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Origin and geochemical evolution of the Michigan basin brine

Wilson, Timothy Peter, Ph.D.

Michigan State University, 1989

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ORIGIN AND GEOCHEMICAL EVOLUTION OF THE MICHIGAN BASIN BRINE

By

Timothy Peter Wilson

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Geological Sciences

1989

ABSTRACT

ORIGIN AND GEOCHEMICAL EVOLUTION OF THE MICHIGAN BASIN BRINE

By

Timothy Peter Wilson

Chemical and isotopic data were collected on 126 oil-field brine samples and were used to investigate the origin and geochemical evolution of water in 8 geologic formations in the Michigan basin. The data were analyzed using graphical, thermodynamic modeling, and statistical methods.

Cl/Br ratios suggest that the Michigan basin brines originated from evapo-concentrated seawater. Two groups of brine are found in the basin, the Na-Ca-Cl brine in the upper Devonian formations, and Ca-Na-Cl brine from the lower Devonian and Silurian aged formations. Water in the upper Devonian Berea, Traverse, and Dundee formations originated from seawater concentrated into the halite facies. This brine evolved by halite precipitation, dolomitization, aluminosilicate reactions, and the removal of SO_4 by bacterial action or by $CaSO_4$ precipitation. The stable isotopic composition (D, O) is thought to represent dilution of evapo-concentrated seawater by meteoric water. Possible brine origins are: (1) seawater evaporation in coastal sabkhas and lagoons, reflux down into the sediments, and

later dilution by meteoric water, or (2) residual fluids squeezed from the underlying Devonian and/or Silurian salts during compaction mixed with dilute water in the overlying formations but maintaining saturation with halite.

Water in the lower Devonian Richfield, Detroit River Group, and Niagara-Salina formations is very saline Ca-Na-Cl brine. Cl/Br suggest it originated from seawater concentrated through the halite and into the $MgSO_4$ salt facies, with an origin linked to the Silurian and Devonian salt deposits. Dolomitization and halite precipitation increased the Ca/Na, aluminosilicate reactions removed K, and bacterial action or $CaSO_4$ precipitation removed SO_4 from this brine. Additional $CaCl_2$ enrichment may have occurred from the diagenesis of the Salina A-1 potash salt. Stable isotopes reflect the seawater origin, but may have been affected by carbonate equilibria at higher temperatures.

Water chemistry in the Ordovician Trenton-Black River formations indicates dilution of evapo-concentrated seawater by fresh or seawater. Possible saline end-members include Ordovician seawater, present-day upper Devonian brine, or Ca-Cl brine from the deeper areas in the basin.

ACKNOWLEDGMENTS

I would like to acknowledge the help given by the following companies and individuals:
The Michigan oil and gas industry, especially the Dart Oil and Gas Company, Shell Oil, Amoco Oil Company, Mossbacher Production Company, Wiser Oil, Miller Oil, and Wenner Production Company.
The faculty and staff at the Department of Geological Sciences, Michigan State University.
Argonne National Laboratory.
Dr. Alden Carpenter, Chevron Research Co.

I would also like to acknowledge the following agencies that funded this project:
The American Chemical Society Petroleum Research Fund.
Geological Society of America.
American Association of Petroleum Geologists.
Amoco Production Company.
Shell Western Exploration and Production Company.
Department of Energy Educational Programs, Argonne National Labortories.
Department of Geological Sciences, Michigan State University.

I would like to express my sincere thanks to the teachers and friends that have helped me in this work: Dr. David Long, Dr. Grahame Larson, Dr. Duncan Sibley, Dr. William Cambray, Dr. John Wilband, Dr. William Cooper, Dr. Richard Cooper, Dr. Richard Heimlich, Mike Takacs, Dale Rezabek, Jim Tolbert, Joe McKee, and Dr. Douglas Lee.

Finally, I would like to express my heartfelt gratitude to my wife Janet, and to Dave. Without your support, friendship, and understanding, this work would not have been possible.

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CHAPTER 1

Geochemistry of water in Devonian aged formations, Michigan Basin.

INTRODUCTION

The origin and evolution of sedimentary basin brine has been the focus of study for a number of years (Russell, 1933; Case et al., 1942; De Sitter, 1947; White, 1957; White, 1965; Torrey, 1966; Dickey, 1966; Graf et al., 1966a, 1966b; Collins, 1975; Collins, 1975; Carpenter, 1978; Carpenter, 1978; Hanor, 1982). Besides understanding the chemistry of these unique fluids, basin waters are of interest because of their involvement in hydrocarbon production and migration (Degens and Chilingar, 1964), deep basin hydrology (Bethke, 1985; Domenico and Robbins, 1985), base-metal mineralization (Roedder, 1967; Billings et al., 1969; Bush, 1970; Carpenter et al., 1974; Long and Angino, 1982), evaporite-cycling (Land, 1987), and sediment diagenesis (Friedman and Sanders, 1967; Bein and Land, 1983; Cercone and Lohmann, 1987). In spite of this interest, the origin and evolution of water in many basins remains unresolved.

Any model for brine origin must explain both the chemical and isotopic geochemistry of the water. The chemical evolution of sedimentary basin brine is thought to reflect two, albeit overlapping, groups of processes (Lerman, 1970). First are the concentrating processes that are responsible for the high salinity of these waters, and include evaporation, evaporite dissolution, and shale membrane filtration. Second, are the modifying processes that occurred during the evolution of the water, and include dissolution-reprecipitation, ion exchange, biological activity, mixing of waters, and shale filtration. These processes may mask the chemical record of formation water origin (Chave, 1960).

The isotopic evolution of sedimentary basin water may also occur by two general processes. Clayton et al. (1966) proposed that the isotopic composition of basin water reflects that meteoric water has flushed through basin rocks, and was subsequently modified by exchange with rock minerals (Clayton et al., 1966). Alternatively, Degens et al. (1964), Knauth and Beeunas (1986), and others (Hitchon et al., 1969; Hanor, 1982), have proposed that the isotopic composition of some formation water reflects mixing, more specifically, the dilution of evapo-concentrated seawater by meteoric water. Hitchon et al. (1969) suggested that the isotopic values of basin waters reflects a combination of these processes including mixing of marine with meteoric waters, exchange with rocks, and shale membrane filtration.

Several studies have demonstrated these general models and have linked brine chemistry to residual seawater (Carpenter, 1978; Stoessell and Moore, 1983; Knauth and Beeunas, 1986, Dutton, 1987), mixed seawater-freshwater (Billings et al., 1969, Dressel and Rose, 1982; Spencer, 1987), and freshwater origins (Clayton et al., 1966; Hitchon et al., 1971; Kharaka and Berry, 1974; Kharaka et al., 1973;

Bassett and Bentley, 1983). However, the chemical and isotopic evolution of formation water in many areas, including the Michigan basin, remains unresolved and may not fit these models. One principle reason for this may be the inability to explain both the chemical and isotopic geochemistry of brine by a single model.

THIS STUDY

The Michigan basin has an important role in the understanding of both brine and basin evolution, because Michigan typifies inter-cratonic sedimentary basins. Similar to other basins, Michigan basin water is Ca-Cl brine, although some formations contain Na-Cl brine. The Michigan brines are somewhat unique however, as they are extremely saline, some having total dissolved solids in excess of 640,000 mg/l (Case, 1945), they have high Ca content (Graft et al. 1966), and because they exist at shallow depths in the basin. Although the Michigan brines have been studied for some time (Lane, 1899; Cook, 1914; Beecker, 1940; Case, 1945; Egleson and Querio, 1969; Sorensen and Segall, 1975; Clayton et al., 1966; Graf et al., 1966a; Graf et al., 1966b), their geochemical and isotopic origin and evolution remains to be clearly identified.

The goal of this study is to determine the geochemical and isotopic evolution of the Michigan basin brines. The chemical and isotopic composition of brines collected from 54 oil wells from 6 Devonian producing formations in

Michigan are used, in combination with brine chemistry from Niagara/Salina and Ordovician aged formations in the basin, which are discussed further in Chapter 2. The geochemical processes for brine evolution considered include seawater evapo-concentration, shale membrane filtration, and water-rock interactions. A tenant followed in this research is that the brine in each formation may have evolved through different processes, therefore, the brine chemistry must be evaluated (whenever possible) on an individual formation basis, rather than collectively in a whole basin manner.

It became evident early in this study that a close agreement exists between the Michigan brine chemistry and evapo-concentrated seawater. This is not totally unexpected, as the basin is noted for its evaporite deposits. Based on this observation, a framework model of evapo-concentrated seawater brine, modified by water-rock reactions is used in this study (Wilson and Long, 1986, Wilson and Long, 1987).

STUDY AREA

The Michigan Basin is a mature, intercratonic sedimentary basin, occupying an area over 200,000 km^2. The basin is located between the Canadian Shield and the Illinois Basin, and is outlined by the arches and platforms shown in Figure 1-1. Over 4000m of Paleozoic sediments exist at the deepest point in the Michigan basin, and range from Jurassic to Cambrian in age (Figure 1-2). The Paleozoic section starts with basinal Cambrian sandstones

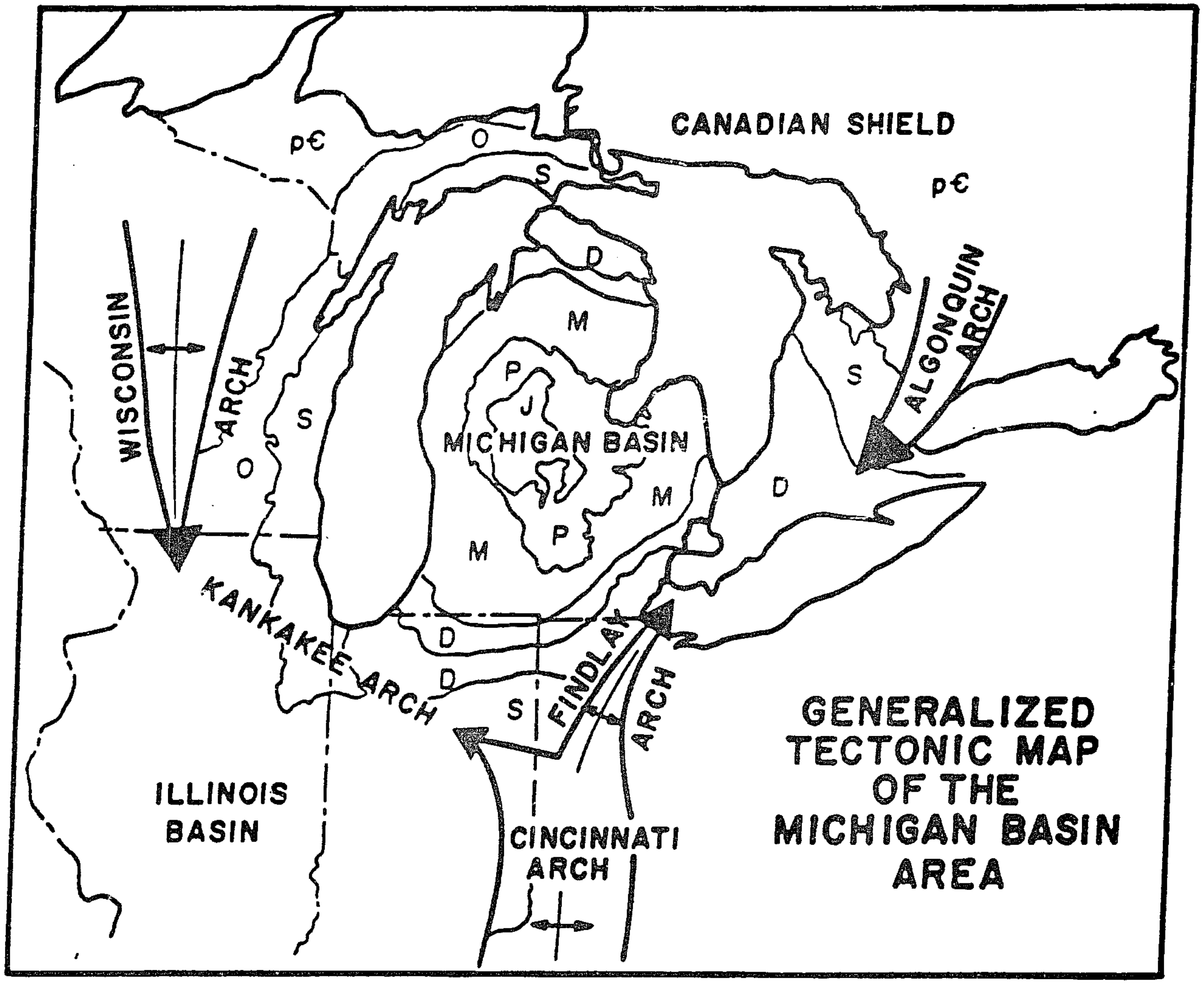

Figure 1-1: Generalized tectonic map of the Michigan Basin area.

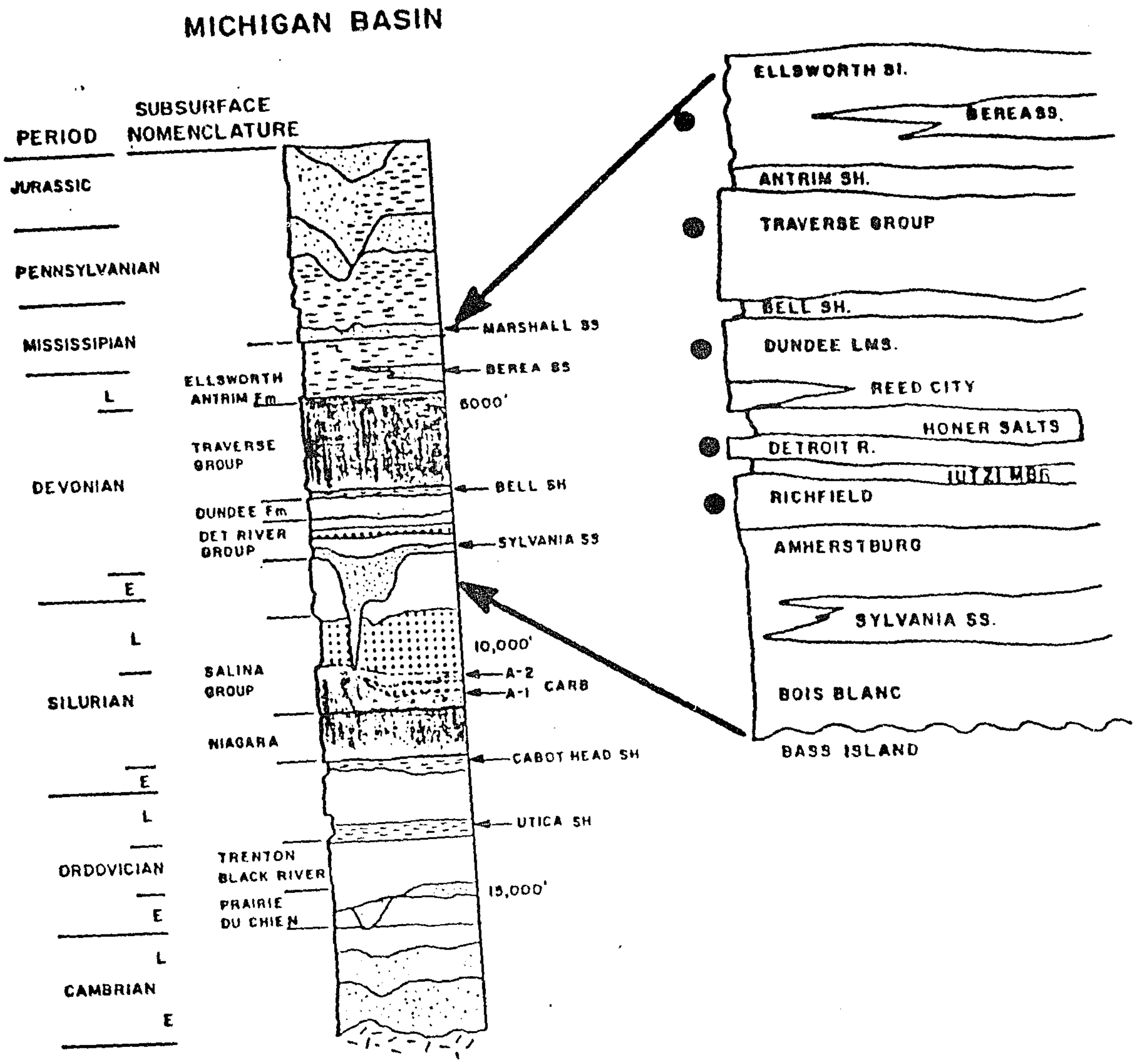

Figure 1-2 : Paleozoic section of the Michigan basin.

overlain by Ordovician limestone-dolostones, which are the oldest rocks to exhibit the basin shape (Nunn et al., 1984). Over 550m of Silurian evaporites and carbonates follow and include dolomite, anhydrite, halite, and potash minerals. Devonian aged carbonates and evaporites, the focus of this paper, follow and are overlain by a thick layer of Carboniferous to Jurassic aged shales and clastic sediments.

The basin is estimated to contain 47% carbonates, 23% sandstones, 18% shales, and 12% evaporites by volume (Cohee and Landes, 1955). Estimated present-day formation volumes (Table 1-1), measured from maps in Gardner (1974) and Curran et al. (1981), indicate that $7.4x10^4$ km^3 of Devonian aged sediment exists in the basin. Assuming an average porosity of 10% and neglecting evaporite layers, the Devonian rocks in Michigan contain approximately $3.5x10^{16}$ liters of water.

The present geothermal gradient in the basin is approximately $22^oC/Km$ (Nunn et al., 1984), but measured temperatures may vary considerably from this gradient (see Appendix B). Hogarth (1985) used conodont color to demonstrate that the paleo-geothermal gradient was similar to the present day gradient, but that Paleozoic sediments may have been buried almost 1 km deeper in the past. Other studies have suggested both deeper burial and higher paleo-geothermal gradients for Michigan (Cercone,1984).

TABLE 1-1
Estimated formation volumes in the Michigan Basin.

AGE& REF.	FORMATION OR GROUP	Km^3 x10^4	SAMPLED	ABSOULTE AGE END x10^6	ABSOULTE AGE DURATIO x10^6
(1)	CARBONIFEROUS			300	46
	GRAND RAPIDS GROUP				
	BAY PORT LMS				
	MICHIGAN FM				
	UNCONFORMITY				
	MARSHALL SANDSTONE	0.46	*		
	COLDWATER SHALE	1.72			
	SUNBURY SHALE	0.08			
	BEREA SANDSTONE	0.08	*		
	BEDFORD SHALE	0.14			
(1&2)	DEVONIAN			376	23
	ELLSWORTH SHALE	1.42			
	ANTRIM SHALE	1.20			
	TRAVERSE GROUP	1.31	*		
	TRAVERSE LMS				
	BELL SHALE				
	NATIONAL CITY GYPSUM	0.04	*		
	DUNDEE FORMATION	0.66			
	ROGERS CITY				
	REED CITY ANHYDRITE	0.14	*		
	LUCAS or DETROIT RIVER				
	HORNER MEMBER TOTAL	1.09			
	HORNER SALTS	0.53			
	IUTZI MEMBER	0.32			
	MELDRUM TOTAL	0.48			
	RICHFIELD MBR.	0.18	*		
	FILER SANDSTONE				
	BOIS BLANC-SYLVANIA	0.89	*		
UNCONFORMITY				399	16

Table 1-1 (cont'd.).

AGE& REF.	FORMATION OR GROUP	Km^3 x10^4	SAMPLED	ABSOULTE AGE END x10^6	DURATIO x10^6
(1)SILURIAN				415	26
	BASS ISLAND	.88			
	SALINA GROUP				
	G UNIT	0.08			
	F EVAPORITE	1.46			
	E EVAPORITE	0.27			
	D EVAPORITE	0.10			
	C CARBONATE	0.17			
	B EVAPORITE	0.91			
	A-2 CARBONATE	0.35	*		
	A-2 EVAPORITE	0.84			
	A-1 CARBONATE	0.34			
	A-1 EVAPORITE	0.55			
	BROWN NIAGARAN	8.79	*		
(1) ORDOVIVIAN				411	21
	UTICA SHALE	0.96			
	PRARIE DU CHEIN	8.88	*		
UNCONFORMITY					

Key:

1: Curran et al. (1981).
2: Gardner (1974).
3: End and duration of geologic periods in Michigan reported in 10^6 years, From Nunn et al., (1984).
SAMPLED: * indicates formations sampled in this study.

Formation waters reported on here are from the Berea Sandstone, the Traverse Group, the Dundee Formation, the Detroit River Sour Zone and Richfield Member of the Lucas Formation, and the Sylvania Sandstone (Figure 1- 2). A summary of the general lithology, structure and textures, thickness, and depositional environments for Devonian formations is given in Table 1-2. Further descriptions can be found in Gardner (1974), Matthews (1977), Door and Eschman, (1981), and Montgomery et al. (1984).

Devonian rocks in Michigan represent a shallow water transgressive-regressive sequence that followed the restricted marine conditions of the Silurian (Gardner, 1974). The Kaskaskia unconformity is considered the lower boundary of the Devonian in Michigan (Gardner, 1974). Overlying this unconformity is the Sylvania Sandstone which represents the start of a transgressive stage of the Early Devonian (Gardner, 1974). The Sylvania is a wind and fluvial transported sand which was reworked by marine currents and was deposited concurrent with offshore carbonates of the Bois-Blanc and Amherstburg Formations (Gardner, 1974).

The cyclic evaporite-carbonate sediments of the Amherstburg and Lucas Formations were then deposited during the Middle Devonian when the basin became restricted. The cyclic deposition is best developed in the Richfield Member of the Lucas Formation, which consists of over 60m of alternating anhydrite and dolomite layers. In the central

TABLE 1-2
SUMMARY OF DEVONIAN FORMATION GEOLOGY

STRATIGRAPHIC UNIT & MAX. THICKNESS	LITHOLOGY	STRUCTURE & TEXTURE	ENVIRONMENT OF DEPOSITION
Traverse Group 800'	Bio-calcarenite limestone, few anhydrite and and porous dolomites on west margin, gray shale facies on east margin.*	bioherms, biostroms wackestones and grainstones	shallow shelf with muddy influx from east. Lagoons on west margin
Dundee Formation 400'	dark limestone with laminar,impure anhydrite and porous secondary dolomites on west.*	irregular beds and banks, bioturbated wackestones and grainstones	subtidal to shallow shelf, with lagoons, and shabkas on basin margins
Horner Member 800'	massive salt with interbeds of anhydrite and dark sour carbonates	impure dolomitic and layered anhydrites, cloudy-clear salt layering	peripheral shabkas and lagoons, and basin centered evaporites
Iutzi Member 150'	massive anhydrite at base, dolomite and some limestones wide spread at top	massive and impure, dolomitic anhydrites and dark micritic carbonates	periphal shabkas and penesaline lagoons
Richfield Member 100'	syngenetic dolomicrite with interbedded, displacement anhydrites.	oolitic, laminated mudcracks, decussate interclasts, nodular mosaic anhydrites	shabka and penesaline lagoons
Amherstburg Member 300'	Dark, carbonaceous wackestones	Bioherms, biostromes bioturbate, bioclastics, and pelletal	shelf to basin, increasingly restricted in upper portion.
Sylvania 300'	White quartzose sandstone, with secondary quartz overgrowths, interbedded with carbonates.	cross beds, planar to irreg. bedding, dessication cracks, frosted and polished grains	dunes, beach, and bar, open marine along hinge line

TABLE 1-2 (cont'd.).

STRATIGRAPHIC UNIT & MAX. THICKNESS	LITHOLOGY	STRUCTURE & TEXTURE	ENVIRONMENT OF DEPOSITION
Bois Blanc 700'	Cherty biocalcaranite, tripolitic chert	irregular to thin bedded mottled wackestone	open marine carbonate shelf silica from adjacent desert land mass

* Carbonates are generally limestone on east, and dolomite on south and west basin margins. They are darker and finer grained in basin center.

SOURCE: Gardner, 1974

basin area the Detroit River Group (Lucas Formation) is found and includes the Horner Member, a up to 200m thick halite-anhydrite-dolomite deposit (Matthews, 1977). The Detroit River carbonates are highly brecciated around the basin margins as a result of later dissolution of the underlying Salina salts (Landes et al., 1945). After the deposition of these evaporites and carbonates, a slow return of normal marine conditions occurred and the Dundee and Traverse sediments were deposited. Both formations consist of a biostromal shelf facies, with argillaceous carbonates found in off-shore areas. Gardner (1974) suggested that extensive sabkhas and lagoons existed around the basin margins during this time (Figure 1-3). Upper Devonian shales cap the section and signal the onset of clastic deposition that continued through the Carboniferous (Door and Eschman, 1981).

