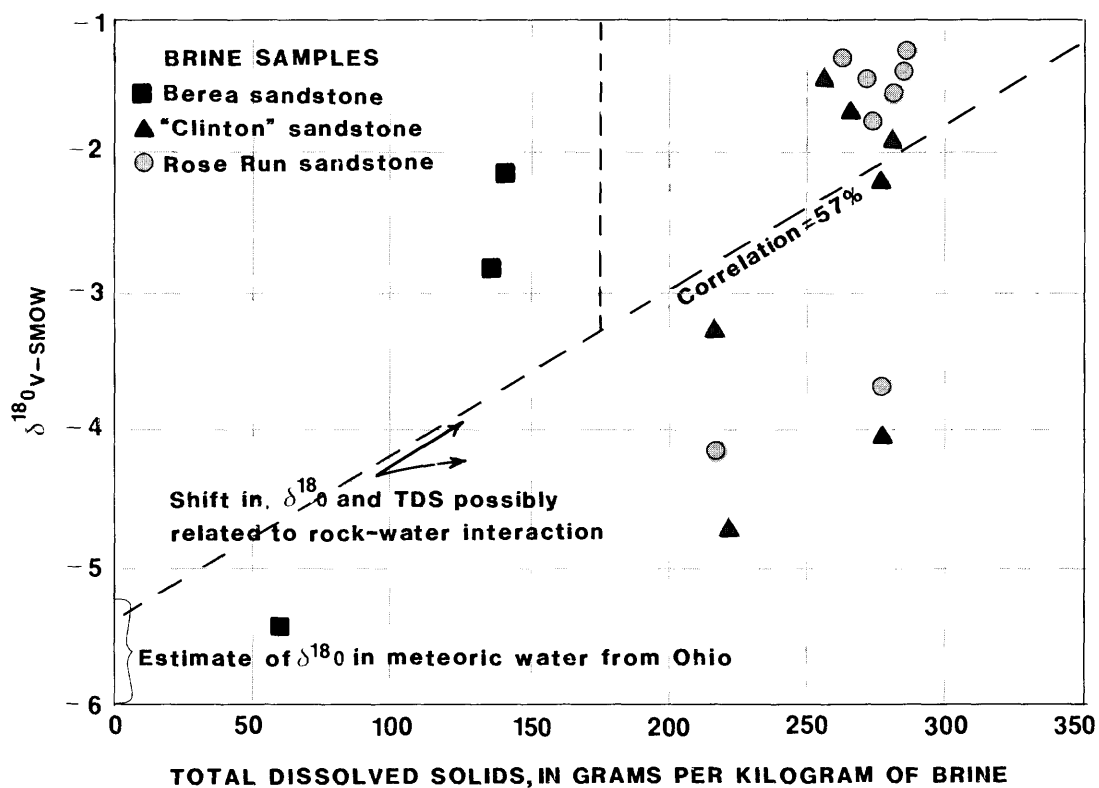
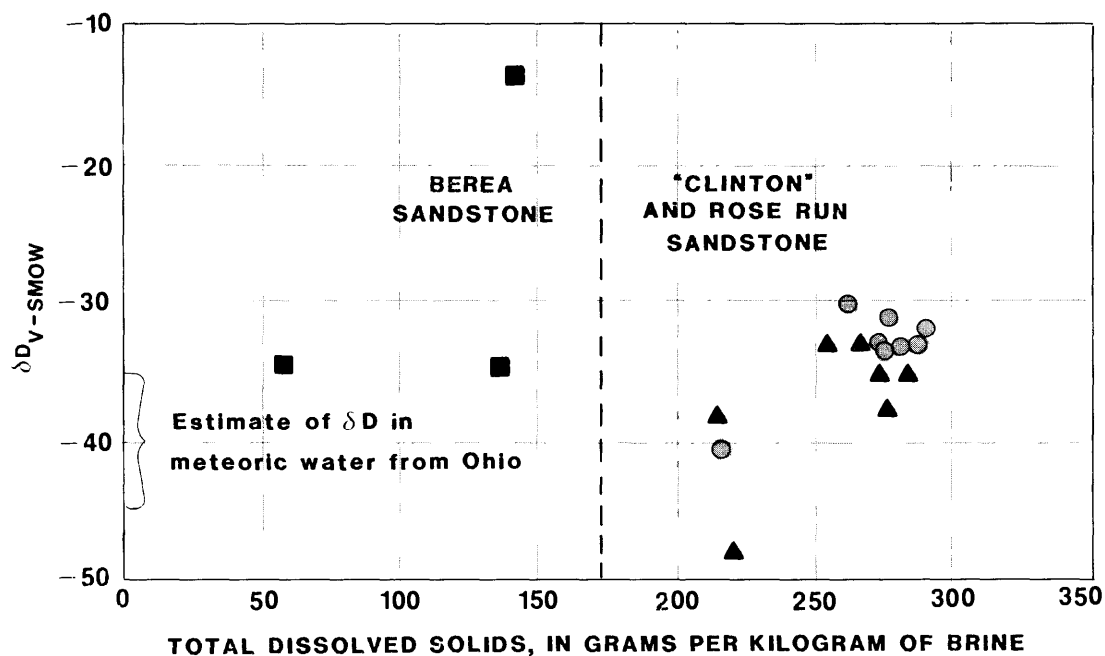


Figure 12.--Graph of δD and $\delta^{18}O$ as a function of total dissolved solids for brine samples.

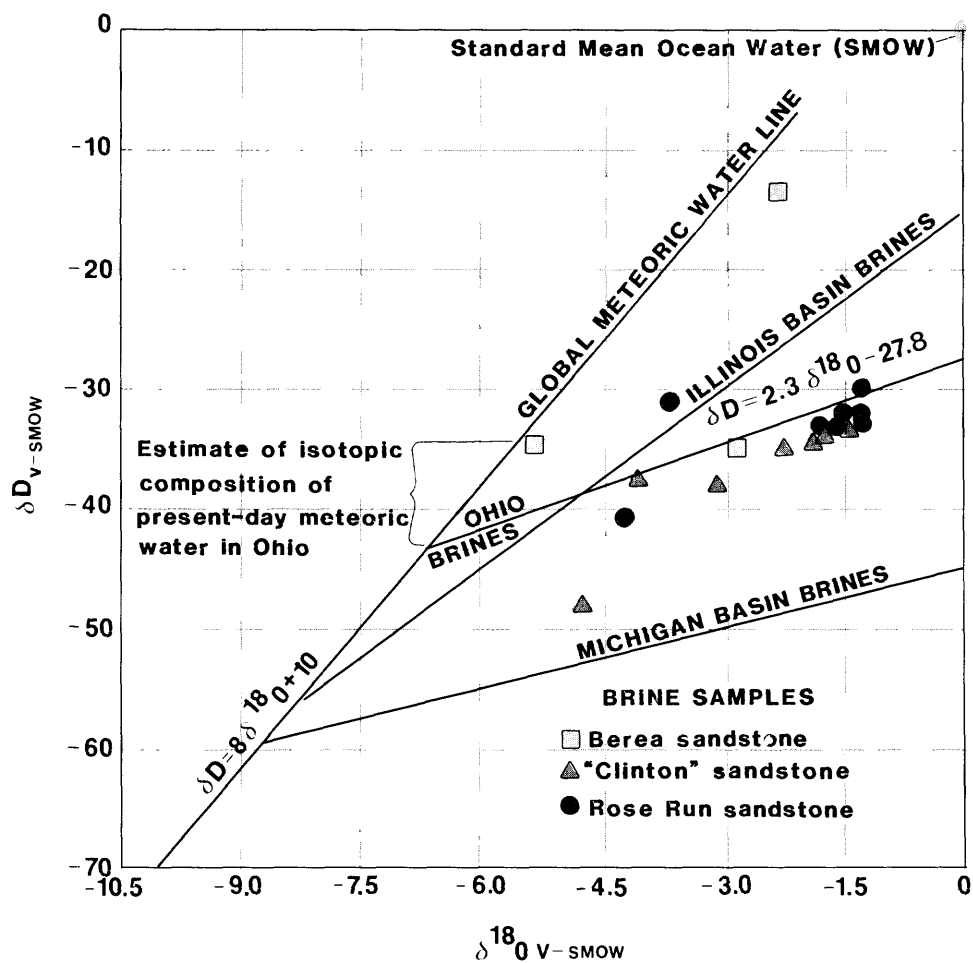


Figure 13.--Graph showing relationship between hydrogen and oxygen isotope composition for Ohio brine samples, brines from Michigan and Illinois basins (Clayton and others, 1966) and the global meteoric water line (Craig, 1961).

Such trends can originate in three ways: (1) By progressive evaporation of water of the composition where the brine line intersects the meteoric water line, (2) by variable mixing of the above meteoric water with some heavier water also plotting along the Ohio brine line, or (3) by rock-water interaction resulting in large increases in the $\delta^{18}\text{O}$ value of the brine with only minor increases in its δD value. As the trend of the Ohio brines, like those of the Illinois and Michigan brines, does not intersect the meteoric water line anywhere near the isotopic composition of seawater, seawater can be completely ruled out as a source of the H_2O , but cannot be ruled out as a source of solutes. A meteoric source of the H_2O is indicated. The Ohio brines intersect the global meteoric water line at the approximate position of present-day precipitation in Ohio, which suggests that the climate where the brine water originated as precipitation was similar to that now.

The brines from the Berea, "Clinton", and Rose Run sandstones are not distinguishable by their hydrogen and oxygen isotopic composition. The only notable difference is that the Berea brines seem to fall along the global meteoric water line.

The origin of the solutes or salts in the brine cannot be deduced from the oxygen and hydrogen isotopic composition of the brine fluids. The chemical and isotopic evolutions of the brines need not be directly related. However, the slope of the Ohio brine data (fig. 13) provides information on the alteration of the water. The slope of 2 is too low to be explained solely by evaporation