The Devonian formation mineralogy is dominated by calcite and dolomite, but also includes anhydrite, halite, quartz sandstone, chert, and illitic-chloritic shales (Gardner, 1974; Matthews, 1977; Nowak, 1978; Door and Eschman, 1981; Montgomery et al., 1984). Dolomite and anhydrite generally increase in abundance near the basin margins, especially towards the west (Gardner, 1974), but also occur in lenticular zones throughout the basin (Montgomery, et al., 1984).

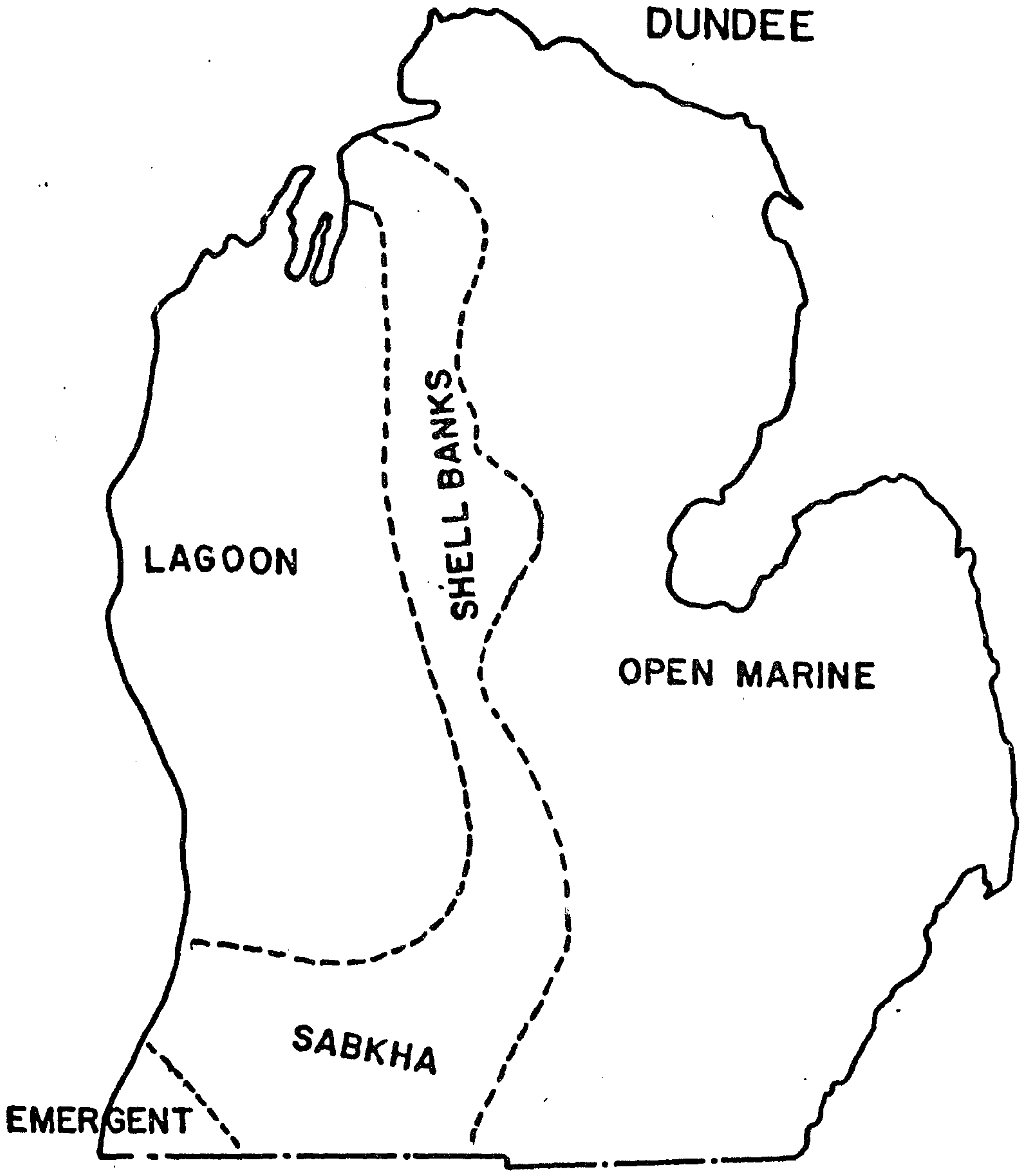

Figure 1-3. Paleo-geography of the Dundee Formation, after Gardner (1974).

Oil production from Michigan Devonian rocks has been important since the early 1900's and occurs in a broad band extending from the central basin westward and southward (Cohee and Landes, 1955; Montgomery et al., 1984). Hydrocarbon production occurs from bioherms and anticlines, dolomitized porosity zones, and from fracture related porosity (Montgomery et al., 1984).

ANALYTIC METHODS

Fifty-four Devonian formation brines were collected as a part of a larger study on Michigan basin brines which included waters from Silurian and Ordovician aged formations. The samples were supplemented with 32 analyses obtained from various oil company and government files including Michigan Department of Natural Resources (M.D.N.R.) open file data. Sample locations are shown in Figure 4. Charge balance errors are less than 5%. Sampled intervals were confirmed by operating personal and drilling records, and by geophysical logs when possible. Well plugging by salts is a serious problem in Michigan and as such, freshwater flushing of oil-wells is a common practice. Care was taken to avoid sampling wells that were recently flushed, wells from fields under water-flood, or those located near brine disposal wells. Because of its long use for brine disposal, Sylvania Sandstone brine was not collected in this study although some data were obtained from M.D.N.R. files.

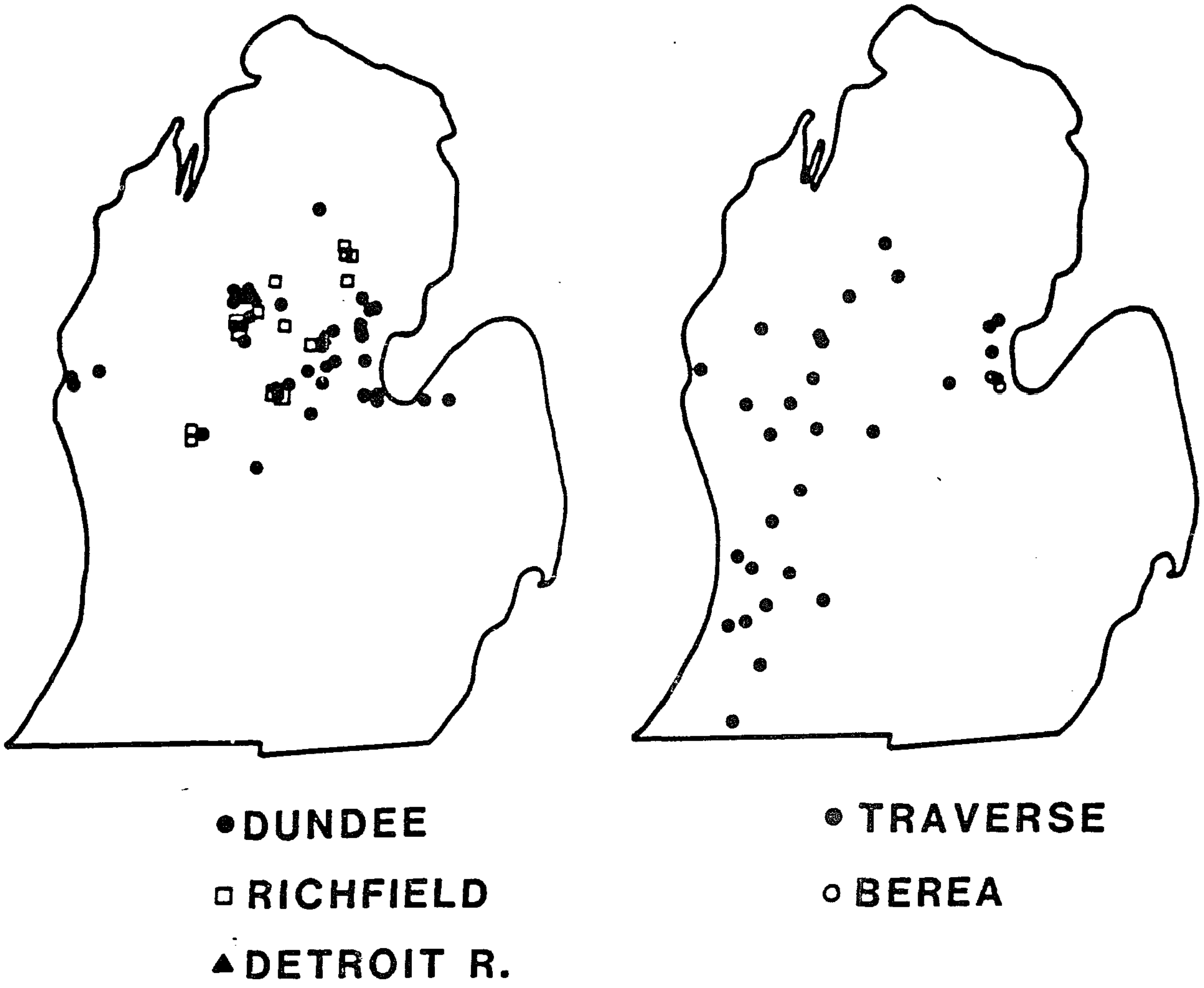

Figure 1-4: Sample locations.

Samples were collected directly from the well head, filtered through glass wool and Watman #1 paper filters, and stored in pre-rinsed plastic bottles. Samples for cation analysis were collected by diluting raw brine 50% with 5% HNO_3, using Class A volumetric pipettes. Undiluted samples were collected for anion analysis and preserved with formeldehyde for SO_4. Untreated samples were collected for D/H, $^{18}O/^{16}O$, and $^{87}Sr/^{86}Sr$ analyses. The pH, Eh, temperature, and when possible, alkalinity, were measured in the field following Lico et al.,(1982), Wood (1981), and Collins (1975). NBS buffers (pH 4 and 7) were used for pH standardization. Formation temperatures were calculated following Vugrinovich (1986) using 10°C at 33m plus 23°C per each km of depth there-after. The components measured and laboratory procedures used are listed in Table 1-3. Inorganic analysis was done at the Geochemical Laboratory, Michigan State University. Stable isotope ratios ($^{18}O/^{16}O$, D/H) were measured at the Environmental Isotope Laboratory, University of Waterloo, Canada, and at Teledyne Laboratories, New Jersey. $^{18}O/^{16}O$ analysis utilized 72 hour equilibration with CO_2, and D/H analysis used a complete distillation technique described in Fritz et al. (1986). Deuterium values were corrected for activities following Sofer and Gat (1975). $^{87}Sr/^{86}Sr$ analysis was preformed at Argonne National Laboratory. Standard chromatography techniques using 2N double distilled HCL and Dowex (8x-200) resin (Stueber et al., 1984) were used to

TABLE 1-3
Components measured and analytic methods.

COMPONENT	METHOD	DILUTION	REFERENCE
pH	electrometric	none	1
Ca, Mg, Sr	flame emmision w/1:10 of 87g/l $LaCl_2$	1:2000	1
Na,K	flame emmision w/1:10 of 25.4g/l NaCl or KCl	1:2000	1
Rb,Cs	flame emmision w/1:10 of 25.4g/l Na-K-Cl	1:26	1
Li	flame emmision w/1:10 of 25.4g/l Na-K-Cl	1:200	1
Cl	Mohr titration	none	1
Br	colorimetric	1:40	2
I	bromide oxidation	1:2	1
B	colorimetric w/carminic acid	1:10	1
Si	colorimetric following extraction	1:200	3
NH_4N	potentiometric titration	1:2	4
SO_4	gravimetric	none	5
Alkalinity	potentiometric titration	none	1
Density	pyconometer @25°C and by calculation $SPG=\log TDS * 7.102\times10^{-7} + 0.996$	none	5
TDS	calculation		

References:
1: Brown et al., (1979) Methods for Determination of Inorganic Substances in Water and Fluvial Sediments, U.S.G.S. Water Resources Investigation Book 5, Chapter A-1, Washington, D.C.
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4: Collins, A.G., Cassaggno, J.L., and Macy, V.W. (1969) Potentiometric determination of ammonium nitrogen in oil-field brines, Environmental Science and Technology, 3, 274-275.
5: A.P.I. (1968) Recommended Practice for Analysis of Oil-field Waters, American Petroleum Institute, Washington, D.C., 2nd edition, 58p..

separate Sr. Rb/Sr ratios are <0.001, suggesting that Rb has not appreciably enriched ^{87}Sr.

GEOCHEMICAL RESULTS

Sample locations, well data, and analytic results for all samples collected in this study are listed in the Appendix of this report. A summary of geometric means, ranges, and concentration ratios are listed in Table 1-4. Total dissolved solids in all samples are in excess of 300 g/l.

Sulfate, alkalinity, and pH values reported for these waters deserve some discussion. Sulfate concentrations are very low, much less than seawater values, with some samples having non-detectable SO_4. Alkalinity is highly variable, ranging from undetectable values up to several hundred mg/l. Several factors may cause errors in the pH and alkalinity measurements. For example, liquid junction potentials and Na poisoning may introduce considerable uncertainty in electrode measurements made in high salinity water (Hawley and Pytkowicz, 1973; Millero, 1979; Harvie and Weare, 1980; Dickson, 1984). Alkalinity may be also affected by borate and organic acids (Willey et al., 1975). Measurement of the organic acid content of these waters has not yet been successful because of salinity interferences (B. Fisher, personal comm.). However, a slight inflection point was found during alkalinity titrations near the apparent pH value of 3.5, perhaps indicating the presence of organic acids (Appendix B). Eh measurements of these waters

TABLE 1-4
Average composition of formation waters

COMPONENT	BEREA	TRAVERSE	DUNDEE	RICHFIELD	DETROIT R.
Cl	195000	172000	171000	194000	212000
Br	1400	1100	1000	2100	3400
Ca	45100	29000	24500	65200	88000
Mg	8250	6600	5100	8700	11800
Na	63000	68200	71000	34200	23100
K	640	1660	1640	7200	13400
Sr	2000	1060	780	1970	2680
Rb	4.	4.	3.	12.	38.
Li	8.	29.	24.	46.	93.
B	-	29	21	119	226
Si	3.	3.	3.	2.	2.
NH_4N	74	125	110	230	550
HCO_3	12	50	30	160	180
SO_4	45	65	180	1200	10
I	23	11	10	23	38
TDS	315000	282000	278000	296000	355000
MCl_2	2980	1840	1660	4020	5420
n	3	30	40	13	2

Key: All values are geometric means in mg/l.
MCl_2 = Ca + Mg + Sr - $0.5HCO_3$ $-SO_4$ as meq/l
n = number of samples analyzed for major components

resulted in highly unstable values that drifted considerably with time. Eh most likely controlled by dissolved Fe (Hem and Crooper, 1959; Back and Barnes, 1965; Langmuir, 1971; Kharaka et al., 1980; Stumm and Morgan, 1981) because in non-treated samples, minerals thought to be Fe-oxide or FeS (depending on formation) would precipitate after a few days time.

DISTRIBUTION OF BRINE CHEMISTRY

Formation waters are often density or chemically stratified in basins, a characteristic that may reflect mass movement or diffusion (Land, 1987; Hanor, 1984). In addition, spatial variations in brine chemistry might reflect different geochemical processes operating within areas of a basin. A summary of the distribution of brine chemistry in the Michigan basin is given here.

Figure 1-5 shows the brine density (specific gravity) versus production elevation for all formation waters collected in this study, including those from Silurian and Ordovician formations. The brine density, and therefore salinity, show a only a slight linear increase with depth. Surface elevations in Michigan range between 200 and 300m above sea-level, and as this diagram shows, very dense, saline brine exists at shallow depths (<500m) below land surface. Although the Michigan basin waters appear density stratified, they do not demonstrate the strong linear increase in salinity with depth characteristic of other sedimentary basins such as Illinois (Graf et al., 1966), and

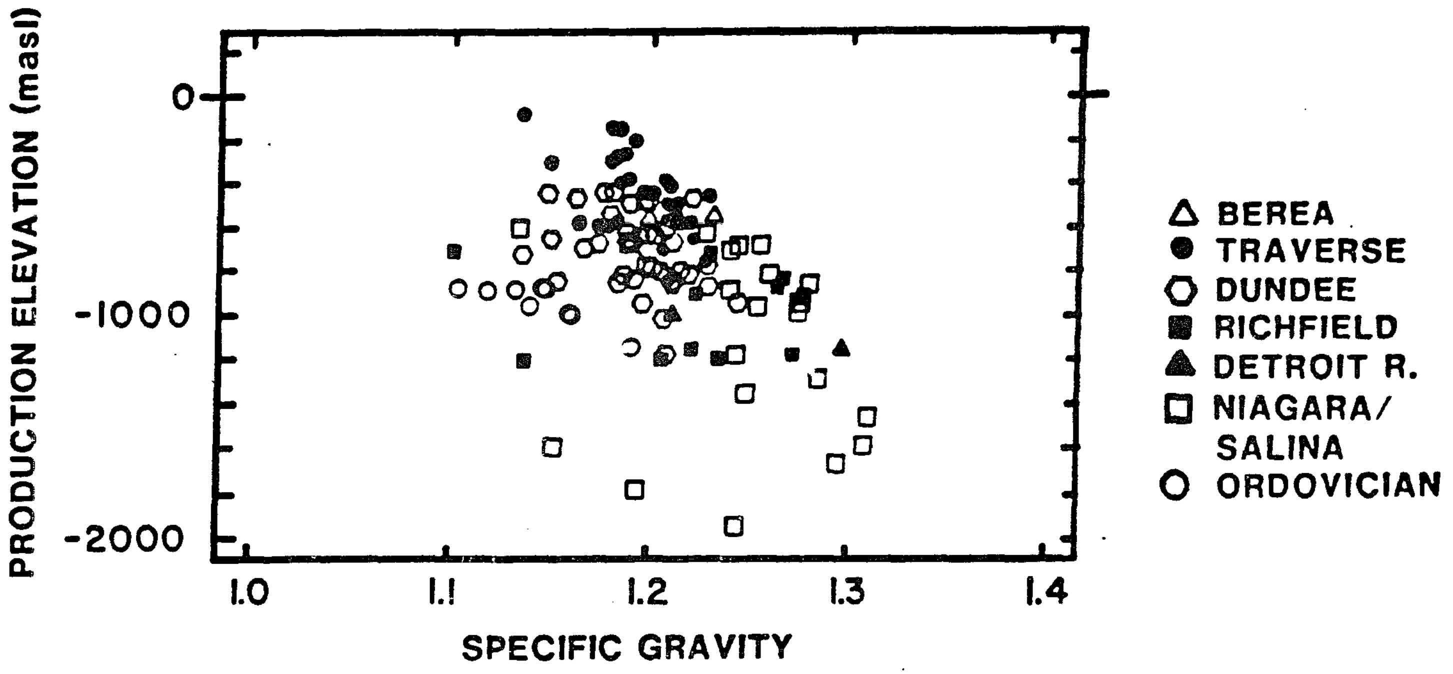


Figure 1-5 : Specific gravity (g/cm^3) versus production elevation (m) in the basin. The elevation of the Great Lakes is approximately 180m.

the West Canada sedimentary basin (Hitchon et al., 1971). This probably reflects the structural shape of the basin and the fact that samples from different formations cannot be collected in a single location in the basin. The Niagaran formation water, for example, was sampled only from near the basin margins (Chapter 2).

Bromide can be used to represent spatial variability in salinity and chemistry of the formation waters. Bromide is selected because the graphical treatment presented below is based on plotting brine chemistry versus Br, and because bromide is strongly related to salinity (log TDS=0.357 * log Br + 4.33, $r^2 = .85$) and covaries directly with many of the major elements (Cl, Ca, Mg, K, Sr, and Na), minor elements (Rb, B, and I), deuterium, and ^{18}O. Therefore, the Br distribution, in a general manner, summarizes the spatial variation of the brine chemistry within the basin.

Bromide concentrations in the combined Traverse-Dundee data increase towards the basin center (Figure 1-6). A similar distribution is suggested for the other formation waters, but the limited data prevent conclusive interpretations from being made. It appears that the brine chemistry is related to location and formation depth, with higher concentrations occurring in the deeper, central-basin areas. Sulfate does not follow this general distribution (Figure 1-6), but generally higher SO_4 concentrations are found in samples collected from shallower depths near the basin margins.

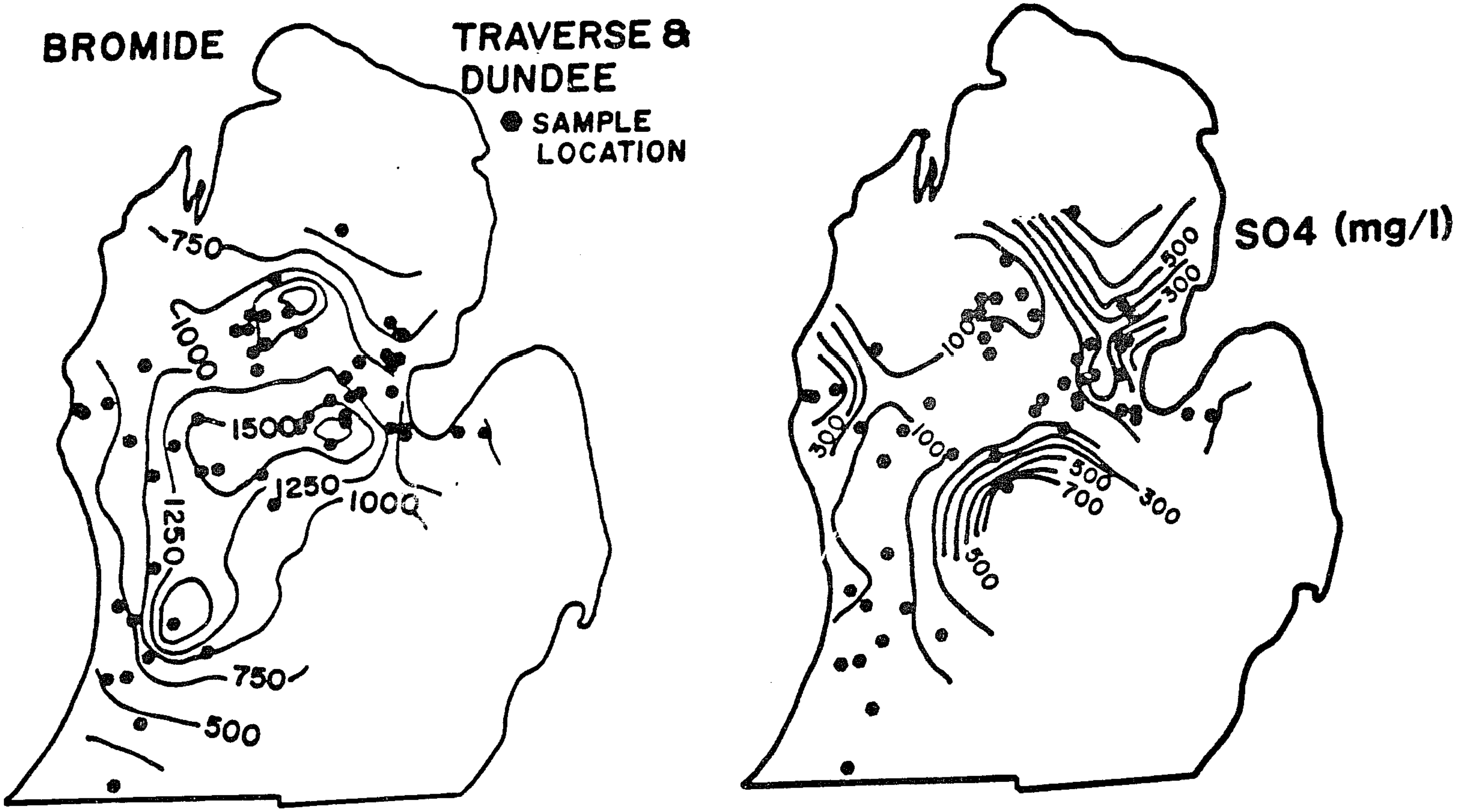


Figure 1-6: Br (mg/l) and SO_4 (mg/l) in the Traverse and Dundee formation waters.