of meteoric water. A slope of zero would be evidence for substantial oxygen isotope exchange during rock-water interaction. Such interaction is typically accompanied by only minor hydrogen isotope exchange. As there is considerable controversy whether rocks ever contain sufficient exchangeable hydrogen to cause any significant positive shift in the hydrogen isotopic composition of the water, it is likely that evaporation is the cause of some of the isotope variation (Carol Kendall, U.S. Geological Survey, written commun., 1984). On the other hand, the low correlation of increasing $\delta^{18}\text{O}$ with salinity and lack of correlation of δD with salinity suggests that rock-water interaction was significant in the isotopic and chemical evolution of the oilfield brines.

Sulfate Sulfur Isotopes as Geochemical Tracers

Sulfur isotopes have also been used as geochemical tracers in ground-water studies. Rye and others (1981) found characteristic ranges of $\delta^{34}\text{S}$ for sulfate in oxidizing and reducing ground waters of the Floridan aquifer system (in Florida) and the Edwards aquifer (in Texas). Oxidizing waters in recharge areas were characterized by a $\delta^{34}\text{S}$ range of + 8.1 to + 19.1 permil relative to CDT (Cañon Diablo Troilite). Reducing ground water was isotopically heavier, and had $\delta^{34}\text{S}$ values that ranged from +18.3 to +26.7 permil. One brine sample from the Charlotte oilfield in Texas had a $\delta^{34}\text{S}$ value of +25.8 permil.

Rye and coworkers suggested the heavy $\delta^{34}\text{S}$ values in reducing waters resulted from a two-stage process involving dissolution of sulfate minerals from evaporites in the host rocks and subsequent $\delta^{34}\text{S}$ enrichment by bacterial reduction of sulfate to sulfide. Sulfate minerals in evaporite sequences within the aquifer systems had the characteristic sulfur isotopic composition of marine sulfate at the time the rocks were deposited (Faure, 1977, p. 411).

The $\delta^{34}\text{S}$ values of Ohio oilfield brines appear in table 10. These data are plotted in figure 14 and show a range of $\delta^{34}\text{S}$ values from +4.6 to +28.4 permil. The $\delta^{34}\text{S}$ data have a poor linear correlation with $\delta^{18}\text{O}$. Despite the scatter of data, the two linear trends may suggest water-rock interaction involving dissolution of sulfate minerals from the host rock formations is responsible for the observed $\delta^{34}\text{S}$ values. The heaviest sulfur is in brine from the Cambrian and Ordovician Rose Run sandstone. These heavy isotopic compositions agree well with that of marine sulfates in Cambrian rocks (fig. 14).

Samples from the "Clinton" sandstone show considerable scatter in $\delta^{34}\text{S}$, but the linear trend of the data suggests a correlation with the lighter sulfur isotopic composition of marine sulfate during the Silurian Period. Unfortunately, only one Berea sample was able to be prepared for sulfur isotope analysis. This one sample agrees with the work of Rye and others (1981), which shows lighter $\delta^{34}\text{S}$ values in ground water from recharge areas. More data are necessary to further test the attributes of $\delta^{34}\text{S}$ as a geochemical tracer. Difficulties in sample preparation and the relatively high cost of isotopic analysis will undoubtedly hinder further testing and application of $\delta^{34}\text{S}$ as a geochemical tracer.

In summary, δD and $\delta^{18}\text{O}$ data indicate meteoric water as a source of the water matrix in Ohio gasfield and oilfield brines. However, δD and $\delta^{18}\text{O}$ values are not useful as tracers of brine from individual stratigraphic horizons. The $\delta^{34}\text{S}$ value for sulfate may provide a means of differentiating near-surface sources of sulfate from deep-seated ("Clinton" and Rose Run) brine sources. The usefulness of $\delta^{34}\text{S}$ as a geochemical tracer is dependent upon the extent of dilution, mixing, and reaction the brine undergoes prior to sampling in an identification study. More samples would be necessary to verify the anomalously light sulfur isotopic composition of Berea brine, and more study is needed to further assess the natural variation in $\delta^{34}\text{S}$ in specific study areas.