MAJOR ION COMPOSITION

Chloride is the dominant anion in all the samples, and as Figure 7 shows, either Na or Ca are the dominant cation. The Berea, Traverse, and Dundee brines are Na-Ca-Cl brine, while the Richfield, Sylvania, and Detroit River Sour Zone are Ca-Na-Cl water, similar to many of the Niagara/Salina formation brines (Chapter 2).

Collins (1975) and Carpenter (1978) demonstrate how formation water chemistry can be compared with evaporating seawater in order to make interpretations as to possible origins and evolutions of brine chemistry. A number of brine studies have since utilized Br/Cl for this purpose (Carpenter, 1979; Rittenhouse, 1967;Collins, 1975; Dressel and Rose, 1982; Spencer, 1987; Dutton 1987; and others). The major ion chemistries are compared with seawater in Figure 8 to 10. The trend lines for evaporating seawater chemistry are from McCaffrey et al. (1988), which agree well with Black Sea data of Zherebtsova and Volkova (1966) and Carpenter (1978). Also shown are the average compositions of the Niagara/Salina formation water samples from (Chapter 2).

The Br, Cl, and Na in the brines compare well with concentrated seawater, while Mg and K are depleted and Ca and Sr highly enriched over the seawater trend. A strong linear relationship exists between log Ca and log Br in the Traverse and Dundee samples (slopes of 0.80 to 0.97, r^2=0.77 to 0.78, respectively) and log Sr-Br (slopes of 1.0 to 1.2, r^2=0.90 to 0.95). Magnesium also plots linear with log Br,

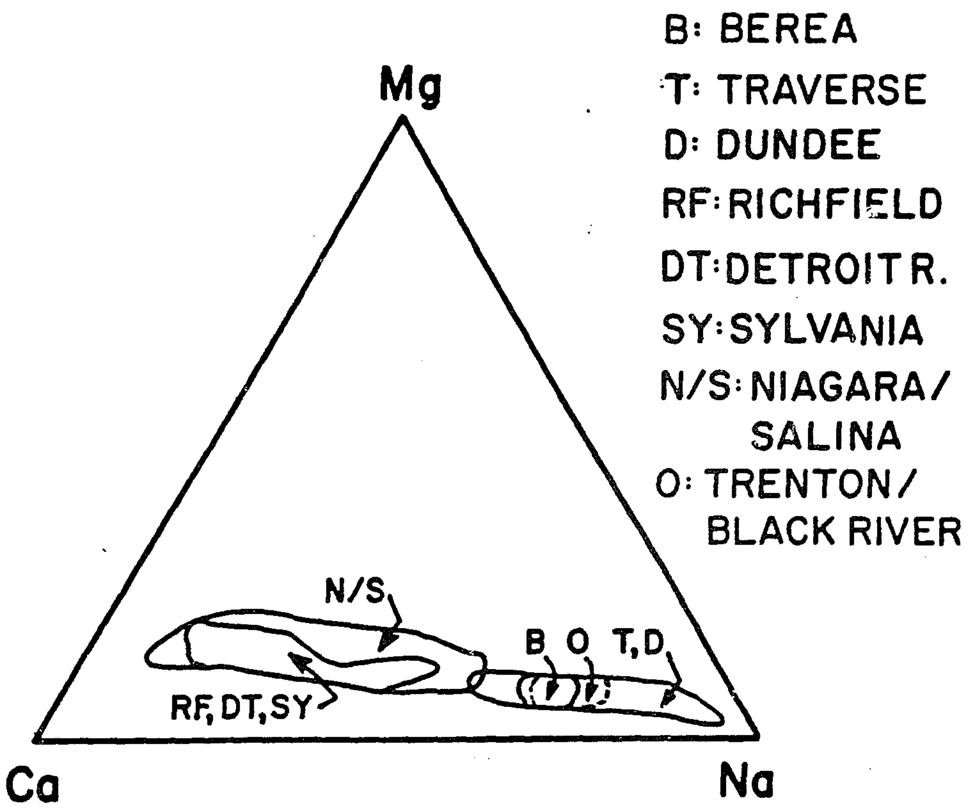


Figure 1-7 : Ternary diagram showing percentages of Ca-Mg-Na (mole percent) in Michigan basin brines.

Figure 1-8. Traverse and Berea Formation water chemistry (log mg/l) compared with evapo-concentrated seawater (dashed line, data from McCaffrey et al, 1988; and Carpenter, 1978). Average Niagara-Salina formation water shown as (⬡) A: log Cl-log Br, B: log Na-Br, C: log K-Br, D: log Ca-Br, E: log Mg-Br, F: log Sr-Br.

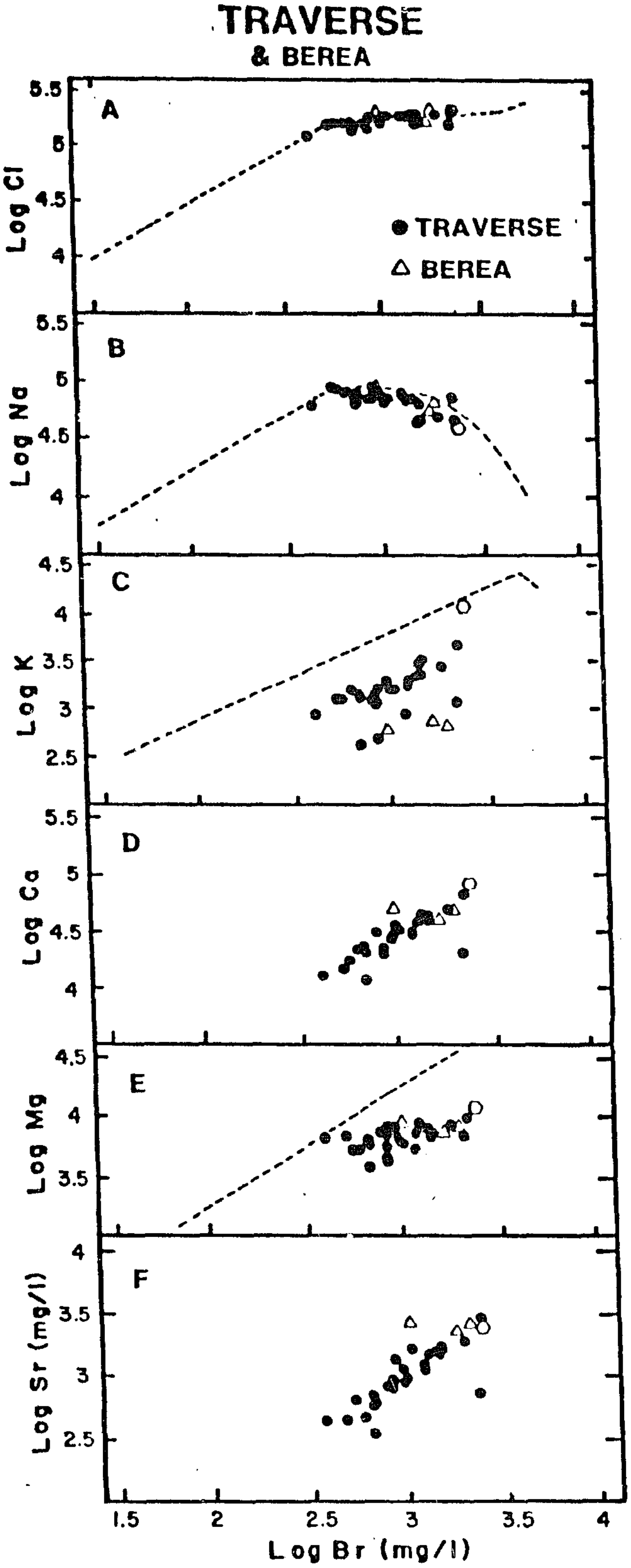

TRAVERSE
& BEREA
A
B
C
D
E
F
● TRAVERSE
△ BEREA
Log Cl
Log Na
Log K
Log Ca
Log Mg
Log Sr (mg/l)
Log Br (mg/l)
5.5
5
4.5
4
3.5
3
2.5
1.5
2
2.5
3
3.5
4

Figure 8.

Figure 1-9. Dundee Formation water chemistry (log mg/l) compared with evaporating seawater. Average Niagara-Salina formation water shown as (⬡) A: log Cl-log Br, B: log Na-Br, C: log K-Br, D: log Ca-Br, E: log Mg-Br, F: log Sr-Br.

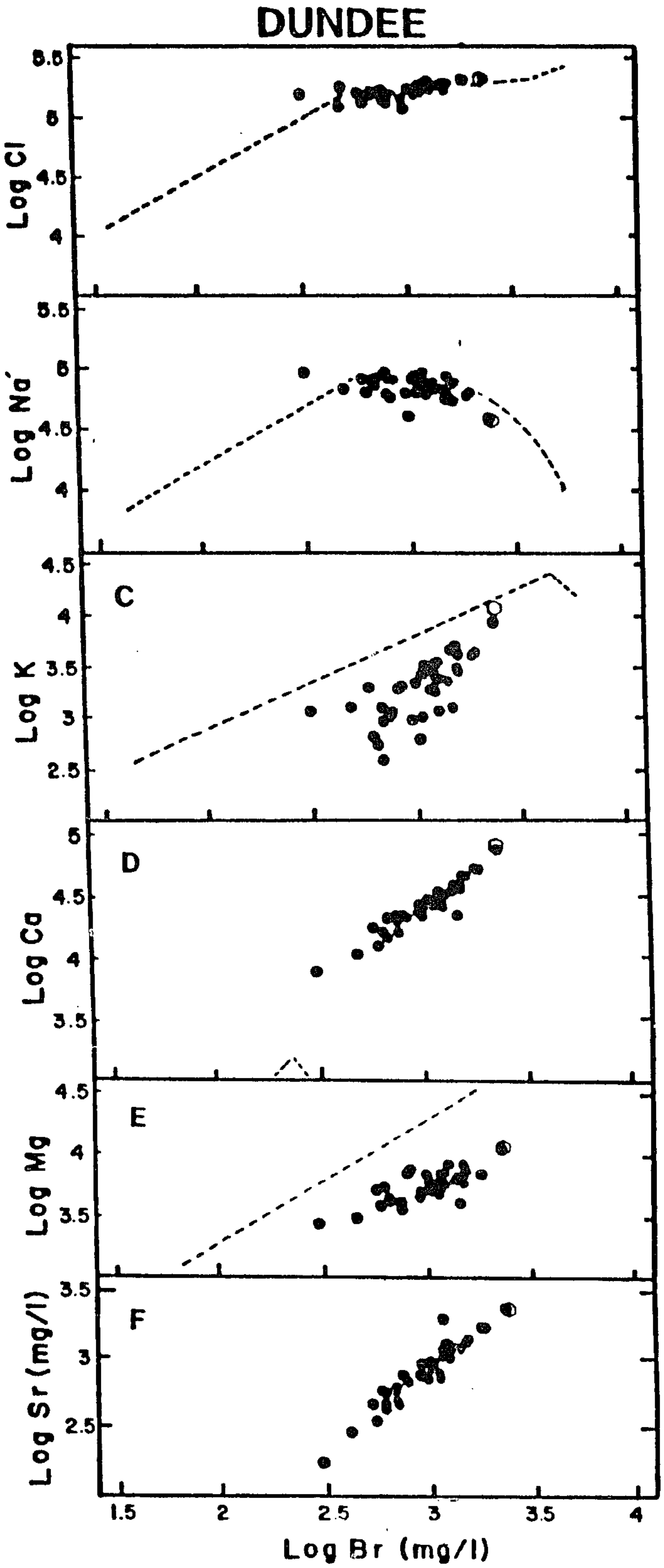

DUNDEE
Log Cl
5.5
5
4.5
4
Log Na
5.5
5
4.5
4
C
Log K
4.5
4
3.5
3
2.5
D
Log Ca
5
4.5
4
3.5
E
Log Mg
4.5
4
3.5
F
Log Sr (mg/l)
3.5
3
2.5
1.5
2
2.5
3
3.5
4
Log Br (mg/l)

Figure 9.

Figure 1-10. Richfield and Detroit River formation water chemistry (log mg/l) compared with evaporating seawater. Average Niagara-Salina formation water shown as (⬡) . A: log Cl-log Br, B: log Na-Br, C: log K-Br, D: log Ca-Br, E: log Mg-Br, F: log Sr-Br.

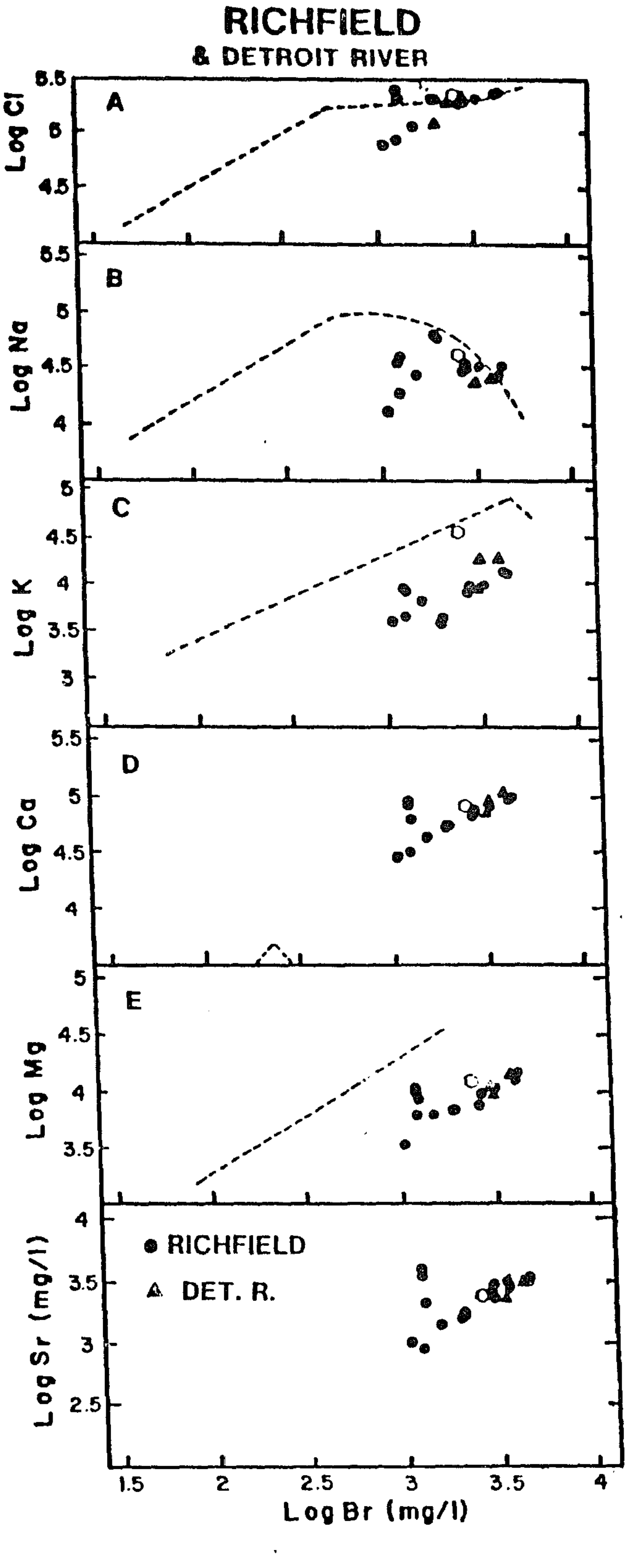

RICHFIELD
& DETROIT RIVER
Log Cl
5.5
5
4.5
A
5.5
B
Log Na
5
4.5
4
C
Log K
5
4.5
4
3.5
3
D
Log Ca
5.5
5
4.5
4
E
Log Mg
5
4.5
4
3.5
Log Sr (mg/l)
4
3.5
3
2.5
● RICHFIELD
▲ DET. R.
1.5
2
2.5
3
3.5
4
Log Br (mg/l)

Figure 10.

but best fit lines have slopes between 0.4 and 0.5 (r^2=0.76 to 0.79).

Carpenter (1978) suggested that a further test of formation brine origin would be to compare MCl_2 with Br and Cl. MCl_2 represents the sum of divalent cation charge balanced by Cl, MCl_2= Ca + Mg + Sr - 0.5*HCO_3 - SO_4 (meq/l). This value is not affected by dissolution-precipitation of carbonates, dolomite, sulfates minerals, or halite. MCL_2 approximately equals Br in seawater, and until carnallite saturation is reached, follows the relationship: Log MCl_2 = Log Br + 0.011 (Carpenter, 1978).

Log MCl_2 is compared with log Br in Figure 1-11a, and with Cl in Figure 1-12. The data plot parallel to, but above, the MCl_2-Br line for seawater, and suggest that an excess of divalent cations or a depletion in Br exists from expected seawater values. Because the MCl_2 value includes the combined error in measuring five components versus the analytic error in measuring Br, MCl_2 was corrected for charge balance by adjusting for excess charge in the analyses (MCl_2'= MCl_2-(EPM cations)+(EPM anions)), which is shown in Figure 1-11b. An excess of MCl_2 is still evident in spite of this correction. The log Cl-MCl_2 relationship (Figure 1-12) gives some insight into this excess. Although similar to the Cl-Br plot in matching the seawater trend, the MCL_2-Cl plot apparently reflects higher degrees of evapo-concentration than are predicted by Cl-Br. This is most evident for some Richfield-Detroit River brines, which

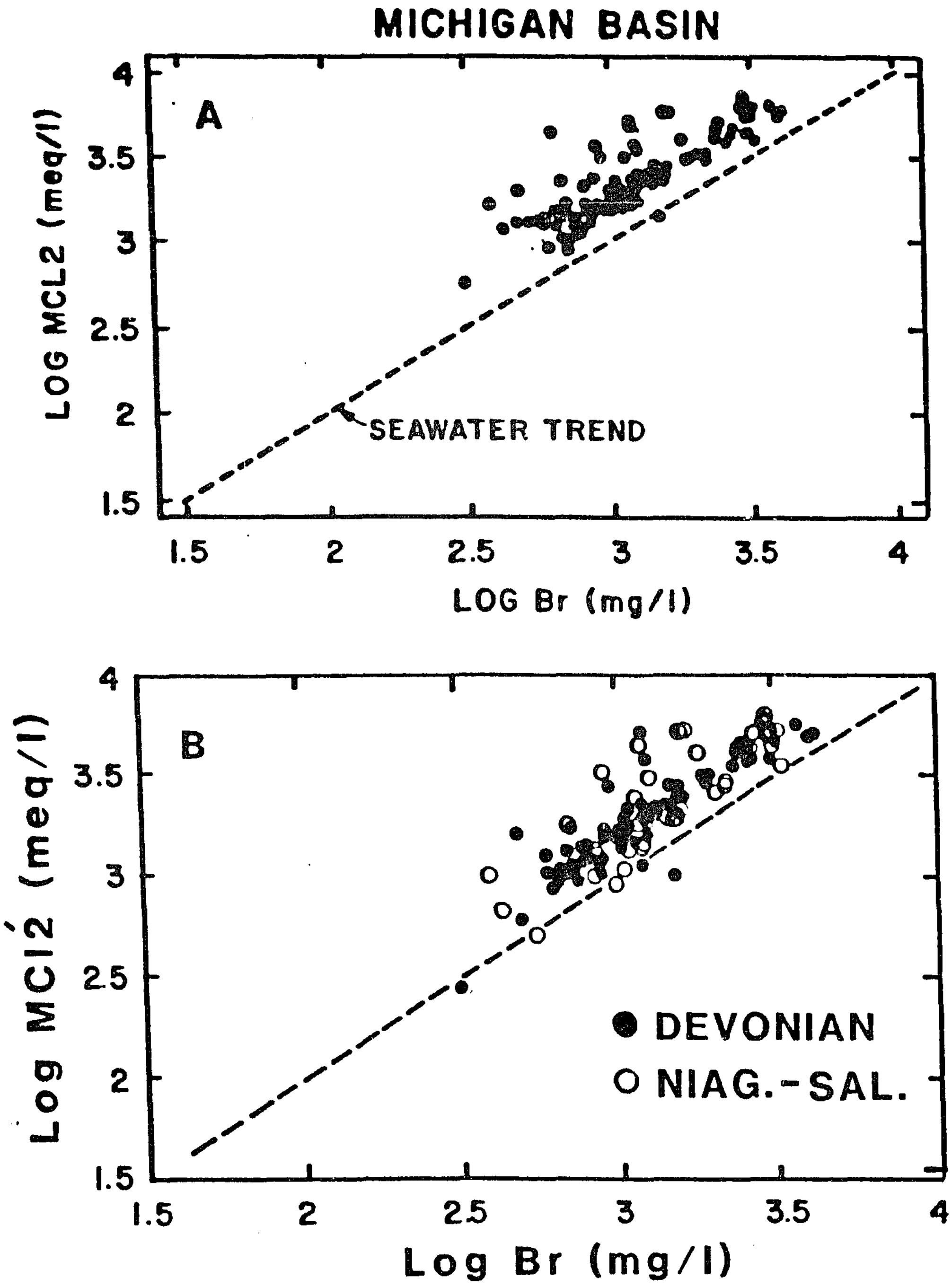


Figure 1-11. (a) Log MCl_2 (meq/l) vs. log Br (mg/l). (b) Log MCl_2 corrected for charge balance vs. log Br (mg/l).

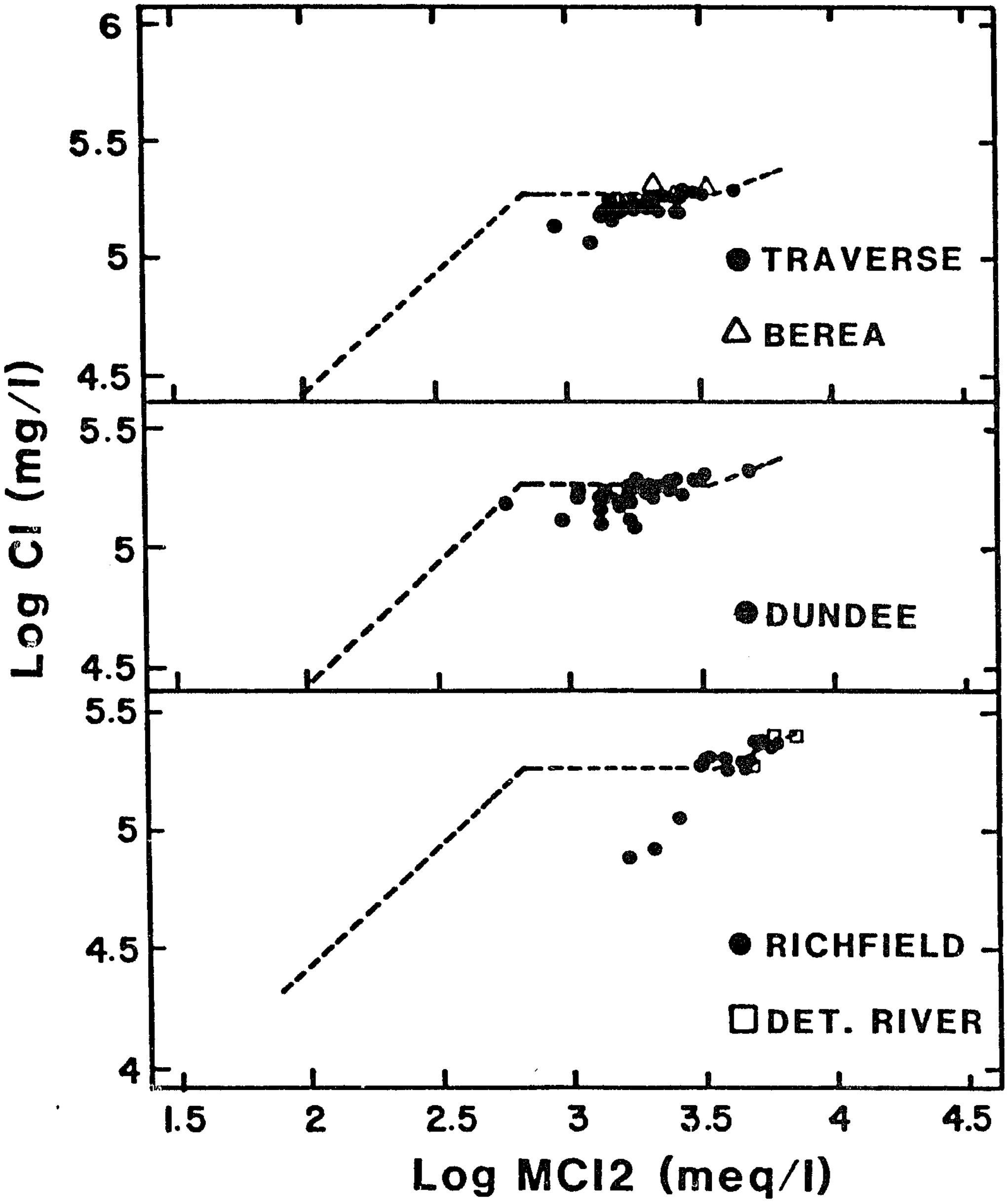


Figure 1-12. Log MCl_2 (meq/l) vs. log Cl (mg/l).

have MCL_2 values identical to seawater concentrated past the start of $MgSO_4$ salt precipitation.