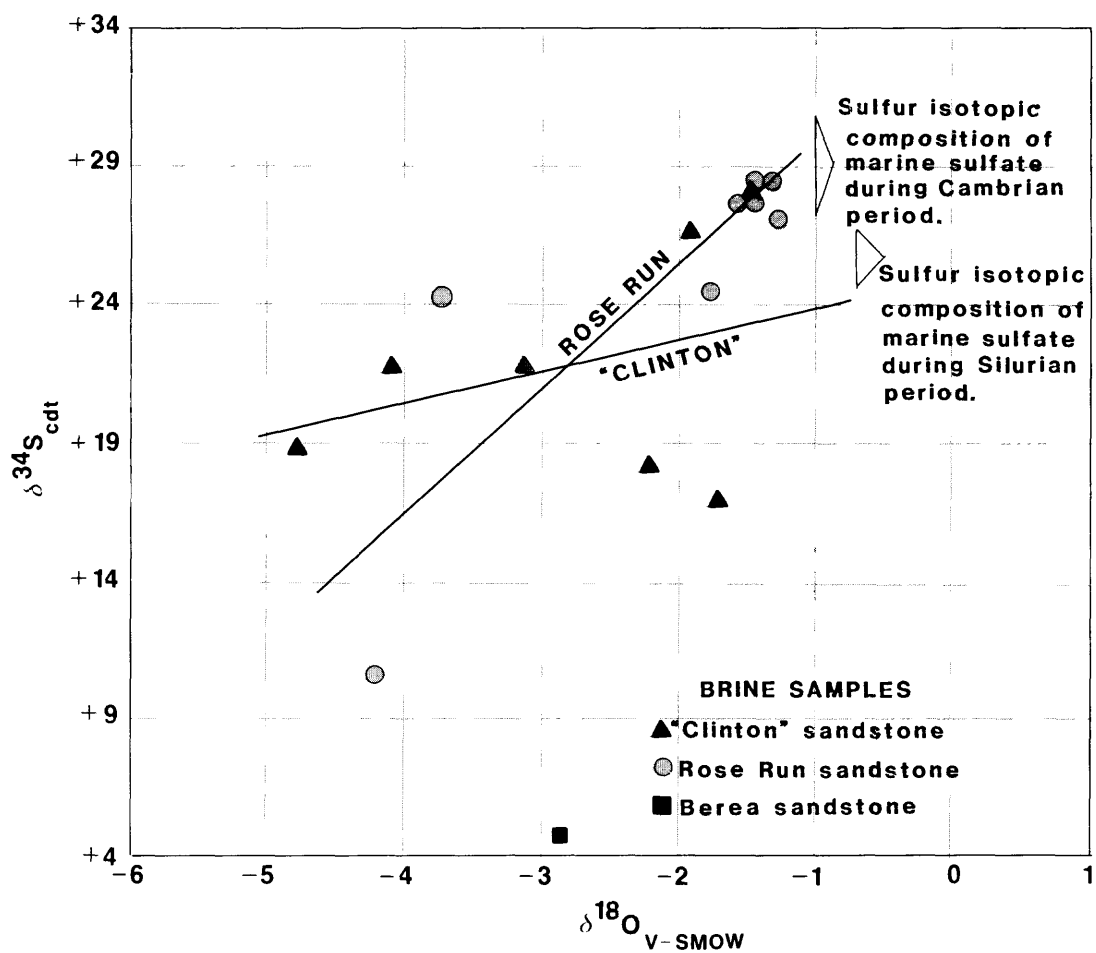


Figure 14.--Graph showing relations between sulfur and oxygen stable isotope ratios for Ohio brine samples and sulfate sulfur in Cambrian and Silurian rocks (Faure, 1977).

SUMMARY

The chemical and isotopic characteristics of brines from three oil- and gas-producing sandstones (the Berea Sandstone and the so-called "Clinton," and Rose Run sandstones of driller's and informal usage) were studied in an effort to chemically identify oilfield and gasfield brines in eastern Ohio.

Concentrations of sixteen dissolved ionic constituents were determined for brines in the three sandstones. In general terms, the chemical constituents in brines from the Berea, "Clinton," and Rose Run sandstones are similar and may be categorized in the following manner:

Category	Constituent	Concentration range (mmol/kg)
Dominant	Na, Cl	>1,000
Major	Ca, Mg	≥100 to <1,000
Minor	K, Br, Sr, Li, Fe, SO ₄	≥1 to <100
Trace	Mn, Zn, Al, I, HCO ₃ , SiO ₂	<1

Variations in brine chemistry exist and are illustrated by Stiff (1951) diagrams. This technique allows comparison of brine analyses for samples within the same sandstone. The Stiff diagrams also serve to highlight differences in brine composition between the three sandstones. Variations in brine chemistry are caused by different geologic, hydrodynamic, and mineralogic conditions in the subsurface rocks from which the brines are derived. Brine chemistry also may be affected by variations in the techniques used by different investigators for collection, preparation, and analysis of samples.

Interformational differences in the mean concentrations of individual constituents were established on a preliminary basis (or on the basis of a limited number of Berea and Rose Run samples) by combining statistical testing with plots of constituent concentration versus sample depth. Brines that have not been diluted or mixed with surface or subsurface waters may be identified using the concentrations of these individual constituents. Mean concentrations of sodium, calcium, chloride, magnesium, potassium, bromide, and sulfate were different in each sandstone. Potassium has unique concentration ranges for each sandstone and is best suited for use in chemical brine identification. Mean values of density and total dissolved solids could also be differentiated between sandstones. Iodide and strontium could be used only to separate Berea from "Clinton" brines. Manganese had similar mean concentrations in Berea and Rose Run brines, and both could be differentiated from the "Clinton." Iron was not useful as a formation indicator.