GEOCHEMICAL ORIGIN

As shown in Figures 1-8 to 1-10, a very good agreement exists between the seawater compositions and the Cl-Br and Cl-MCl_2 values in these Michigan brines, suggesting that the geochemical origin of the brines is evapo-concentrated seawater. Based on Br concentrations, the Michigan brines have apparently evolved from seawater concentrated from the start of halite precipitation into the $MgSO_4$ salt facies.

Close inspection of Figures 1-8 to 1-10 shows that some of the samples with lower Br concentrations plot below the seawater trend line, suggesting they have been diluted. This dilution appears related to well location and production depth, as samples with lower Br concentrations were collected from shallow depths near the basin margins (Figure 1-6). The higher SO_4 values found near the basin margins (Figure 1-6) might reflect $CaSO_4$ dissolution resulting from infiltration. The data shows however, that the Devonian brines have not been greatly diluted with seawater or freshwater, as most of the samples agree well with the seawater line. Certainly, the large scale dilution found in the West Canada sedimentary brines (Spencer, 1987), Mississippi Gulf Coast brines (Carpenter et al., 1974), and the Pennsylvania brines (Dressel and Rose, 1982) is not found in Michigan.

GEOCHEMICAL EVOLUTION

While the Cl/Br suggest the brines originated from the evapo-concentration of seawater, the differences from expected seawater concentrations of Ca, Mg, K and Sr demonstrate that the brines have evolved by other processes; most important may be water-rock reactions and mixing. The extent of evolution is illustrated by the $^{87}Sr/^{86}Sr$ of the brines and by MCl_2 enrichment described earlier. The results of a preliminary study of the strontium $^{87}Sr/^{86}Sr$ isotopic composition of the brines are shown in Figure 1-13, where the samples are plotted on the seawater strontium isotopic curve from Burke et al. (1982) according to the geologic age of the producing formation. As is discussed below, evapo-concentrated seawater should be almost devoid of Sr, therefore, the Sr in these brines must reflect reactions with carbonates or other minerals. A generally good agreement exists between the seawater curve and many of the samples, especially for samples from the Richfield and Dundee suggesting that the brines have reacted with Devonian aged carbonates to gain Sr. This conclusion is tempered by several facts, most important is that the $^{87}Sr/^{86}Sr$ of seawater was apparently the same many times during the Paleozoic. However, several of the samples (Traverse and Berea formations) are more radiogenic than the seawater curve, perhaps the result of reactions with shale minerals (Stueber et al., 1984). Reaction with aluminosilicates is

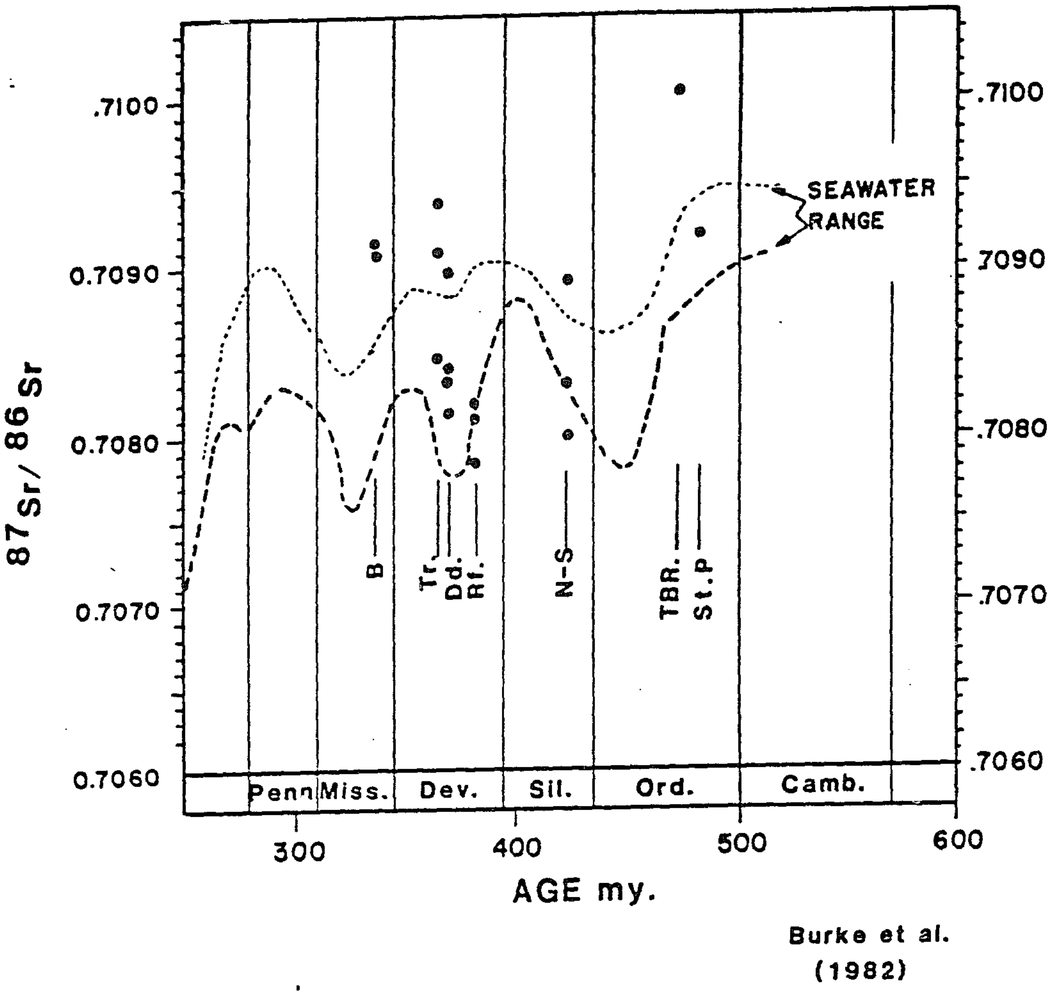


Figure 1-13: $^{87}Sr/^{86}Sr$ of Michigan basin brines vs. producing formation age. Also shown is the variation of the $^{87}Sr/^{86}Sr$ ratio of seawater during the Phanerozoic Eon (Burke et al., 1982).

also consistent with the depletion of K from expected seawater concentrations (Figures 1-7 to 1-9).

The enrichment in MCl_2 over expected seawater values (Figure 1-11) also demonstrates that the brines have evolved from seawater. One explanation might be that MCl_2 is not enriched, but rather, Br is deficient in these waters. Few mechanisms are known that deplete Br from natural waters, for example, bromide is considered conservative in evapo-concentrating seawater as it is removed only after potash-magnesia salts precipitate (Holser, 1979). Kozin (1960), and Krejci-Graf (1963) (in Van Everdingen, 1968) suggested that Br and Cl may exchange onto clays. However, the effect of anion exchange on Br-Cl in formation waters is unknown, and it seems unlikely that exchange could noticeably deplete Br from these waters. Finally, analytical error magnified by the large dilution required for the analysis of highly concentrated brine may explain some of the MCL_2-Br difference. Although correcting for charge balance decreases the MCl_2-Br difference it does not eliminate it. Therefore, the MCL_2-Br difference (Figure 1-11) is assumed to result from an excess of divalent cations in these waters, balanced by Cl or anions other than $SO_4^=$ and $CO_3^=$. Divalent cation enrichment may result from water-rock reactions involving aluminosilicate or evaporite minerals, or perhaps by shale filtration. Enrichment may also result from mixing with MCL_2 rich water from other formations. Although the MCl_2 enrichment appears large in the Michigan brines it is not uncommon for sedimentary basin water to exhibit divalent cation enrichment. Figure 1-14 shows that West Canada basin waters (Hitchon et al., 1971), the Mississippi Gulf Coast brines (Carpenter et al., 1974), and the Illinois basin brines (Graf et al., 1966) are enriched in MCl_2 over seawater.

WATER-ROCK REACTIONS

Differences between the Ca, Mg, Sr, K, and MCl_2 content of these brines and evapo-concentrated seawater may reflect water-rock interactions. Reactions considered here to explain these differences include dolomitization, aluminosilicate reactions, ion-exchange, and evaporite mineral diagenesis (Collins, 1975; Land, 1987; Hanor, 1982).

DOLOMITIZATION

The strong relationships between Ca-Br and Mg-Br (Figure 1-8 to 1-10) is suggestive of dolomite equilibria (Collins, 1975; Carpenter, 1978). Carpenter (1978) demonstrated that an approximate 1:1 relationship between Ca and Br results from dolomitization by evapo-concentrated seawater, rather than from shale filtration (Anderson et al., 1966).

The influence of dolomitization on the brine chemistry was evaluated as follows. The difference between Mg in each sample and equivalently concentrated seawater was calculated based on the measured Br in each sample. This Mg deficiency was assumed to result only from dolomitization and so was converted to a predicted Ca concentration based on a 1 for 1

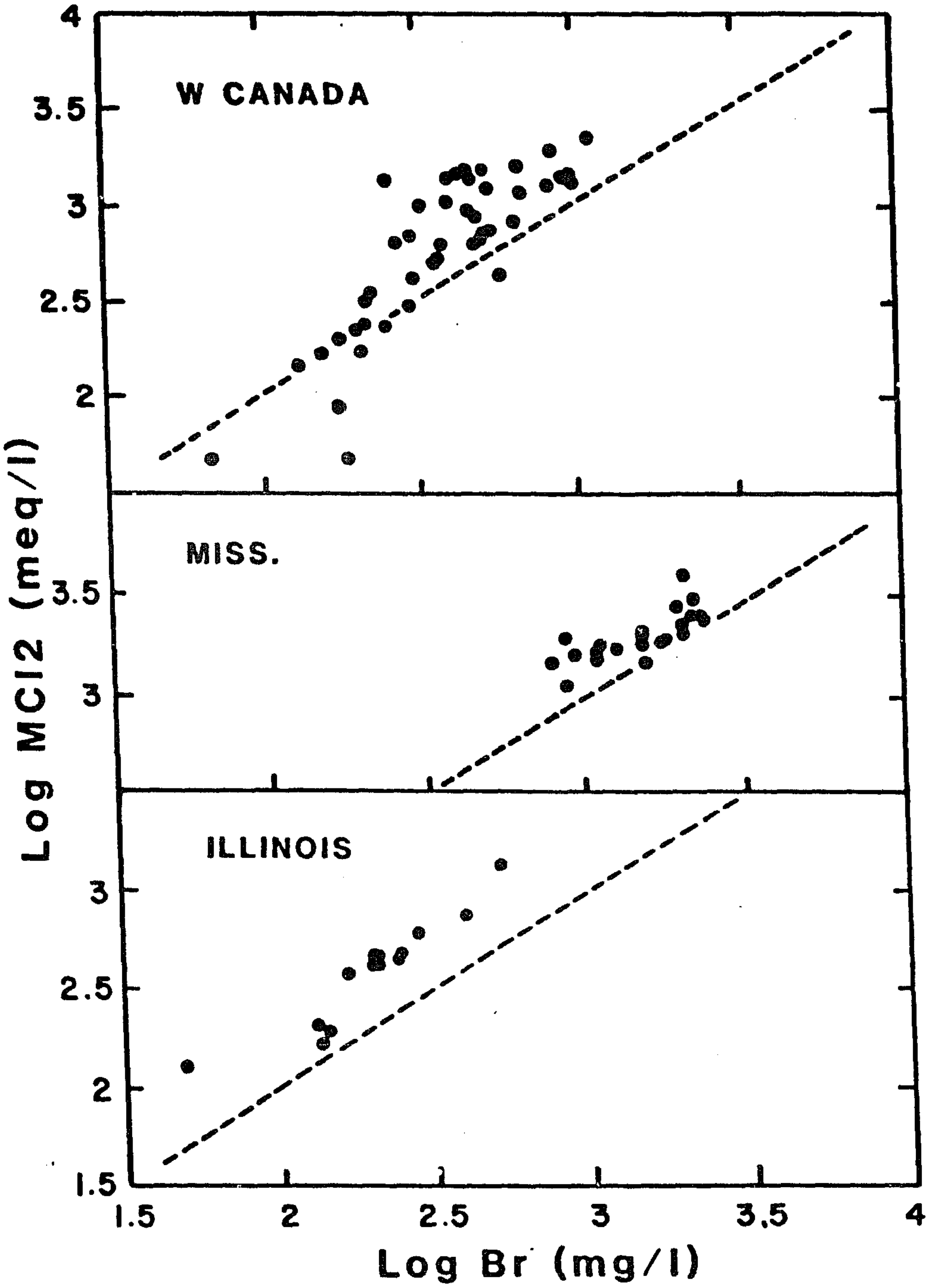


Figure 1-14. Log MCl_2 (meq/l) vs. log Br (mg/l) in formation waters of W. Canada, Mississippi, and Illinois basins.

mole replacement. The predicted Ca are adjusted for $CaSO_4$ dissolution, and then compared with the measured Ca in Figure 1-15.

Generally, a very good agreement exists between the predicted and measured Ca, suggesting that dolomitization by concentrated seawater explains Ca and Mg in these waters. This suggests that the 1:1 relationship between Ca and Br simply reflects Ca taking the place of the Mg in seawater, which originally co-varied directly with Br due to evapo-concentration. An interesting feature of the Mg-Br relationship is that Mg/Br do not approach 1, as do Ca/Br. If Mg depletion and Ca enrichment occurred before evaporation, then both Ca and Mg would plot (vs. Br) near a slope of 1. The Ca-Mg chemistry might reflect that dolomitization occurred concurrent with, or after evapo-concentration.

If dolomitization occurred concurrent with evapo-concentration, then the seawater trend line for Mg in Figures 1-8 to 1-10 may not truly represent the chemistry of evaporating seawater in carbonate basins. Rather, the paths that Ca and Mg in these brine plot along may represent the path seawater follows when equilibrium with dolomite and calcite is maintained during evaporation. Alternatively, dolomitization may have occurred after evapo-concentration; the more highly concentrated brines were involved in more dolomitization and thus show a greater depletion in Mg. This may reflect a greater ability

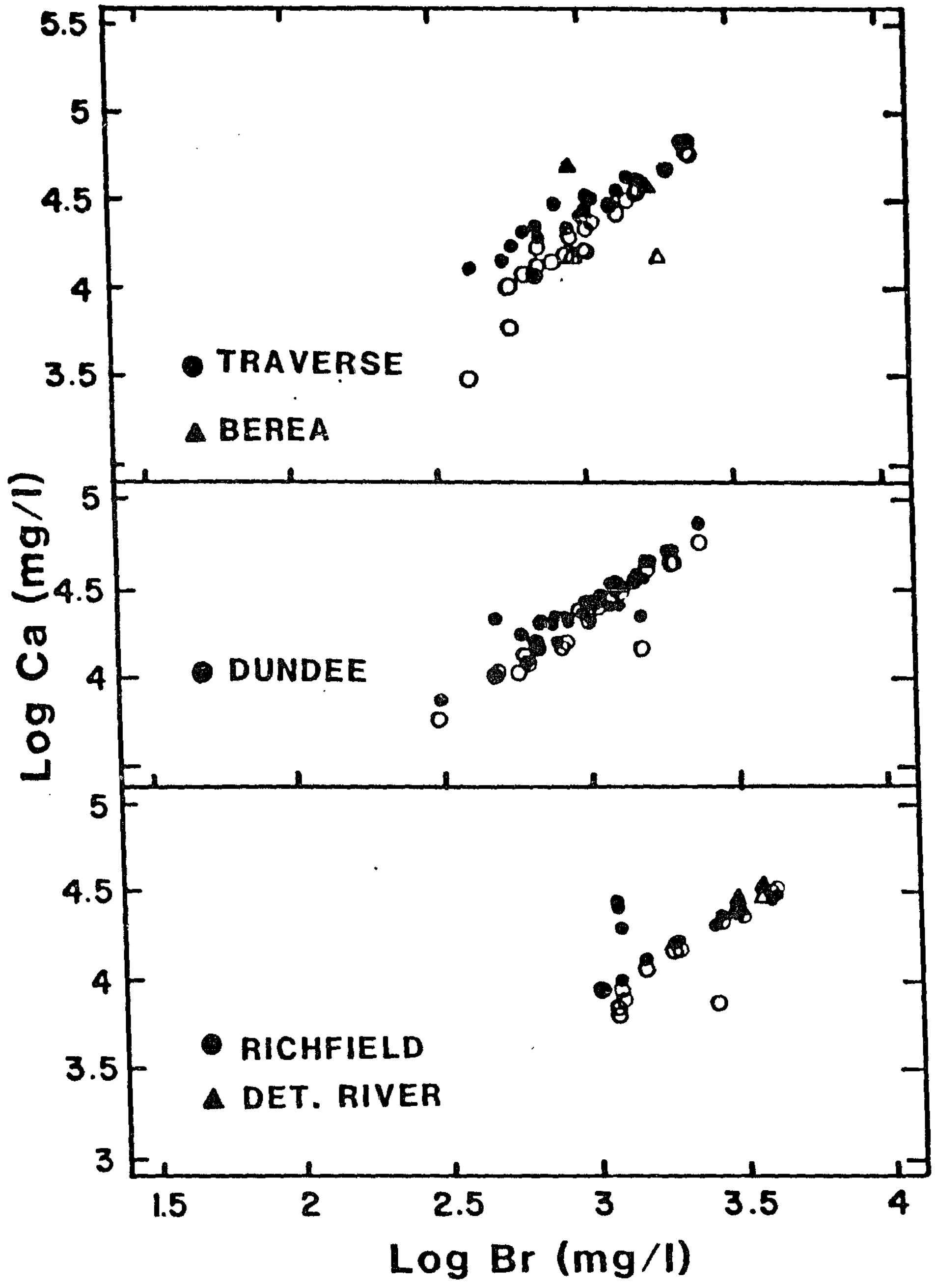


Figure 1-15. Results of dolomitization model. Log Ca (mg/l) vs. log Br (mg/l). Filled symbols are measured Ca, open symbols are predicted Ca.

of highly saline waters to dolomitize, or that the higher salinity waters have simply interacted to greater extents with formation minerals.

The dolomitization model (Figure 1-15) under-predicts Ca in some samples, especially in the less saline Traverse samples. Combined analytic error in Ca, Mg, SO_4, and Br measurements may explain some of this difference, but not all. More likely, other process have added Ca or depleted Mg from these brines. Explanations to considered are the formation of Fe-rich dolomite ($2CaCO_3 + Mg_{(1-x)} + Fe_x = CaMgFe(CO_3)_2$) or Mg-clay minerals. Both the formation of Fe-rich dolomite or Mg-clays would reduce the Mg depleted from seawater by dolomitization, thus resulting in an underprediction of Ca by the model. The Fe content of Devonian dolomites in Michigan is presently not known, but it may be large. For example, Trenton Formation dolomites (Ordovician Age) are reported to contain over 8% $FeCO_3$ (Taylor, 1982).

To further demonstrate dolomite equilibria, the brine chemistries were modeled using the PHRQPITZ program (Plummer et al., 1989). PHRQPITZ is a specific interaction model which uses Pitzer's equations for determining activity coefficients, following Harvie and Weare (1980). Activity coefficients of Na and Cl are adjusted for temperature, but are temperature invariant for the other ions. Only temperature is considered in adjusting equilibrium constants. The Devonian brines of Michigan are a good test for calculating dolomite equilibria in high ionic strength solutions because: 1) dolomite and calcite are common coexisting minerals throughout these formations, 2) the brines appear to have been affected by dolomitization, and 3) because of their suspected seawater origin, the brines have been in contact with the formation minerals for considerable time.

The results of the chemical modeling when the measured pH and alkalinity values are used initially show the brines are slightly undersaturated with calcite (average calcite saturation index = -0.71, s^2=0.80) and dolomite (average dolomite saturation index=-1.149, s^2=1.357). Considering the possible errors in pH and alkalinity measurements, chemical modeling was repeated assuming calcite equilibria. Under this assumption an average dolomite disequilbrium index of 0.017 (s^2=0.230) is calculated, suggesting that the brines are in equilibrium with dolomite (Figure 1-16a).

Strontium is highly enriched in the Michigan brines over seawater and follows a 1:1 relationship with Br, similar to that of Ca (Figures 1-8 to 1-10). This is in great contrast to seawater, which is devoid of Sr at these levels of evapo-concentration (Zherebtsova and Volkova, 1966). The high Sr content of these brines is probably the result of carbonate mineral reactions which can be evaluated using Sr/Ca ratios. Sass and Starinsky (1979) demonstrated that distinct ranges of Sr/Ca result in brines affected by dolomitization of calcite or aragonite, the transformation

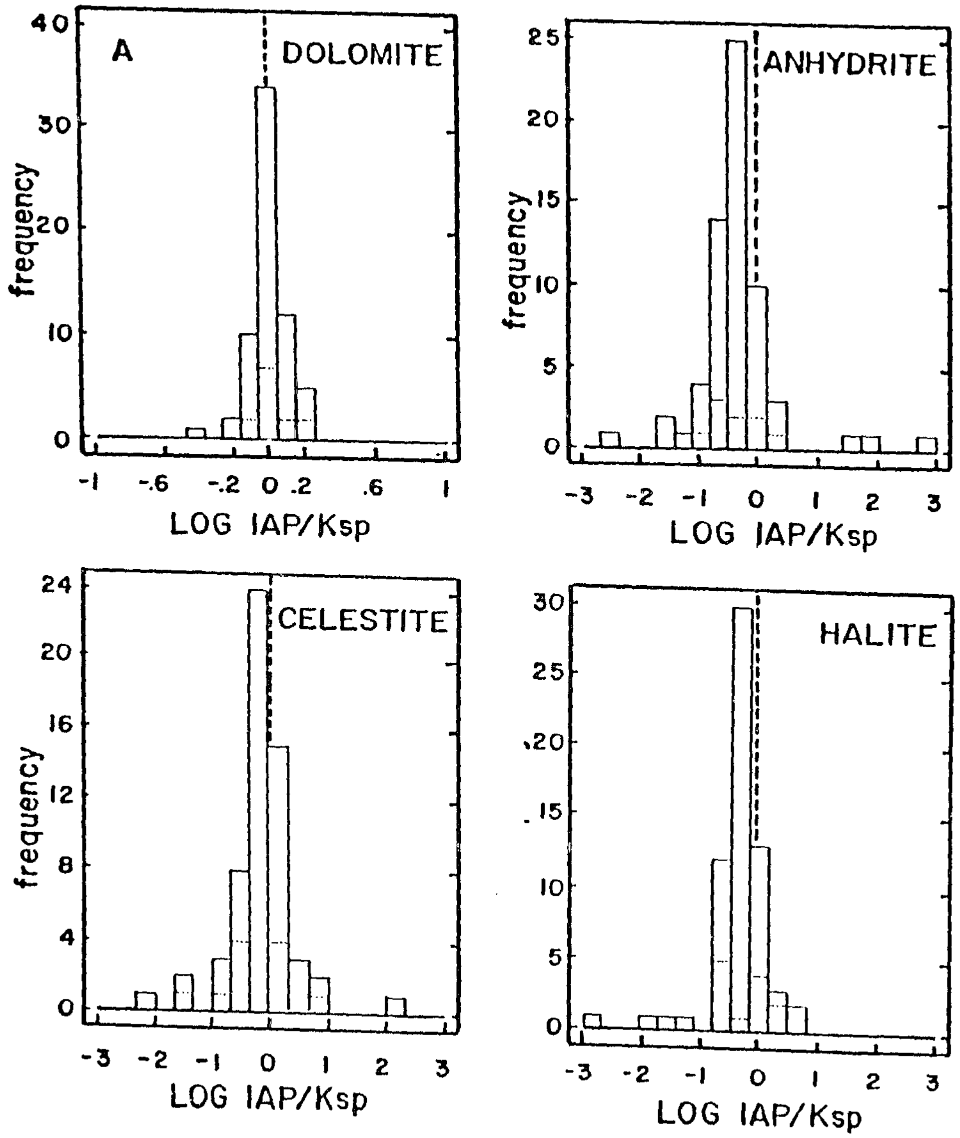


Figure 1-16: Histograms of saturation indices (log IAP/Ksp) for Michigan basin formation waters.

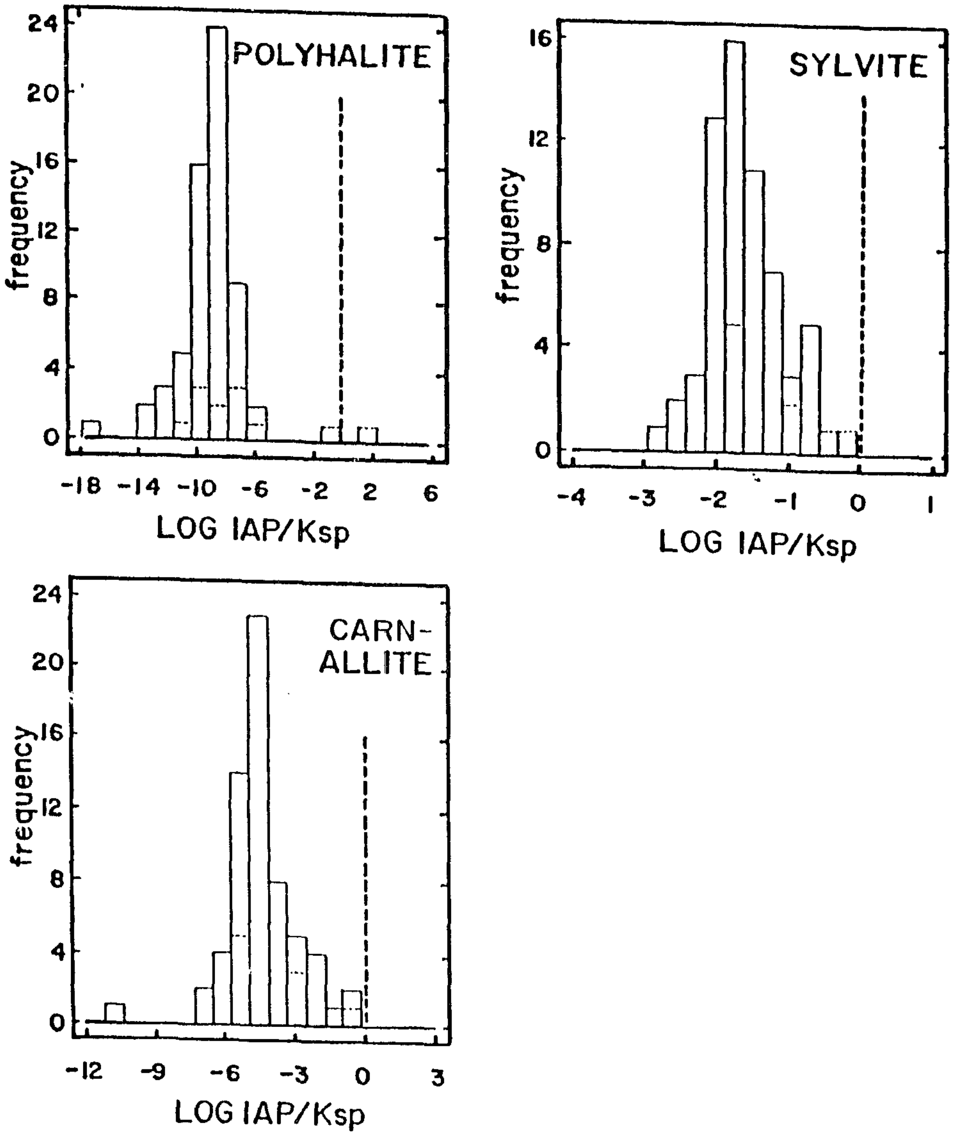


Figure 1-16: Histograms of saturation indices (log IAP/Ksp) for Michigan basin formation waters.

of aragonite to calcite, and solution-reprecipitation of calcite. The Devonian formation waters have molar Sr/Ca of 0.01 to 0.023, with values independent of formation. These values agree with the Sr/Ca predicted for dolomitization of aragonite, and in a few cases, solution-reprecipitation of calcite. Dolomitization of aragonite suggests that carbonate diagenesis affected the brines early in their history, before the aragonite was affected by other reactions. If solution-reprecipitation of calcite was important then a Sr-rich calcite precursor is suggested. The use of Sr/Ca ratios to interpret seawater derived brines such as these is somewhat tenuous, however, as these brines would have been associated with carbonate minerals during all phases of diagenesis. The Sr/Ca may therefore, be the sum of the many different reactions that affect carbonates and only appear to reflect the diagenetic reaction involving the largest exchange of Sr.

The $^{87}Sr/^{86}Sr$ ratios presented earlier (Figure 1-13) suggest that these brines may have reacted with carbonates of similar geologic age to the producing formations of the brines. This conclusion is tempered however, because seawater has had similar Sr ratios many times throughout the Paleozoic. Until more data are collected on the Sr isotopic ratios of the basin minerals, such conclusions are tenuous.

ALUMINOSILICATE REACTIONS

Aluminosilicate mineral reactions may be important in explaining the potassium depletion and the MCl_2 enrichment. Reactions might include albitization of plagioclase, formation of K-feldspar, illite, and chlorite (Kharaka et al., 1973; Merino, 1975; Land and Prezbindowski, 1981).

Authigenic feldspars have been found in carbonate rocks (Kastner, 1979), but have rarely been reported in petrologic studies of Devonian carbonate rocks in Michigan (Sibley, personal comm.). Most likely, authigenic K-minerals would be associated with clastics in the basin such as the Berea and Sylvania Sandstones. Nowak (1978) reported Na and K feldspars in Paleozoic shales of the basin, but it is not clear if these were considered authigenic or primary minerals. Authigenic(?) muscovite is also reported in the Berea formation by Sawtelle (1958). Because feldspar abundances and petrogenesis in Michigan basin rocks has not been documented, it is not possible at this point to quantify their effect on K in these brines.

Most likely, the formation of illite and the subsequent reaction with carbonates has caused the potassium depletion, for example: $2K^+ + CaCO_3 + 3Al_2Si_2O_5(OH)_4 = 2KAl_2(AlSi_3)O_{10}(OH)_2 + Ca^{2+} + 4H_2O + CO_2$. Illitic shales dominate the upper Devonian and Carboniferous rocks, and are present throughout the section as discrete layers and dispersed minerals (Nowak, 1978). Gardner (1974) reports upper Traverse Group contains up to 80% shale in the central basin. The interaction of a K-rich seawater brine with clays may help explain the dominance of illite in the Upper Devonian shales, which are presently at shallow depths (<500 m) and low temperatures (<22°C), conditions thought to be kinetically unfavorable for the smectite-to-illite transformation (Burst, 1969; Perry and Hower, 1970; Hower et al., 1976). If the shales originated as expandable clays, then the interaction with K-rich hypersaline waters might explain the dominance of illite in the basin. Illitization is also supported by the depletion of K in brines from the upper Devonian formations which contain clastics, for example, K depletion is greater in the Berea, Traverse, and Sylvania brine than in the Dundee and Richfield-Detroit River samples (Figures 1-7 to 1-9).

The reaction given above demonstrates illite diagenesis may be tied into the excess MCl_2. An elemental balance model, similar to that used for Ca-Mg, was attempted to determine if illitization could explain the K depletion and the "excess" Ca not explained by dolomitization. During this reaction, the depletion of 2 moles of K from seawater produces 1 mole of Ca. When the amount of K depleted from seawater (based on Br) is plotted versus the "excess" Ca, a large number of samples are found to follow the predicted 2:1 molar relationship. Generally however, an excess of Ca still exists. Whether this excess represents other aluminosilicate reactions is not clear, but the results suggest illite diagenesis may explain the K depletion and much of the excess Ca.

OTHER SALTS

The diagenesis of evaporite minerals may also be important in the evolution of Michigan brines. Anhydrite is abundant throughout the Devonian formations in Michigan, both near the western margins of the basin and in the central-basin area (Gardner, 1974). As an example, the "massive anhydrite" layer at the base of the Ituzi Member of the Lucas Formation is over 30m thick and contains some 10^3 Km^3 of anhydrite (Table 1-1). Reactions involving anhydrite or other evaporite minerals could have supplied Ca and possibly enriched MCl_2 in the basin waters.

Reactions to consider include the gypsum to anhydrite transformation and the replacement of gypsum by glauberite or polyhalite. During the gypsum-anhydrite conversion, each $1m^3$ gypsum liberates $0.486m^3$ of $CaSO_4$ saturated water which can dissolve anhydrite along with other more soluble evaporite minerals (Borchert and Muir, 1964). The significance of this potential Ca supply is realized by considering that the hypothetical transformation of the "massive anhydrite" layer from gypsum would have liberated some $7.8x10^{11}$ liters of $CaSO_4$ enriched water.

The replacement of anhydrite or gypsum by glauberite or polyhalite liberates Ca rich fluid by: $2CaSO_4(H_2O)_2 + 2Na^{2+} = Na_2Ca(SO_4)_2$ (glauberite) + Ca^{2+} + $2(H_2O)$, and $4CaSO_4(H_2O)_2 + Mg^+ + 2K^+ = K_2MgCa_2(SO_4)_4$ (polyhalite) + $2Ca^+$ + $8(H_2O)$. Inspection of Figure 1-8 to 1-10 shows that the Na concentrations generally match seawater values, although random samples show a depletion in Na. The Na depletion may reflect glauberite formation, and perhaps ion exchange of Na for Ca. Glauberite is not a primary evaporite mineral, but forms during the "breakdown of gypsum-anhydrite in association with NaCl solutions" (Borchert and Muir, 1964). Glauberite has yet to be reported in Michigan, but it is found in many evaporite deposits such as the Ochoa Series in Texas (Borchert and Muir, 1964). Polyhalite has been found to replace gypsum in the Silurian salts of Michigan (Dellwig, 1955), and may, in part, explain some of the observed K depletion in the Devonian brines. Although these reactions may not produce large amounts of Ca enriched water, they represent an additional mechanism for divalent cation enrichment (MCl_2) in brine.

In order to determine the control by other mineral phases, equilibrium modeling was attempted in this study. Modeling was done as described earlier using the PHRQPITZ routine of Plummer et al. (1989), and assumed calcite equilibrium. This assumption had little effect of the calculated saturation indices of non-carbonate minerals. Histograms of saturation indices (log IAP/Ksp) calculated for common minerals in the Michigan basin are shown in Figure 1- 15. The model results suggest that the brines may be in equilibrium with halite, anhydrite, gypsum, and celestite in addition to dolomite described earlier. The brines are apparently undersaturated with glauberite, polyhalite, carnallite, and sylvite.

MODEL FOR THE BRINE EVOLUTION BASED ON GEOCHEMICAL DATA

The chemical data and geologic information presented above suggest that brines in the Devonian Formations of the Michigan basin evolved from evapo-concentrated seawater. A Devonian seawater origin is consistent with the basin history and geology, as Devonian rocks in Michigan reflect evaporative conditions. This is illustrated by the dispersed and bedded evaporite minerals in the basin and by the coastal environments interpreted to have existed in the basin (Gardner, 1974; see Table 1-2). Evapo-concentration of seawater would have occurred in the coastal sabkhas and lagoons located around the basin margins (Figure 1-3), and perhaps in the central-basin area during lower sea level stands. Dense, Na-Mg-K-Cl-SO4(?) seawater brine would have refluxed down into the carbonate sediments towards the basin center, mixing with and displacing less dense water residing in the sediments. The more highly concentrated brine would have migrated farther down into the central-basin area as suggested by the Br distribution (Figure 1-6). The underlying Devonian and Silurian salt beds would have trapped the brine and prohibited deeper reflux from occurring. Water-rock reactions, occurring both during and after the brine generation then modified the original seawater composition. Important reactions include dolomitization, which affected the Ca, Mg, and Sr, aluminosilicate diagenesis, which affected potassium and MCl_2, and sulfate reduction or precipitation of $CaSO_4$ during dolomitization, which removed SO_4. Sulfate reduction is a common processes known to operate in areas such as sabkhas, and may have played a more important role in the basin than previous studies have suggested (Matthews and Querio, 1974).

STABLE ISOTOPE RESULTS

Figure 1-17 shows the D/H and $^{18}O/^{16}O$ isotopic ratios (vs. SMOW) in the Devonian formation waters collected in this study. The results are similar to those of Clayton et al. (1966). Also shown is the global meteoric water line (GMWL) from Craig (1961), and two pathways for seawater during evapo-concentration up to halite saturation, from Holser (1979) and Pierre (1982), respectively.

The Michigan brines plot very near the end of the evaporation trend lines and extend back to the GMWL (Figure 1-17a). The Berea, Traverse, and Dundee samples plot intermediate of the more saline Richfield, Detroit River, and Niagara-Salina samples and the GMWL (Figure 1-17b). The isotopic composition of "apparent modern-day meteoric water" (AMMW) is found where the best fit line to the data intersect the GMWL. Four AMMW values and "basin" lines can be calculated (Table 1-6), depending on the formation selected and if D is corrected for activity ($\delta^{a}D$). Correlation coefficients show a wide range of goodness-of-fit for calculated lines, with the best correlation obtained using $\delta^{a}D$ vs. $\delta^{18}O$ in Devonian formation water samples only. AMMW values are near estimated present-day average meteoric water falling on mid-Michigan ($\delta^{18}O=-7.3^{o}/oo$, $\delta D=-50.6^{o}/oo$,

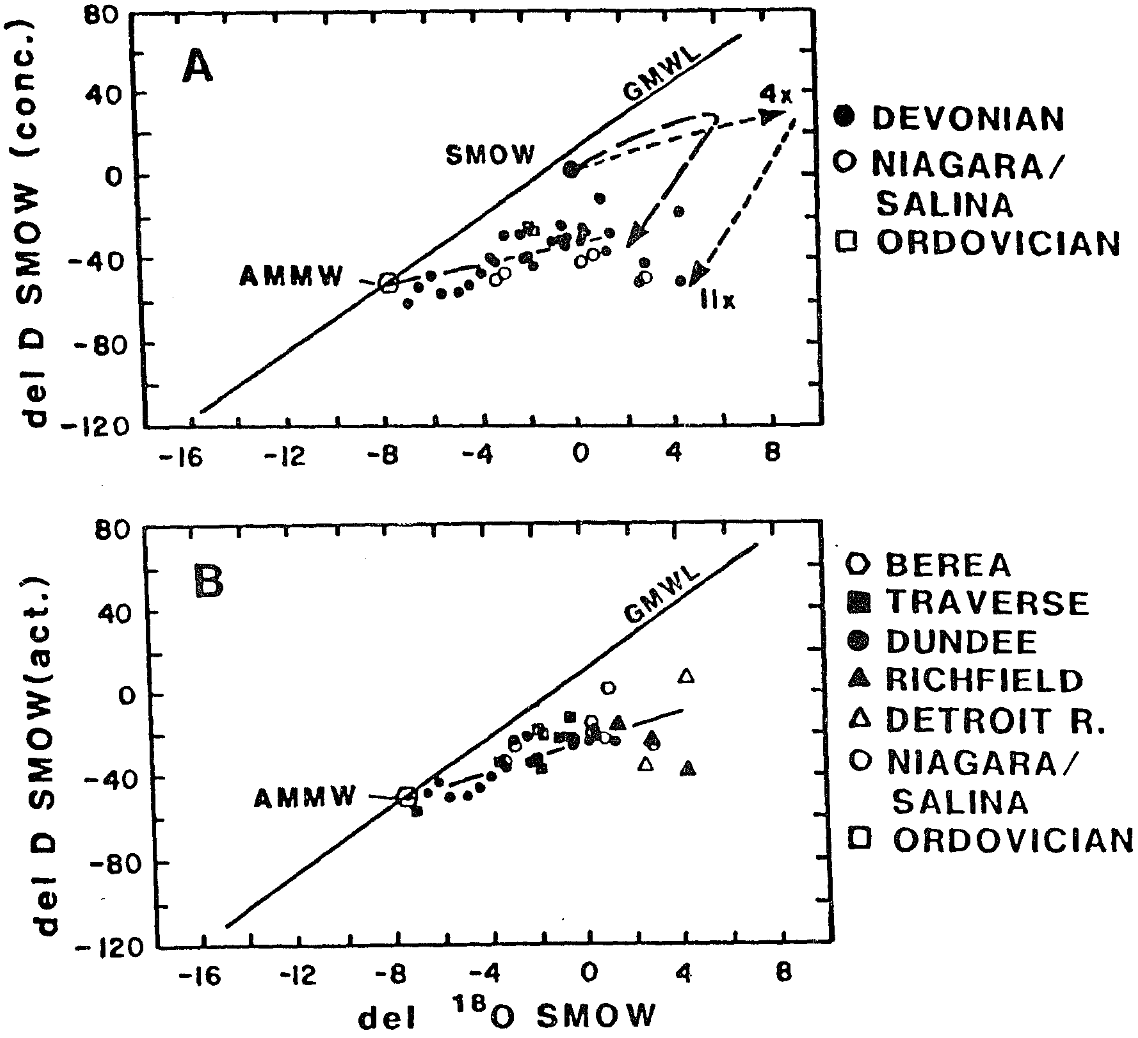


Figure 1-17. (a) del D^{o}/oo (SMOW) concentration scale, (b) and del D^{o}/oo (SMOW) activity scale, vs. del ^{18}O^{o}/oo (SMOW) of Michigan basin waters. Also shown is the best-fit line to the data, and two examples of seawater compositions during evapo-concentration, from Holser (1979) and Pierre (1982).

TABLE 1-5
Apparent meteoric water compositions.

BEST FIT LINE	r^2	AMMW		n
		del $^{18}O^{a}$	del D	
A: del ^{c}D = 1.912 del ^{18}O + -34.537	0.46	-7.32	-48.53	40
B: del ^{a}D = 3.197 del ^{18}O + -22.909	0.67	-6.85	-44.82	40
C: del ^{c}D = 2.508 del ^{18}O + -33.314	0.61	-7.89	-53.10	29
D: del ^{a}D = 3.489 del ^{18}O + -23.791	0.74	-7.49	-49.93	29
E: del ^{c}D = 3.646 del ^{18}O + -38.59	0.79	-11.16	-79.28	26

Equation Key:
A: all data, del D on concentration scale
B: all data, del D on activity scale
C: Devonian formation water data only, del D on concentration scale
D: Devonian formation water data only, del D on activity scale
E: data from %Clayton et al. (1966), del D on concentration scale
AMMW: Apparent modern-day meteoric water, calculated from intersection of best-fit line with the GMWL
n: number of samples

Long et al, 1989). Also listed in Table 1-6 is the equation for the best fit line from Clayton et al. (1966). Because Clayton et al. (19966) used samples mainly from the Devonian formations, their line is similar to the best-fit lines calculated for Devonian samples from this present study. However, the Clayton et al. (1966) line intersects the GMWL at slightly more negative values than present-day meteoric water.

INTERPRETATION

Based partially on the δD-$\delta^{18}O$ values in Michigan basin brines, Clayton et al. (1966) argued that meteoric waters had flushed the basin and that Michigan brines formed, in part, by shale membrane filtration. A meteoric water origin was suggested because the best fit line to the isotopic data intersects the GMWL at a δD value similar to modern-day precipitation falling on Michigan. Their model however, calling for the evolution of freshwater and seawater into brine, is not consistent with the evaporated seawater origin interpreted from the chemical data in this present study.

Knauth and Beeunas (1986) proposed that the isotopic composition of many sedimentary basin brines reflects dilution of evapo-concentrated seawater rather than the evolution of meteoric water into brine. The isotopic composition of seawater first apparently increases in D and ^{18}O during evaporation until approximately gypsum saturation is reached (4x concentration). With continued evaporation the isotopic values decrease; due in part to back exchange with the atmosphere and changing H_2O activities. The isotopic composition of seawater after halite saturation is reached (10x concentration, near the end of the evaporation lines in Figure 1-17) is however, generally not predictable and may be highly variable. The dilution of a residual seawater brine by AMMW then causes formation waters to plot along the best-fit "basin" line (Knauth and Beeunas, 1986).

The isotopic composition of the Michigan brines may be explained by Knauth and Beeunas (1986) model. Perhaps the best evidence for this is the lower salinity of the samples plotting close to the GMWL. This is demonstrated by Figure 1-18, which shows $\delta^{a}D$ plotted versus log Br (mg/l) for the brines collected in this study. The strong linear relationship (r^2=0.8) that exists between these two conservative components shows that samples with more negative δD values have lower Br and salinity. Considering this and the spatial distribution shown in Figure 1-6a, water with lower Br and more negative D values are produced from near the basin margins. Thus, at first consideration, the isotopic data for the Devonian brines are consistent with evapo-concentrated seawater that has been diluted near the basin margin by infiltrating meteoric water. The end member waters and the extent of dilution are however, not entirely evident.

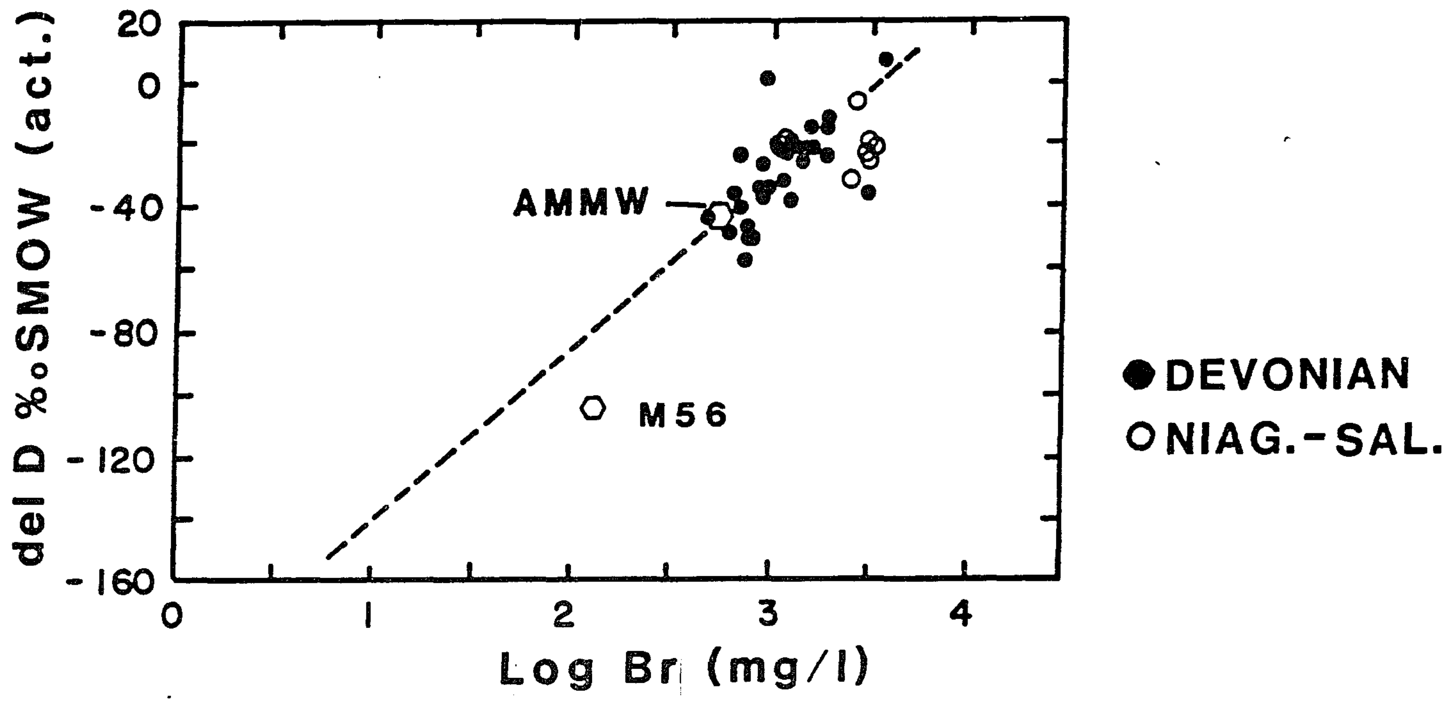


Figure 1-18. del ^{a}D^{o}/oo (SMOW) vs. log Br (mg/l) in all Michigan basin waters. Also shown is the best-fit line (r^2=.8) to the Devonian formation data, and sample M56 from %Clayton et al. (1966).