For applications dealing with brine migration and brine contamination, the use of concentration ratios as geochemical tracers was evaluated for brines with some history of dilution and mixing with surface and subsurface waters. The K:Na ratios are capable of differentiating between brines from all three sandstones and therefore offer a potentially important method for brine identification. Ratios of K:Br, Na:Cl, Ca:Mg, Na:Ca, Cl:Ca, Mg:Br, Na:Br, Mg:K, Cl:Br, and Ca:K are most useful for differentiating the Berea from the "Clinton" and the Rose Run. The K:Cl and Ca:Br values are most useful for differentiating Rose Run brines from Berea and "Clinton" brines. The Cl:Mg and Na:Mg values are not useful as geochemical tracers.

The isotope geochemistry of oxygen and hydrogen provides evidence that the water in Ohio oilfield and gasfield brines is meteoric. This finding is in agreement with isotopic data for oilfield brines in Michigan and Illinois. The shallowest Berea brine most closely matches the present-day isotopic composition of meteoric water in Ohio. Deeper-seated "Clinton" and Rose Run brines show a linear-trending oxygen isotope shift away from the global meteoric-water line. Increased water-rock interaction in the "Clinton" and Rose Run sandstones is a possible explanation for the linear trend. Similarities between brine water and meteoric water should preclude using oxygen and hydrogen isotopes as a means of identifying brines in the three formations, particularly if dilution with surface or ground water has occurred.

A moderate range of $\delta^{34}\text{S}$ (SO_4^{2-}) values (+4.6 to +28.4 permil) was determined for oilfield brines and gasfield brines in Ohio. The heaviest sulfate sulfur (+24.1 to +28.4 permil) was found in brine from the Cambrian and Ordovician Rose Run sandstone in Coshocton County. The $\delta^{34}\text{S}$ (SO_4^{2-}) values for the Coshocton County Rose Run brines show good agreement with the $\delta^{34}\text{S}$ of marine sulfates in Cambrian and Ordovician rocks. This finding provides additional evidence for rock-water interactions being responsible, in part, for the observed brine chemistry. The characteristically heavy sulfate sulfur isotope values found in the "Clinton" and Rose Run brines may prove useful for differentiating isotopically light, near-surface sources of sulfate (ground-water recharge) from brine-derived sulfate.

CONCLUSIONS

Chemical "fingerprinting" is feasible as a means of identifying oilfield and gasfield brines in eastern Ohio, and the use of selected ratios of chemical constituents has important potential as a "fingerprinting" technique. However, effective application of chemical brine tracing would require that a comprehensive data base of the chemical characteristics of brines from individual formations be established. Such a data base would support studies of brine pollution on local and regional scales. A data base of chemical characteristics of brines also would aid in horizon identification during drilling and in studies of the

compatibility of brines with the various chemical treatments and fluids used during the oilwell and gaswell drilling, completion, and production process. Thus, the lifetime of a well and the recovery of hydrocarbons may be enhanced.

The use of potassium chemistry and the concentration-ratio concept for geochemical tracing of brines requires further testing. Additional brine analyses are needed for the Berea and Rose Run Sandstones; new data could be used to test the validity of the findings in this report.

Future sampling, brine analysis, and data evaluation must be done using a standard set of techniques and could be conducted on the basis of individual production fields. Samples of brine from several wells in each major field would be most desirable. Consideration may be given to sampling other producing formations, (such as the Newburg zone of the equivalent of the Lockport Dolomite, Oriskany Sandstone, and Cussewago Sandstone).

Future case studies of pollution resulting from brine disposal or well leakage could be done in such manner as to incorporate chemical testing with an evaluation of the surface- and groundwater hydrology of the study area.

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