DISCUSSION

Although the Knauth and Beeunas model is accepted here, an inconsistency occurs in that while the isotopic data may represent dilution, the chemical data apparently does not. If dilution has been masked in the Cl and Na data shown in Figures 1-8 to 1-10, then the co-varying relationships between Br and Ca, Sr, Mg, K, and MCl_2 may represent dilution and not enrichment by evapo-concentration. If this is indeed the case, then the isotopic data might show that the upper Devonian brine (Berea, Traverse, and Dundee) formed by dilution of saline water having an isotopic composition of around $\delta D=-20^{o}/oo$, $\delta^{18}O=2^{o}/oo$, similar to some of the more concentrated Richfield, Detroit River, or Niagara/Salina brines. In other words, the brine in upper formations of the basin may have evolved from water derived from deeper formations. Two explanations for the lack of agreement between isotopic and chemical data are possible, either the isotopic data do not represent dilution by AMMW, or halite equilibria has removed chemical evidence of dilution from the Na-Cl data. Failure for the isotopic data to reflect dilution might mean the isotopic composition of the brine is primarily that of evapo-concentrated seawater, or alternatively, the components expected to behave conservatively during dilution (D,O,Br), in reality, do not. In order to explore these questions further, the possible end member waters, both saline and AMMW must be characterized, and the question of what would be required to link the chemical and isotopic data together must be addressed.

SALINE END MEMBER

In contrast to its chemical composition, the isotopic composition of the saline end member water (seawater) is difficult to quantify. The isotopic composition of evaporating water is a function of the initial composition, humidity, rate of evaporation, isotopic values in the vapor phase, and degree of mixing (Lloyd, 1966; Sofer and Gat, 1972 and 1975; Nadler and Margatiz, 1980). Because of the complex interplay of these factors, the isotopic path of seawater during evaporation may be unique for any basin, and may vary within a basin. This variability is demonstrated by the two different evaporation paths shown in Figure 1-17, and by the results of Nadler and Magritz (1979) who measured the isotopic composition of Mediterranean seawater during evaporation. Their data show that after reaching halite saturation, residual seawater brine had a δD (concentration scale) composition more negative than the non-evaporated seawater source. Considering that most of the Michigan brines are concentrated far past the start of halite precipitation (10x), very little can be said about the isotopic composition of the parent seawater bitterns for the Michigan brines. Additionally, the isotopic values of seawater before evaporation may have been different from present-day SMOW. It has been suggested, for example, that seawater may have been 1 to 2‰ lighter in ^{18}O during the

Devonian (Fritz, 1971; Popp et al., 1986). A change of this magnitude in both $\delta^{18}O$ and δD would make Devonian seawater plot very near the main group of Michigan brines in Figure 1-17. Thus, the isotopic composition of Michigan basin brines may be nearly that of the parent seawater from which they were derived, or alternatively, if concentrated seawater brines were diluted with Devonian seawater, then dilution may not be visible in the isotopic data.

APPARENT MODERN-DAY METEORIC WATER

The isotopic and chemical nature of AMMW must also be considered. A wide variety of meteoric water compositions must have fallen on the basin throughout geologic time. Thus, the chemical and isotopic composition of AMMW may not be that of "modern-day" meteoric water. The relationship between D and Br (Figure 1-18) can be used to help evaluate AMMW composition. Deuterium, like Br, is generally considered conservative in formation waters, although deuterium may exchange with clays, gases, and may br enriched by organic matter decay (Fritz et al., 1986; Hitchon and Friedman, 1969). The best fit line to the D-Br data shows a good correlation (r^2 =.8), somewhat better than for δD vs. $\delta^{18}O$ (Table 1-6). This line predicts that AMMW with a δD of $-50^o/oo$, the AMMW value (Table 1-6), should contain about 450mg/l Br (525 mg/l using the concentration scale). The source for a Br enriched meteoric water of this composition is unknown. To evolve meteoric water into such a water by salt dissolution, saturation with halite containing uncommonly high concentrations of Br is required, in this case, at least 1260ppm Br. Recent models that describe halite recrystallization (Stoessell and Carpenter, 1986) and the effects of diffusion during the interaction of saturated brine with halite may explain Br enrichment (Wilson and Long, 1985), but the occurrence of these processes in natural systems has not been demonstrated.

The D-Br line (Figure 1-18) extends back to very negative δD values at low Br values characteristic of meteoric water, for example, δD=-195^{o}/oo when Br=1mg/l. This value is characteristic of glacially derived water rather than present-day meteoric water. Infiltration of isotopically light water is also supported by sample M56 (Figure 1-18) taken from Clayton et al. (1966), which was not used in determining the best fit line shown. This Traverse water sample was collected at the extreme western edge of the basin (18N, 17W) and is thought to be glacial meltwater (δD=-109 ^{o}/oo, δ^{18}O = -13.11 ^{o}/oo, Br= 134 ppm) which had dissolved halite (115 g/l) and anhydrite (3.6 g/l minimum) (Graf et al., 1966). Sample M56 plots near the best-fit line, suggesting that dilution by isotopically light water causes the D-Br relationship. If the dilute end member water has a more negative isotopic composition then AMMW then a much smaller amount of meteoric water is needed to explain the isotopic trend, which may help explain the lack of dilution in the Cl-Na data.

LINKING ISOTOPIC AND CHEMICAL DATA

Considering the problems involved in defining the chemical and isotopic compositions of the end member waters, it may not be possible to link the two types of data together in a single model. A question therefore, is what would be required if the two types of data represent the same evolutionary path?

This question is explored in Figure 1-19, where, because the isotopic composition of the saline end member is not known, the following model was considered. Two Dundee formation water samples (water A, #3029, and water B, #3081) are used, along with apparent meteoric water (AMMW) from Table 1-5. The composition of these two samples, which were collected from the basin center and margin, respectively, and various mixtures are listed in Table 1-6. If dilution of a single saline end member by AMMW explains these samples, then continued dilution of sample A by AMMW should account for the chemical and isotopic composition of the intermediate sample B. Bromide and deuterium are the only elements that can be considered conservative in mixing, as Cl could be supplied by halite dissolution and ^{18}O could be altered by reactions with carbonates and other minerals.

First, the deuterium in sample B is predicted based on dilution of sample A, with dilution calculated using bromide. Based on Br, the dilution of sample A by AMMW (Br=0) predicts that sample B would plot at point C on Figure 1-19a after a 50% mix (Br=640mg/l, Cl=92,500mg/l).

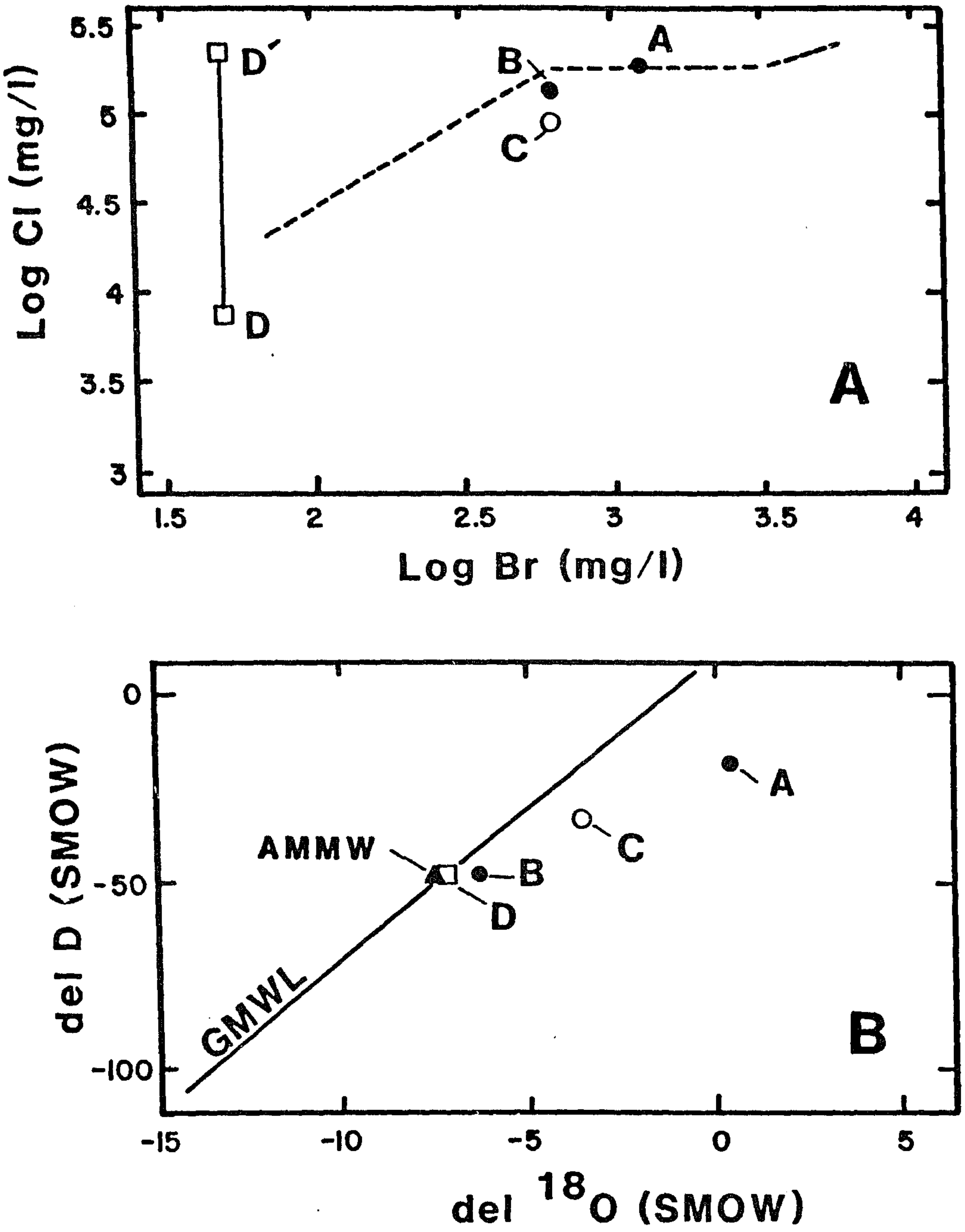


Figure 1-19. Possible mixing scenarios between Dundee brines and AMMW. (A) Log Cl (mg/l) vs. log Br (mg/l), and (B) del D^{o}/oo vs. del ^{18}O^{o}/oo (SMOW)

TABLE 1-6
Results of mixing example.

POINT	^cD	δ^aD	$\delta^{18}O^a$	$\delta^{18}O^c$	Br	Cl	f
A (sample 3029)	-26.1	-18.6	0.43	1.06	1240	185,000	
B (sample 3081)	-52.6	-48.6	-6.53	-6.21	620	92,500	
C (not corrected for brine salinity)	-39.6	-35.8	-3.53	-3.42	620	158,000	0.5
C (corrected for brine salinity)	-39.6			-3.53	620	92,500	0.5
D (not corrected for brine salinity)	-52.7	-52.6	-7.76	-7.73	22	3330	0.18
D (corrected for brine salinity)	-52.6			-7.76	19	2775	0.15
AMMW (activity scale from line D, table 5)		-49.9	-7.49		0	variable	
AMMW (concentration scale, from line C, Table 5)	-53.1			-7.89	0	variable	

Key: Br and Cl as mg/l, del D and del ^{18}O as ^{o}/oo, SMOW.
Point C = composition resulting from dilution of Br
Point D = composition resulting from dilution of D
^cD, $^{18}O^c$ = deuterium and oxygen on concentration scale.
^aD, $^{18}O^a$ = deuterium and oxygen on activity scale.
f = fraction of brine sample A in mixture, 1-f = fraction of AMMW in mix.

Point C clearly does not match sample B in Cl, but if AMMW had dissolved 63.5 g/l halite, or if halite dissolution occurred after mixing to increase Cl to 131,000 mg/l, than both Br and Cl in sample B can be explained. However, as shown in Figure 1-19b, the mixture has a $\delta^{C}D=-39.6^{o}/oo$ and $\delta^{18}O=-3.22^{o}/oo$ (concentration scale, $\delta^{18}O$ corrected from activity following Sofer and Gat, 1972), which is 3 permil enriched in $\delta^{C18}O$ over water B. Whether this reflects enrichment of $\delta^{18}O$ by carbonate mineral reactions is discussed below.

Next, the Br in sample B is predicted based on dilution of sample A, with dilution calculated using deuterium. When calculating the isotopic composition of mixtures of brine and dilute water, it is important to recognize that a given volume of a highly concentrated brine contains significantly fewer water molecules than the same amount of AMMW. For example, a liter of brine A contains about 70% of the H_2O molecules in a liter of pure water. Consideration of this is made in the isotopic mixing calculation by using:

$$F*A*({}^{C}D_{brine})+(1-F)*1*({}^{C}D_{freshwater})= {}^{C}D_{mix}$$

where F is the fraction of brine mixed, and A is the ratio of water molecules in the concentrated brine solution compared with freshwater (water molecules per kg brine solution / water molecules per kg freshwater). The value of A in AMMW is assigned 1. The results of calculated mixing considering this factor are listed in Table 1-6.

The mixing of 15% sample A with 85% AMW can predict the δ^cD in sample B. Because sample B does not fall exactly on a straight mixing line between sample A and AMMW, sample B can be matched only in δ^cD, and only approximately matched in $\delta^{18}O$. This mix plots at point D in Figure 1-19b. However, point D plots in Figure 1-19a at Br=19mg/l, Cl=2775mg/l (δ^cD=-52.6, $\delta^{c18}O$=-7.76°/oo). Because the final Cl content would depend on the amount of halite dissolved, the mixture may plot anywhere along the line D-D′. In this case the mixture chemistry would reflect halite dissolution, and clearly does not match the composition of sample B.

In sum, it does not appear possible to predict both the Br and δ^cD in sample B by using a single mixing ratio. Similar results are obtained when mixing samples that have δ^cD more intermediate between sample A and AMMW, however, it is noted that the closer the δ^cD value of the intermediate water is to sample A, the closer the agreement becomes with dilution based on Br.

These calculations suggest that <u>if</u> dilution of a saline end member water by AMMW explains the Devonian formation brine, as suggested by the isotopic data, then it must have been accompanied by halite dissolution and ^{18}O enrichment. Halite dissolution is certainly possible, considering the presence of halite in the basin, and the geologic evidence that Salina salts were extensively dissolved from around the basin margins during the Devonian time (Landes et al., 1945). The next consideration, therefore, is whether ^{18}O

enrichment has occurred from reactions with oxygen bearing minerals. Enrichment of ^{18}O was proposed by Clayton et al. (1966), who suggested that isotopic equilibrium with carbonate minerals causes the $\delta^{18}O$ in brines to shift from the meteoric water line (Figure 1-17). Hitchon and Friedman (1969) calculated that West Canada formation waters may have been enriched by as much as +9^{o}/oo in $\delta^{18}O$ as a result of equilibration with carbonate rocks. Land (1980) demonstrated that pore-waters in carbonates will rapidly increase in ^{18}O during mineral re-crystallization, and Knauth and Beeunas (1986) show how ^{18}O enrichment of formation waters can result from gypsum dewatering as well (Knauth and Beeunas, 1986).

Isotopic equilibrium with carbonate minerals is evaluated in Figure 1-20, where $\delta^{18}O$ values are plotted versus estimated formation temperatures. Data on the isotopic composition of Devonian carbonates in Michigan are severely lacking, however, Gardner (1974) reports an average $^{18}O/^{16}O$ of -5.75$^{o}/_{oo}$ (PDB) for micritic calcite from the Detroit River Group. This values is similar to that used by Clayton et al. (1966)(-5.39^{o}/oo PDB) and can be used to calculate water $\delta^{18}O$ as a function of temperature using: **alpha*($\delta^{18}O_{rock}$+1000)=($\delta^{18}O_{water}$+1000).** The fractionation factor (alpha) is calculated using: **$10^3\ln$ alpha=$2.78\times10^6T^{-2}$ - 2.89**, from O'Neil and Epstein (1966). Figure 1-20 shows the brines exhibit a wide spread of $^{18}O/^{16}O$ ratios over the narrow range of formation temperatures, and plot across the

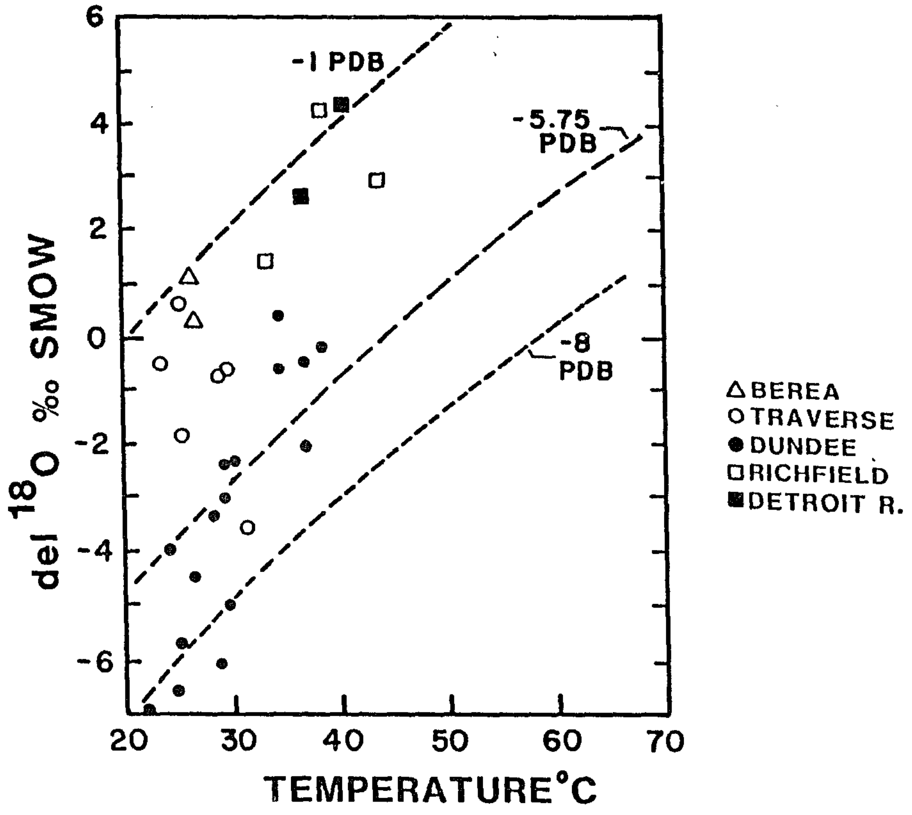


Figure 1-20. del ^{18}O °/oo (SMOW) vs. estimated formation temperature. Shown as a dashed line are the del ^{18}O values for water predicted to be in equilibrium with calcite of -1, -5.75, and -8 °/oo PDB.

calculated equilibrium line. Calculated values fall between lines for calcite of -1°/oo PDB and -8°/oo PDB. Although the data seem to follow the general trend of the equilibrium lines, there is not a single ^{18}O value for calcite that can explain the range of brine compositions. A better fit would be obtained if (1) higher temperatures (paleo-temperatures?) are used for samples collected from the basin interior, or (2) the fractionation factor (alpha) increases more with temperature. Non-uniform higher temperatures in the basin interior may reflect that brines in these areas were buried deeper in the past. The explanation of a fractionation factor that increases more as a function of temperature than the one used here might indicate that dolomite equilibrium plays a role in controlling $^{18}O/^{16}O$ in these waters, as equations for dolomite-water fractionation apparently have larger slopes than for the calcite-water system (Land, 1982). Further information on basin mineral and cements and paleo-temperatures are needed before this question can be completely addressed. However, the enrichment of the oxygen isotopes in the brines by carbonate equilibrium remains a possibility.

MODEL FOR THE BRINE EVOLUTION BASED ON ISOTOPIC DATA

The isotopic evolution of Michigan formation waters is an enigmatic problem. One explanation is that the Michigan brines largely retain their original seawater isotopic signature (perhaps modified by water-rock equilibria), and dilution has been limited, primarily to near the basin margins. This explanation is consistent with the geochemical model presented earlier, and would be most applicable for brines in the lower Devonian formations (Richfield, Detroit River).

The isotopic data can also be interpreted to show that large scale dilution of a seawater brine by AMMW has occurred. Considering this, a second scenario may be that the upper Devonian brines originated by mixing of higher concentrated brine, perhaps derived from lower Devonian or Niagara/Salina formations, with AMMW. In this case the co-varying relationships between Ca, Sr, K, Mg and Br (Figures 1-7 to 1-9) reflect dilution, and not enrichment by evapo-concentration. Additionally, halite equilibria is needed to remove evidence of dilution from Cl/Br and Na/Br ratios; dilution has been limited to where Br remains at values characteristic of evapo-concentration; and reactions with carbonate rocks have increased ^{18}O in the brines and may have affected Mg. Each of these conditions appear possible.

If mixing explains the elemental and isotopic trends, then evidence of mixing would be expected in the Sr isotopic ratios when plotted versus Sr content (Figure 1-21). Mixing of two waters having different isotope ratios and Sr concentrations should result in a straight line in a plot of $^{87}Sr/^{86}Sr$ vs 1/Sr (Faure, 1986). The amount of data available limits the interpretations that can be made, but a direct linear mixing trend is not observed in this plot. Rather, the data appear to group by formation in a band

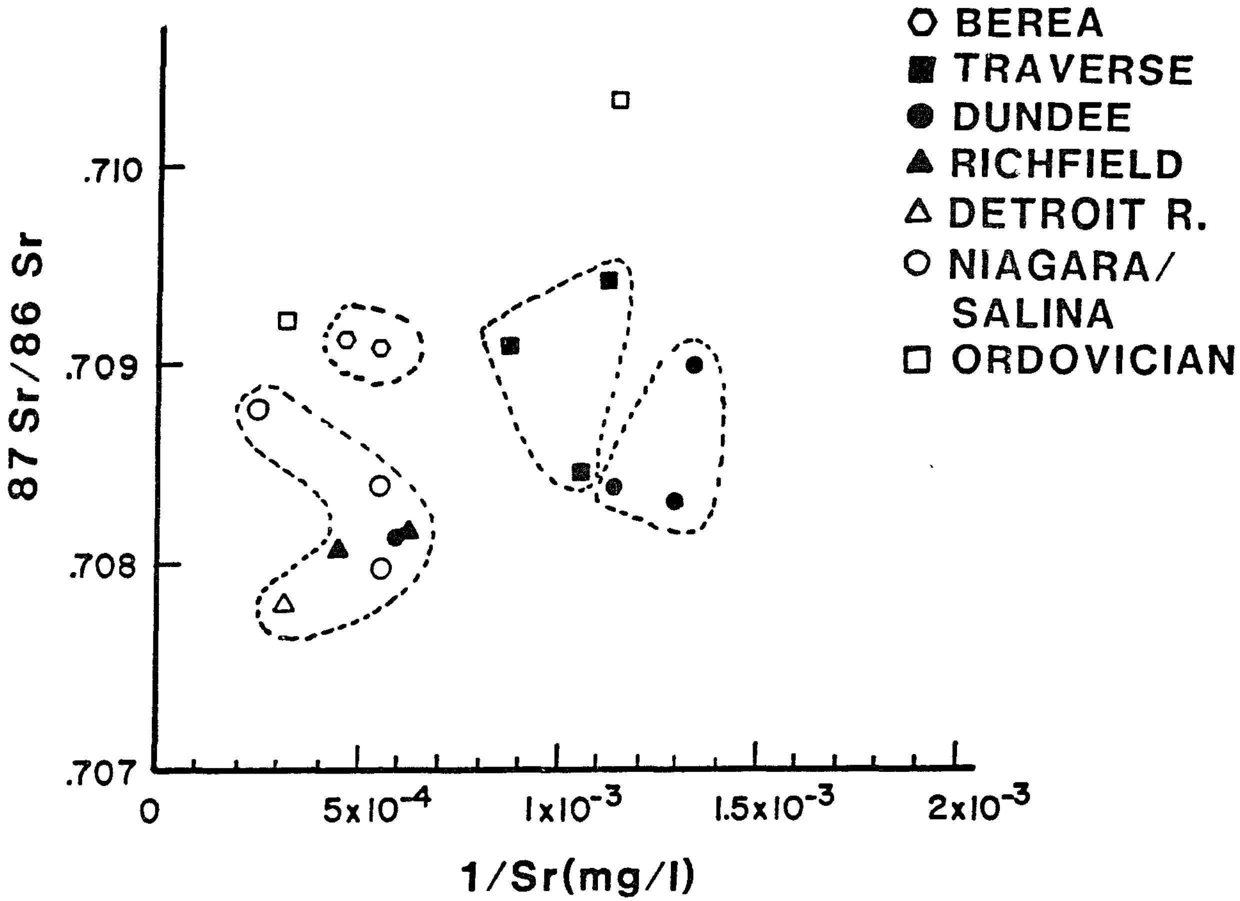


Figure 1-21: Plot of 1/Sr (mg/l) vs. $^{87}Sr/^{86}Sr$ of the Michigan basin brines.

having similar isotopic values (0.7082 to 0.7092) independent of Sr concentration. One interpretation is that this diagram does show dilution of a Richfield-Detroit River or Niagara/Salina formation brine,by a dilute water having a isotopic composition similar to the brine. Near-surface ground water in Michigan may have these characteristics because their Sr composition would be governed by reactions with Paleozoic carbonates in the bedrock and till. As an example, Lake Huron water is reported to have a $^{87}Sr/^{86}Sr$ ratio of 0.7086 (Faure et al., 1963), similar to many of the deep brine samples reported here. Enrichment in ^{87}Sr caused by water-rock reactions, especially those involving shales (McNutt et al., 1987; Stueber et al., 1984), may explain the dispersion from a linear mixing trend.

Several other observations lend support to a mixing evolution for the upper Devonian formation brines. First, it is questionable that evaporative conditions in the Traverse and Dundee formations ever reached the high degrees needed to explain the Br in the brines. Conditions that favor seawater evapo-concentration into the late halite and $MgSO_4$ salt facies is certainly more consistent with the Salina geology in Michigan.

Additionally, the Niagara-Salina and Richfield-Detroit River formation waters are highly enriched in MCl_2 (Figure 1-11, Chapter 2). Although the mineral reactions discussed previously might explain some MCl_2 enrichment, especially in light of the enrichments found in other basins (Figure 1-4), dilution of a MCl_2 enriched brine derived from the Silurian salts is also possible. Based on the measured formation volumes listed in Table 1-1, fluids representing less than 10% of the present volume of Silurian salts can account for the volume of Devonian formation waters (assuming average porosity of 10%). Any remnant brine squeezed from the Silurian salts that has migrated upwards during sediment compaction may have caused the MCl_2 enrichment. These fluids would have mixed with dilute waters present in the Devonian sediments, or were later diluted near the basin margins. It is not known however, if such dense brine could have moved upwards to the Devonian sediments in a slowly compacting basin such as Michigan (Bethke, 1985), which suggests a modification to this scenario. The MCl_2 enrichment may have simply been carried along through time with each incursion of seawater into the basin. Although not based on chemical evidence, Briggs et al. (1980) suggested that highly concentrated seawater bitterns remained in the central-basin are of Michigan between incursions of seawater in the Silurian. Similar fluids may have resided in the lower areas of the basin during the Devonian. Burial and compaction may later move the fluids towards the basin margins, mixing with meteoric water.

SUMMARY

The data presented here suggest that Devonian formation brines in Michigan originated from evapo-concentrated seawater. This is supported by the halide chemistry, as well as by relationships between the other elements and Br. Although somewhat more equivocal, isotopic data support dilution of an evapo-concentrated seawater bittern by meteoric water. The original evapo-concentrated seawater chemistry was modified by extensive water-rock interactions. Most important appears to be dolomitization and aluminosilicate reactions such as illitization.

Two scenarios are presented to explain the chemical and isotopic origin. Either the brines formed syngenetically with Devonian formation rocks or they are in part derived from the underlying formations, such as the Richfield, Detroit River, or Niagara-Salina. The data do not seem to unequivocally distinguish between these origins.

Several chemical and geologic observations however, favor a syngenetic evolution for the upper Devonian formation water, and make this the preferred model. Most important are the difference in cation composition and degree of concentration reached by the upper Devonian formation brines (Dundee-Traverse-Berea) brines, versus the water in the underlying formation waters (Richfield-Sylvania-Detroit River and Silurian). These differences suggest an independent evolution for these two groups of brines. The similarity in chemistry and lack evaporitic conditions (Sawtelle, 1958) suggests that Berea Formation waters perhaps migrated from the upper Devonian formations. The fact that the lower Devonian formation brines (Richfield, Detroit River) are more highly concentrated Ca-

Cl solutions that have similar isotopic compositions that do not suggest dilution, and are associated with Devonian and Silurian evaporite deposits supports that these waters share a common origin, possibly being remnant brine derived from the evaporite deposits.

In the syngenetic origin model, the upper Devonian brines originated during deposition of formation sediments in coastal sabkhas and lagoons as well as during restricted periods of the Devonian. Dense seawater brines would have refluxed down into the lower areas of the basin and reacted with the formation carbonates and clays. Underlying salt layers would have kept the brines from refluxing further downward. The brines largely retain their parent seawater isotopic composition, perhaps being modified by carbonate equilibria, and some were later apparently diluted to minor degrees with meteoric water.

In the second scenario, the brines in the upper Devonian formations originated, in part, from fluids derived from the lower Devonian or perhaps the Silurian salts. Divalent cations in the fluids would have been enriched either as the result of the reactions suggested earlier, or by reactions involving the Silurian potash deposits. These fluids would have moved into the Devonian sediments during compaction and mixed with meteoric water. In this case, the diluted bitterns have maintained equilibrium with halite and carbonate rocks.

CHAPTER 2

Origin and evolution of water in Niagara-Salina and Ordovician aged formations, Michigan Basin

INTRODUCTION

Sedimentary basins contain a variety of sediment types reflecting many geologic histories, and as such, no single rock type or diagenetic history will characterize a single basin. Similarly, it is possible that no single origin or evolution can explain the chemistry of all waters within a basin. Although water chemistry may evolve by reactions with sediments and by mixing, the water within each formation of a basin may retain a chemical signature that reflects an origin or evolution unique to the basin. This suggests that to best determine their geochemical origin and evolution, basin waters should be studied on an individual formation basis whenever possible.

The Paleozoic rocks in the Michigan basin (Figure 2-1) reflect the many geologic conditions that existed in the basin, such as periods of shallow and deep water carbonate deposition, hyper-saline evaporite deposition, clastic deposition, and periods of emergence. The origin of saline waters contained within the basin has been linked to periods of intense seawater evaporation (Chapter 1). Under a more detailed examination however, differences in water chemistry are observed between the individual formations of the basin. Figure 2-2 illustrates the the major cation composition of

MICHIGAN BASIN

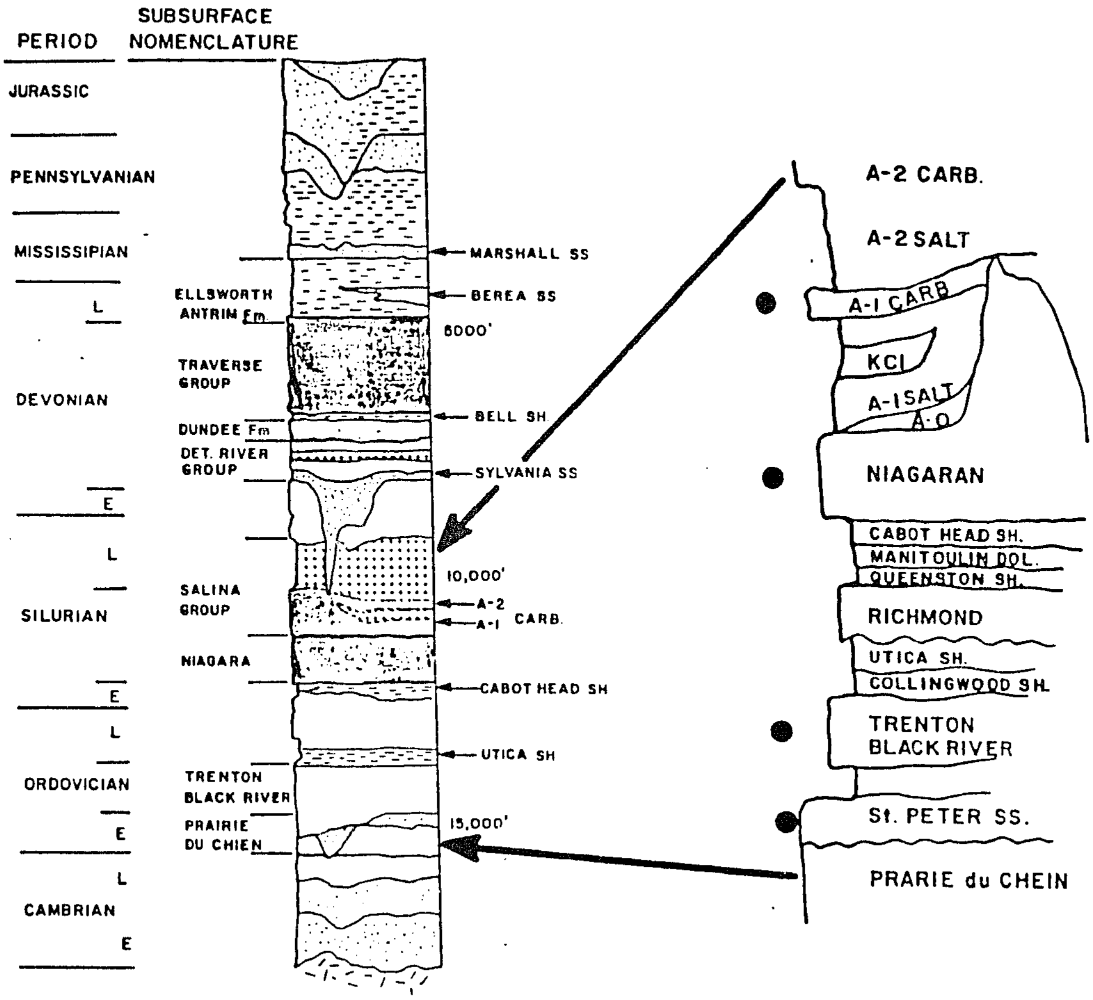


Figure 2-1. Stratigraphic column of the Michigan basin.

brine from the different formations in Michigan. Brine chemistry in the basin ranges between Na and Ca dominated water as a function of formation. These differences reflect the different evolutions of the water within each formation, and might be explained by formation history, mineralogy, hydrology, and geochemical reactions.

This paper reports on formation waters in the Ordovician and Silurian aged formations in the Michigan basin. These formations differ in their geology and history, and as Figure 2-2 demonstrates, in their water chemistry. Silurian formations produced water mainly from Niagaran aged reefs that encircle the basin. These deeply buried reefs and are encased in salts that significantly reduce their hydrologic connection with overlying formations, and produced some of the most highly saline $CaCl_2$ brine known (Case, 1945). In contrast, Ordovician aged Trenton and Black River formations produce water from a major fracture system in the basin, located outside of, and at shallower depths than, the Niagaran reefs. The Ordovician rocks in this area are not capped by the Salina salts and the fault system allows ready connection to other formations. These Ordovician formations contain NaCl brine that is less saline than the Niagara/Salina formations, being more similar to water from the upper Devonian formations in the basin (Figure 2-2). This paper proposes that water in the Silurian and Ordovician formations of the Michigan basin originated from evapo-concentrated seawater,

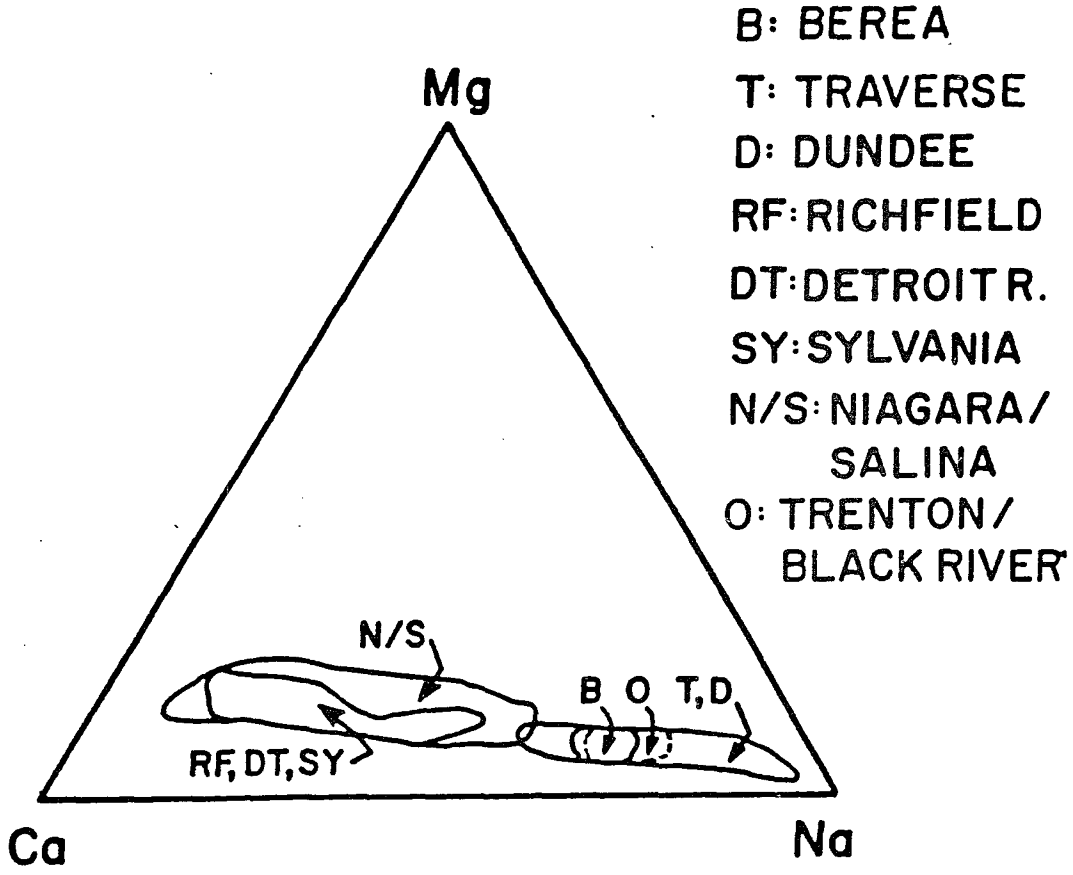


Figure 2-2. Ternary diagram showing percentages of Ca-Mg-Na (mole percent) in Michigan Basin brines.

similar to the origin proposed for water in other formations in the basin (Chapter 1). Both formations retain unique chemical signatures, however, the Ordovician formation brine suggests an evolution by mixing, while the Niagara/Salina formation water retains a chemical signature reflecting their seawater origin and an evolution by water-rock reactions.

STUDY AREA

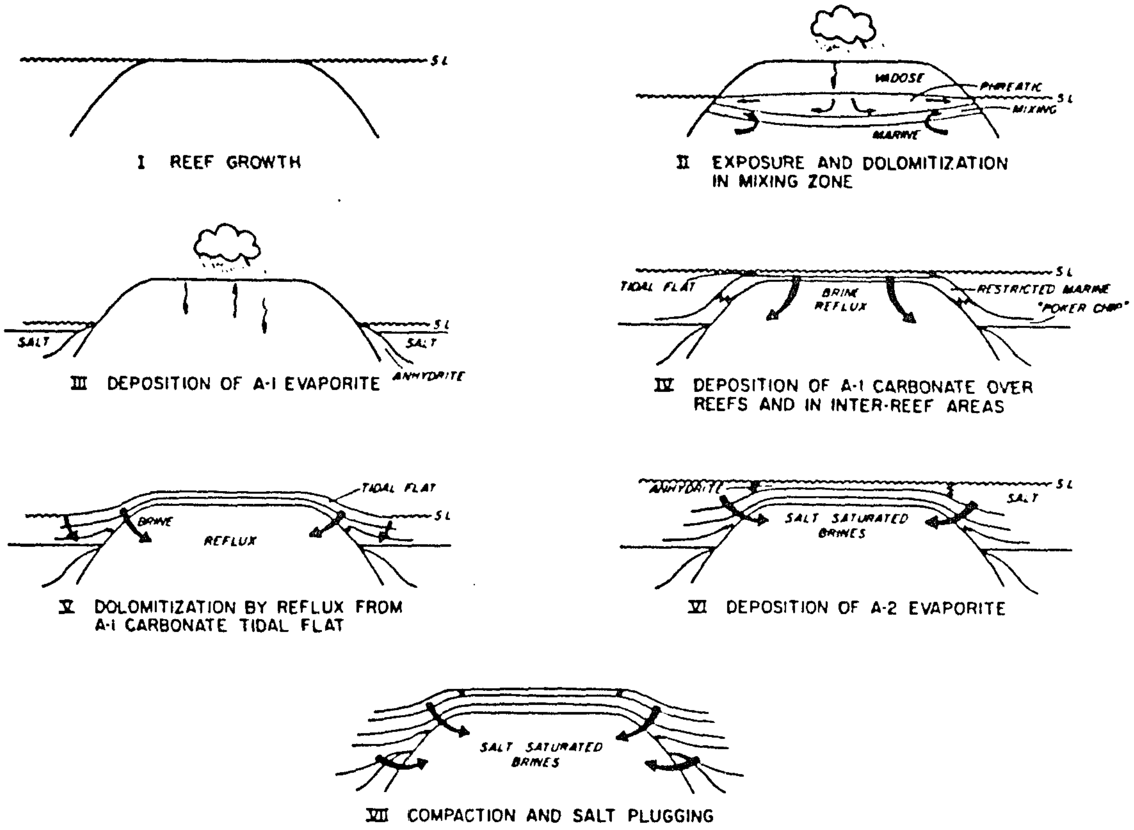
NIAGARA/SALINA REEFS

Formation waters studied here are produced from middle Silurian aged Niagaran carbonate reefs (Figure 2-1). Because the reefs are built upon the Niagaran dolomites and intersect the Salina A-1 Carbonate unit within the salts, the true producing formation of the water is in question. Therefore, these samples are termed Niagara/Salina (N/S) brines. Niagaran reefs encircle the basin in a belt some 16 to 40 km wide, with individual reefs occupying from <1 to over 5000 acres, averaging about 80 acres in size (Gill, 1979). Three reef types have been identified based on diagenetic and geologic criteria (Gill, 1979). First are the reefs located nearest the basin margins which contain mostly water, are highly dolomitized, and have little or none of their porosity plugged with salt. The second reef group is located more basinward and is less dolomitized. They contain hydrocarbons and have only minor amounts of porosity plugged with salt. The third group includes the innermost pinnacle reefs which contain mostly gas or are barren, are slightly dolomitized, and in some cases, their porosity is completely plugged with salt.

REEF HISTORY

The Niagaran reefs have interacted with a variety of water types during their history (Fisher, 1977; Nurmi and Friedman, 1977; Gill, 1979; Sears and Lucia, 1980). Figure 2-3 outlines the reef history and is from Sears and Lucia (1980). Reef growth began after deposition of the Middle Niagaran Lockport Formation carbonates, which formed a stable ramp platform in the basin (3-I). Reefs formed along the shallower basin margins, in mid-shelf areas, and in deeper water as pinnacle reefs. During reef growth, frame building organisms that formed the bulk of the reefs built upwards in response to rising sea level.

Sometime after the pinnacle reefs reached heights of about 45m, seawater levels lowered and exposed the reefs. Dolomitization of the reefs is thought to have occurred during this period by a mixed water system (3-II). Extreme basin isolation followed during which time concentrated seawater interacted with the reefs as the Salina A-1 salts were deposited around the reefs (3-III). A subsequent rise in sea level allowed thinly laminated algal stromatolites, mudstones, and conglomerates of the A-1 Carbonate to be deposited first over the salts and later around the reef base (3-IV). The A-1 Carbonate was apparently deposited in two stages, over the reefs during the periods of high sea levels, and inter-reef during lower stands. Tidal flats



I REEF GROWTH

II EXPOSURE AND DOLOMITIZATION IN MIXING ZONE

III DEPOSITION OF A-1 EVAPORITE

IV DEPOSITION OF A-1 CARBONATE OVER REEFS AND IN INTER-REEF AREAS

V DOLOMITIZATION BY REFLUX FROM A-1 CARBONATE TIDAL FLAT

VI DEPOSITION OF A-2 EVAPORITE

VII COMPACTION AND SALT PLUGGING

Figure 2-3. Diagenetic history of Niagaran reefs in Michigan, from Sears and Lucia (1982).

formed during low seawater stands and resulted in dolomitization of the upper portions of the reefs and the inter-reef areas by refluxing seawater brine (3-V). Following this, the A-2 and ensuing Salina salts buried the reefs (3-VI). Salt saturated brines are thought to have infiltrated the reefs during the deposition of the A-1 and A-2 salts (3-VII) and during salt compaction. McCollough (1977) suggested that concentrated seawater from the deposition of the A-1 salts was responsible for the salt plugging of porosity in the Niagaran reefs.

Although a variety of waters, interacted with the reefs during their early history, including fresh-water, normal marine, and hypersaline seawater, fluid movement through the reefs occurred later as well. Gill (1979) suggested that freshwater entered the Niagaran rocks at the basin margins sometime during the Late Silurian to Middle Devonian time, and flushed the outer reefs opening their porosity (Figure 2-4). After the pore filling salts were removed, up-dip migrating fluids and hydrocarbons became entrapped in the reefs (Gill, 1979). In addition, Cercone and Lohmann (1987) reported that late burial diagenetic assemblages in the reefs (geopetal sediment, pyrite, bituman, dolomitic cements, equant calcite spar) formed as a result of high temperature (>80°C) deep basinal brines that migrated through the Niagara and the A-1 Carbonate formations.

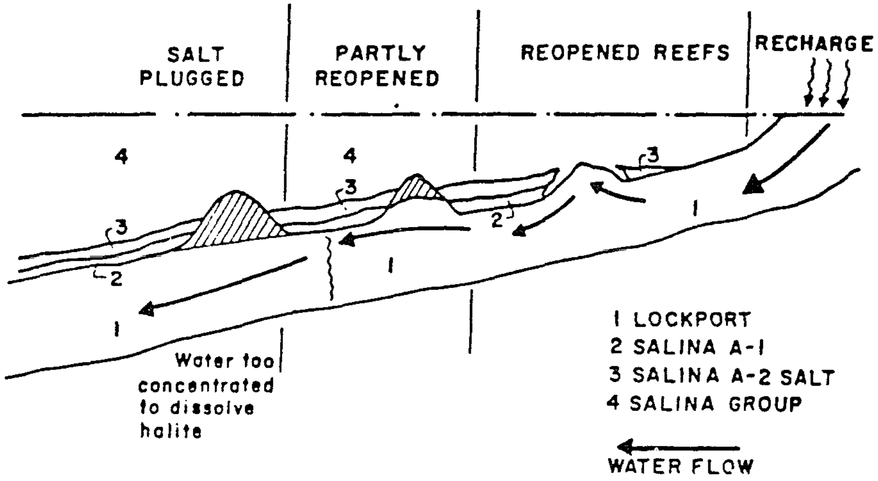


Figure 2-4. Proposed model for freshwater flushing of Niagaran reefs in Michigan, from Gill (1977). Recharge may have entered the Niagaran rocks along marginal arches, flowed down into the basin, and dissolved salt from reefs along the basin margins.

SALINA SALTS

The Salina salts, especially the A-1 salt, may play an important role in the generation of the Michigan Basin brines. Over 500m of Salina salts exist in the Michigan basin in 6 individual units (the Salina A to F salts). The salt origin has been linked to the restricted conditions caused, in part, by the Niagaran reef system described above (Dellwig, 1955). Minerals reported in the Salina salts include halite, anhydrite, sylvite, carnallite (Dellwig, 1955; Kunasz, 1970), polyhalite (Dellwig, 1955), Ca-borate nodules (Nurmi and Friedman, 1977), authigenic quartz and chalcedony (Gill, 1979), hematite, pyrite, and both illitic-chloritic shale (Lounsbury, 1963).

The Salina A-1 salt is the only known potash bearing formation in the basin (Nurmi and Freidman, 1977; Elowski, 1980; Sonnenfeld, 1985). The geologic history of these salts is somewhat equivocal. Matthews (1970) and Matthews and Egleson (1974) thought the A-1 salts represent the start of a megacycle of deep-water evaporite deposition in the basin, while Nurmi and Freidman (1977) suggested that the A-1 potash salts precipitated in a highly desiccated, shallow marine basin. Figure 2-5 illustrates the geology and stratigraphy of the Salina A-1 unit in relationship to the Niagaran reefs and the Salina A-1 carbonate. The sylvinite (a mixture of NaCl and KCl) bearing units of the A-1 salt cover an area of 33,700 km^2, and occur in multiple beds between 1m and 4m thick that coalesce into a single bed 15-20m thick near the northwest area of the basin (Matthews and

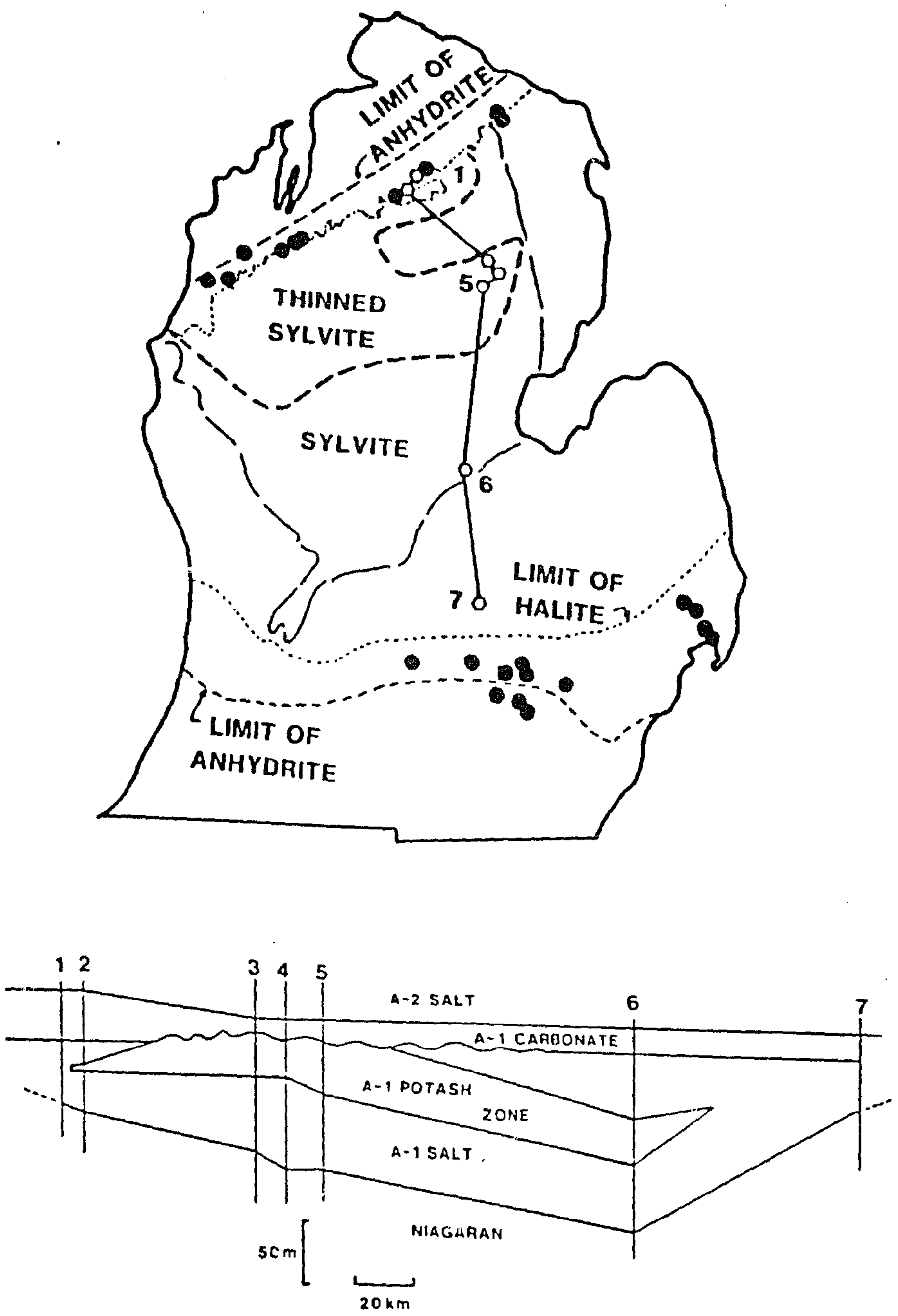


Figure 2-5. Salina A-1 salt stratigraphy, after Matthews and Egleson (1977).

Egleson, 1974). In the northern area of the basin the sylvite is thinned and truncated by an erosional surface that intersects the A-1 carbonate. A notable feature of the A-1 salt is the lack of Mg-K-SO4 evaporites, as the sylvite layers are apparently encased completely in halite. This observation led Matthews and Egleson (1974) to suggest that the Michigan evaporites belong to the class of highly $MgSO_4$ deficient deposits categorized by Braitsch (1971).

ORDOVICIAN FORMATIONS

Hydrocarbon and brine production from Ordovician aged formations has, until recently, been centered along the Albion-Pulawski-Scipio fault trend in Southern Michigan (Figure 2-6). This is a highly dolomitized, 35 mile long fault zone located along an upwarp in the basin. This upwarp now has a general synclinal form along its crest, attributed to dolomitization and fracturing of the fault area (Ells, 1967). Hydrocarbon production is from the Trenton and Black River Formations, both of which are composed of fossiliferous, finely crystalline limestone (wackestone) and dolomite, locally rich in argillaceous minerals (Taylor, 1982). Because of their interconnection and because wells are often open to both zones, these samples are termed the Trenton-Black River (TBR) brines in this study.

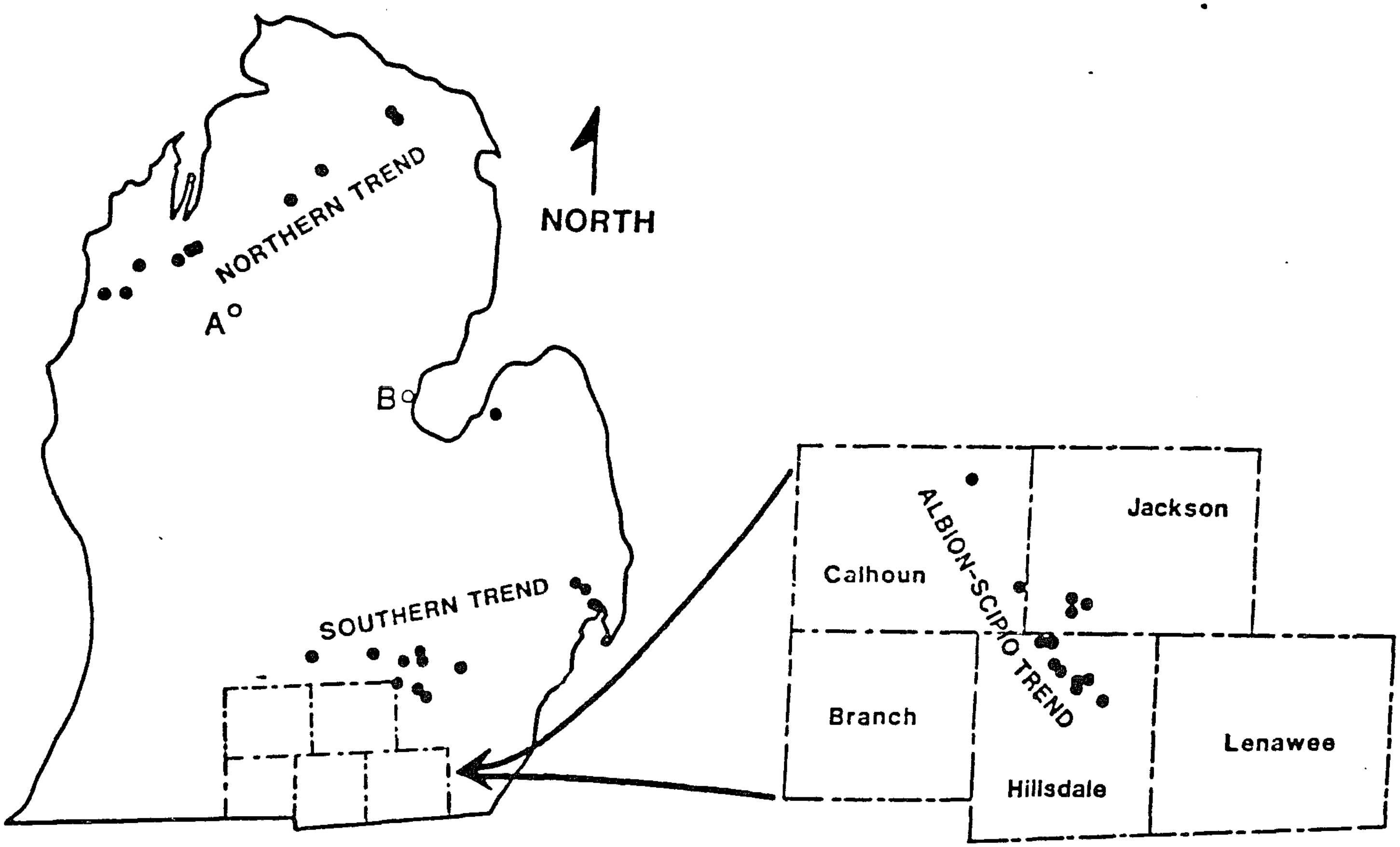


Figure 2-6. Sample location map. St. Peter Sandstone sample from (A), and the Case (1945) sample from (B).

The faulting, or reactivation of pre-existing faults in this area apparently created channels for fluids that dolomitized the fault zone (Taylor, 1982). In addition to this fracture related dolomite, two other generations of dolomites occur in the Trenton rocks (Cohee et al., 1958; Taylor, 1982). A ferroan dolomite zone, approximately 15m thick, exists in the upper section of the Trenton. This dolomite, referred to as cap dolomite, is present only near the basin margins and grades downward into limestone (Taylor, 1982). A second generation of regional dolomite is found in the extreme western and southwestern area of the basin, where Trenton rocks are almost completely dolomitized (Taylor, 1982). The fracture related dolomite differs from the cap and regional dolomites, as it is non-ferroan, coarse grained, and xenotropic (Taylor, 1982). Shaw (1975) suggested that fracture related dolomitization occurred between Silurian and Devonian time, at a minimum fluid temperature of 80°C. This is also the minimum temperature suggested by Cercone and Lohmann (1987) for the late diagenetic fluids that affected the Silurian reefs.

Gas has recently been produced from the lower Ordovician St. Peter Sandstone and Prairie du Chien formations, from the northern area of the basin. These formations contain generally quartz sandstone and dolomitic sandstones.

METHODS

Seven brine samples from the Trenton-Black River formations were collected from the Albion-Scipio trend of southwest Michigan, and were supplemented with 5 analyses obtained from Michigan Department of Natural Resources Geological Survey open files, and from files of various oil producing companies. In addition, one sample of water from the St. Peter Sandstone[1] was collected from a gas well in Missaukee County in central Michigan. Sixteen samples from Niagaran reefs in both the northern and southern reef trends, and a sample from the A-2 Carbonate (#2020) were also collected. These were supplemented with 9 analyses from M.D.N.R. files, and the analyses reported by Case (1945, listed in Table 2-4). Figure 2-6 shows the sample locations. All analyses made in this study have charge balance errors of less than 5%, although some of the collected analyses had charge balance errors between +6% and +8%. Comparison with analyses made in the present study shows that samples with poor charge balances differed mainly in Cl. These collected analyses were used only in graphical treatments of the data.

1:The sample well is the Dart Edwards 7-36 (T22N, R7w, sec. 36). The drillers log records this well as being finished in the Prairie du Chien Sandstone. Sibley (personal communication) suggests that the producing formation is really the St. Peter Sandstone, or perhaps the Bruegers Sandstone.

Brine sampling was preformed in the manner explained in detail in Chapter 1. Samples were collected directly from the well head whenever possible, allowed to separate, and were filtered through glass wool and Watman #1 filters. Field measurements included temperature, pH, Eh, and when possible, alkalinity. The N/S samples were diluted in field to avoid possible problems with salt precipitation, a common occurrence in Niagara/Salina reef wells. At each location, one sample was diluted 50% with 5%HNO_3 for cation analysis and another diluted 50% with distilled H_2O for anion analysis. Hydrocarbon-brine mixtures would occasionally not separate in the field, and in these cases, combined hydrocarbon-water samples were collected in plastic bottles, sealed, and allowed to separate in the laboratory, before being treated as described above.

Because of the hydrocarbon and salinity characteristics, fresh water and other additives are often introduced into N/S wells to prevent salt and paraffin build-up. Every attempt was made to avoid sampling any well injected with additives, or to sample before injection occurred. Additional problems were encountered with sampling TBR wells. The Albion-Scipio trend has produced hydrocarbons since the early 1930's, and for the past several years brine has been re-injected into the TBR formation. The limited number of samples obtained from the Trenton-Black River formation reflects the difficulty in finding production wells sufficiently distant from injection wells to insure representative samples could be collected.

The samples were analyzed using A.A.S, titrimetric, and gravimetric methods reported in Chapter 1. Five N/S brines and 3 TBR brines were further analyzed for the stable isotope ratios of D/H and $^{18}O/^{16}O$ at the Environmental Isotope Laboratory, University of Waterloo, Waterloo, Ontario. Results are reported in δ $^{o}/oo$ values normalized to SMOW. Measured isotopic values were converted between activity and concentration scale following Sofer and Gat (1972).

GENERAL RESULTS

Well information, analytical, and isotopic results are listed in Appendix C. Table 2-1 is a summary of average compositions of the Niagara/Salina and Ordovician TBR waters, and also lists the one St. Peter Sandstone sample collected in this study. Geometric means are listed because the data were found to be log-normally distributed.

The Niagara/Salina brines are highly concentrated with TDS values typically in excess of 400 g/l. The high salinity is best exemplified by the Niagaran brine reported by Case (1945) that has a T.D.S. of 640 g/l (Table 2-4). The TBR waters are less concentrated with salinities between 300 and 360 g/l. Figure 2-7 shows the relative precentages of Na, Ca, and Mg (mole percentage) in the Niagara/Salina and Ordovician waters used in this study, and demonstrates that most of the N/S samples, and the St. Peter Sandstone

TABLE 2-1
Average composition of Niagara/Salina and Ordovician formation waters, Michigan Basin

Component	NIAGARA-SALINA	ORDOVICIAN (TBR only).	ORDOVICIAN St. Peter
Cl	210,000	126,000	250,000
Br	2400	1030	3100
Ca	74,000	22,800	90,100
Mg	11,500	5130	9710
Na	31,400	30,000	28,200
K	9250	3680	19,500
Sr	2190	750	3160
Rb	24	8	58
Li	60	38	44
B	127	13	107
Si	2	3	20
NH_4N	550	80	247
HCO_3	90	40	10
SO_4	50	205	-
I	25	11	20
TDS	345,000	207,000	404,000
MCl_2	4720	1580	5367
n	26	11	1

Key: All values as mg/l, except MCl_2 (meq/l).
HCO_3: Alkalinity as HCO_3
$MCl_2 = Ca + Mg + Sr - 0.5HCO_3 - SO_4$
n = number of analyses for major components
St. Peter Sandstone sample, #8040

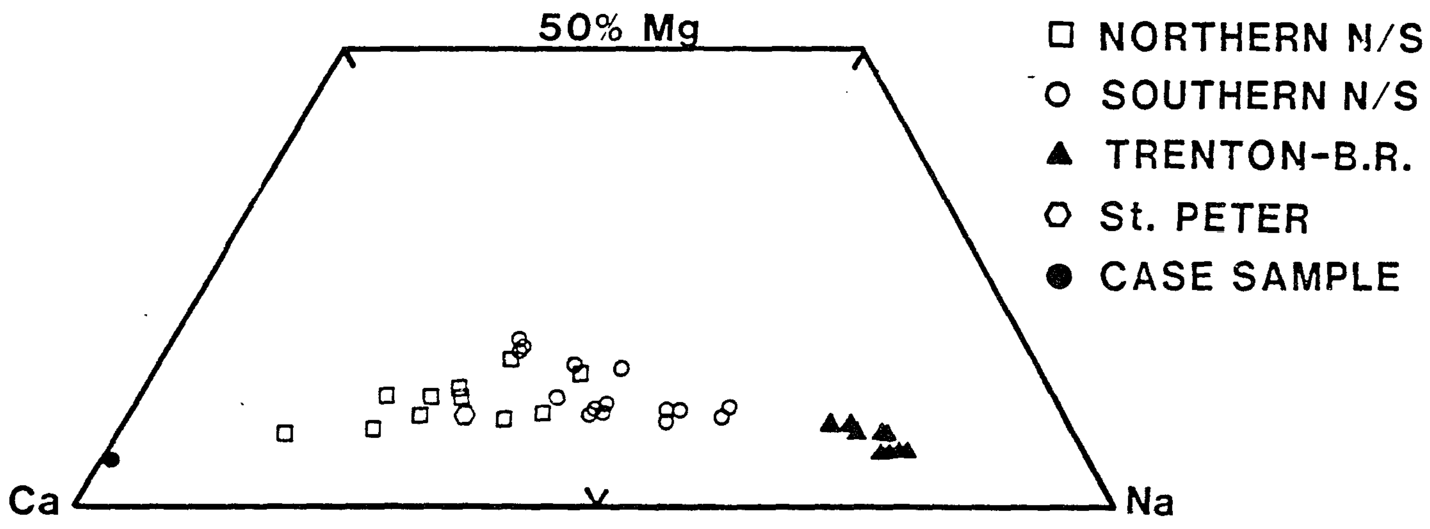


Figure 2-7. Ternary diagram showing percentages of Ca-Mg-Na (mole percent) in Niagara/Salina and Ordovician aged formations in the Michigan basin.

sample are Ca-Cl brine, while the TBR brines are Na-Cl. The N/S samples are separated by reef trend (north vs. south), and as can be seen, the northern samples appear to be contain a higher relative percentage of Ca then do the southern reef samples. Differences between northern and southern reef samples are also observed in the other elements, discussed below. Chloride is the dominant anion in these waters, while SO_4 and alkalinity are minor components and in some samples are below detection. The Case (1945) samples show anomously high alkalinity values, however, these may be related to dissolved organic acids (Case, 1945; Willey et al.,1975).

NIAGARA/SALINA FORMATION RESULTS

Previous work (Chapter 1) has shown that the Michigan basin brines may have evolved from evapo-concentrated water and in following that observation, the Niagara/Salina samples are compared with evapo-concentrated seawater in Figure 2-8 (d-f). The seawater concentration trend lines shown are from data in McCaffrey et al. (1988) and Carpenter (1978). The data shown in the graphical plots are separated into northern reef trend and southern reef trend samples with the mid-basin samples (sample #2020, and the Case, 1945 analysis) combined with the southern trend samples. A generally good agreement is evident between Cl-Br in the brines and seawater (Figure 2-8a). Several of the northern trend samples plot on the seawater line past the start of $MgSO_4$ precipitation, while several samples having lower

Figure 2-8. Niagara/Salina formation waters (log mg/l) compared with evapo-concentrating seawater (dashed lines, data from McCaffrey et al. 1988; and Carpenter, 1978). A: Log Cl-log Br, B: Log Na-Br, C: Log K-Br, D: Log Ca-Br, E: Log Mg-Br, F: Log Sr-Br.

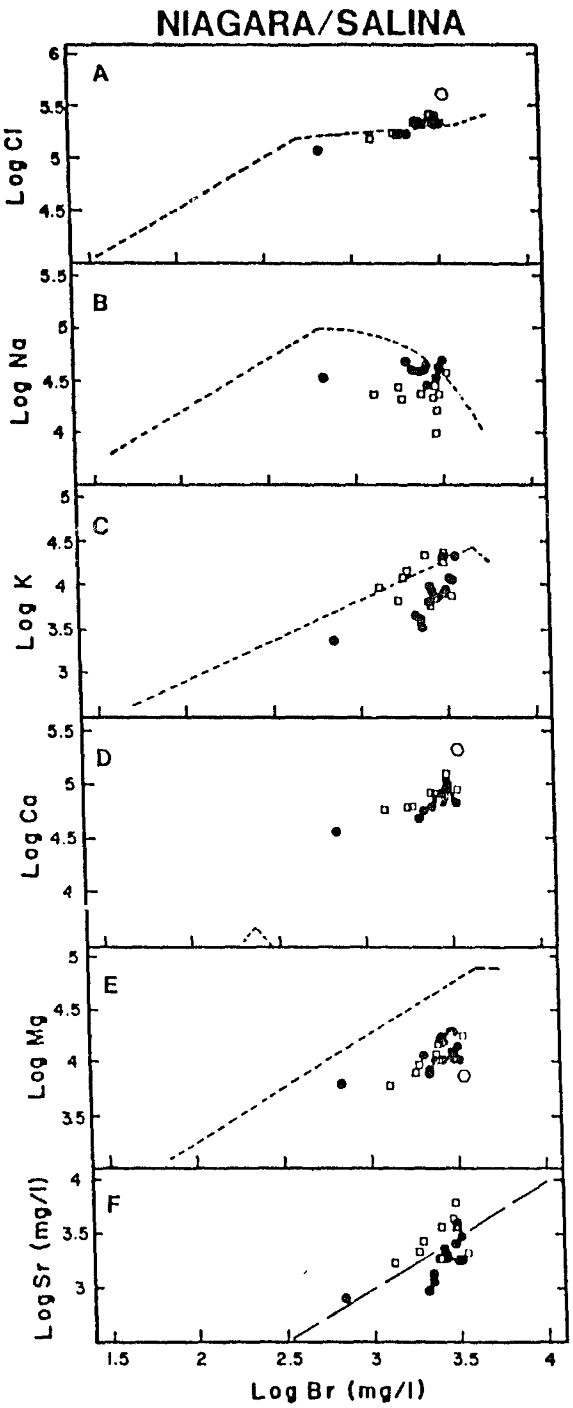

NIAGARA/SALINA
A
Log Cl
B
Log Na
C
Log K
D
Log Ca
E
Log Mg
F
Log Sr (mg/l)
Log Br (mg/l)
1.5
2
2.5
3
3.5
4

Figure 2-8

amounts of Br plot below the seawater line. The Case (1945) sample plots above the seawater trend line and has a Br concentration similar to seawater concentrated to the K-salt facies.

The log Na-Br plot also demonstrates the close agreement with seawater and a division between northern and southern reef trend samples (Figure 2-8b). Most of the southern reef samples, and some of the northern samples, plot as a cluster very near the seawater trend line. However, several northern samples are depleted in Na or Br, and plot as outliers from this cluster. This figure also demonstrates how the N/S brines plot as clusters on the log-log plots rather than as distinct linear trends characteristic of the other formation waters in the basin (Chapter 1).

Figure 2-8(d-f) shows that Ca, Mg, and Sr co-vary directly with Br, with Ca and Sr being highly enriched and Mg depleted from expected seawater values, characteristics similar to those found in the Devonian formation brines (Chapter 1). A near 1:1 relationship exists between Ca-Br and Sr-Br in most samples, similar to other Michigan formation waters (Chapter 1). However, Mg values generally plot more as a cluster below the seawater line rather than in a linear trend. Potassium plots in two groups, one group, generally the southern reef samples, are depleted in K and plot below the seawater trend line. The second group, generally the northern samples and the Case (1945) sample, plot very near the seawater trend line.

An important relationship used in examining evapo-concentrated seawater brine is MCl_2, defined as: MCl_2=Ca+Mg+Sr-HCO_3-SO_4 (in meq/l, Carpenter, 1978). MCl_2 represents the divalent cations balanced by Cl, and during evapo-concentration of seawater, the MCl_2(meq/l)/Br(mg/l) remains approximately 1. MCl_2 is conservative and is not affected by dolomitization, $CaCO_3$, $CaSO_4$, and halite precipitation-dissolution, and sulfate reduction. When the log MCl_2 values are plotted versus log Br (Figure 2-9), the N/S brine appear to be either enriched in MCl_2 or are depleted in Br from concentrated seawater. This is also the case for the TBR samples and the Devonian formation water in the basin (Chapter 1). When log MCl_2 is plotted versus log Cl (Figure 2-9b), the N/S brine apparently agree with the seawater concentration line, similar to the Br-Cl plot (Figure 2-8a). Chapter 1 discusses some of the reasons why MCl_2 may appear to be enriched or Br depleted in these waters, but the agreement with seawater in both the MCl_2-Cl and Br-Cl plots suggests that MCl_2 values are enriched in these waters.

ORDOVICIAN FORMATION RESULTS

The Ordovician formation samples are compared with seawater in Figure 2-10(a-f). The TBR samples plot below the seawater Cl-Br line and extend down toward seawater (Figure 2-10a). A similar relationship is found when the

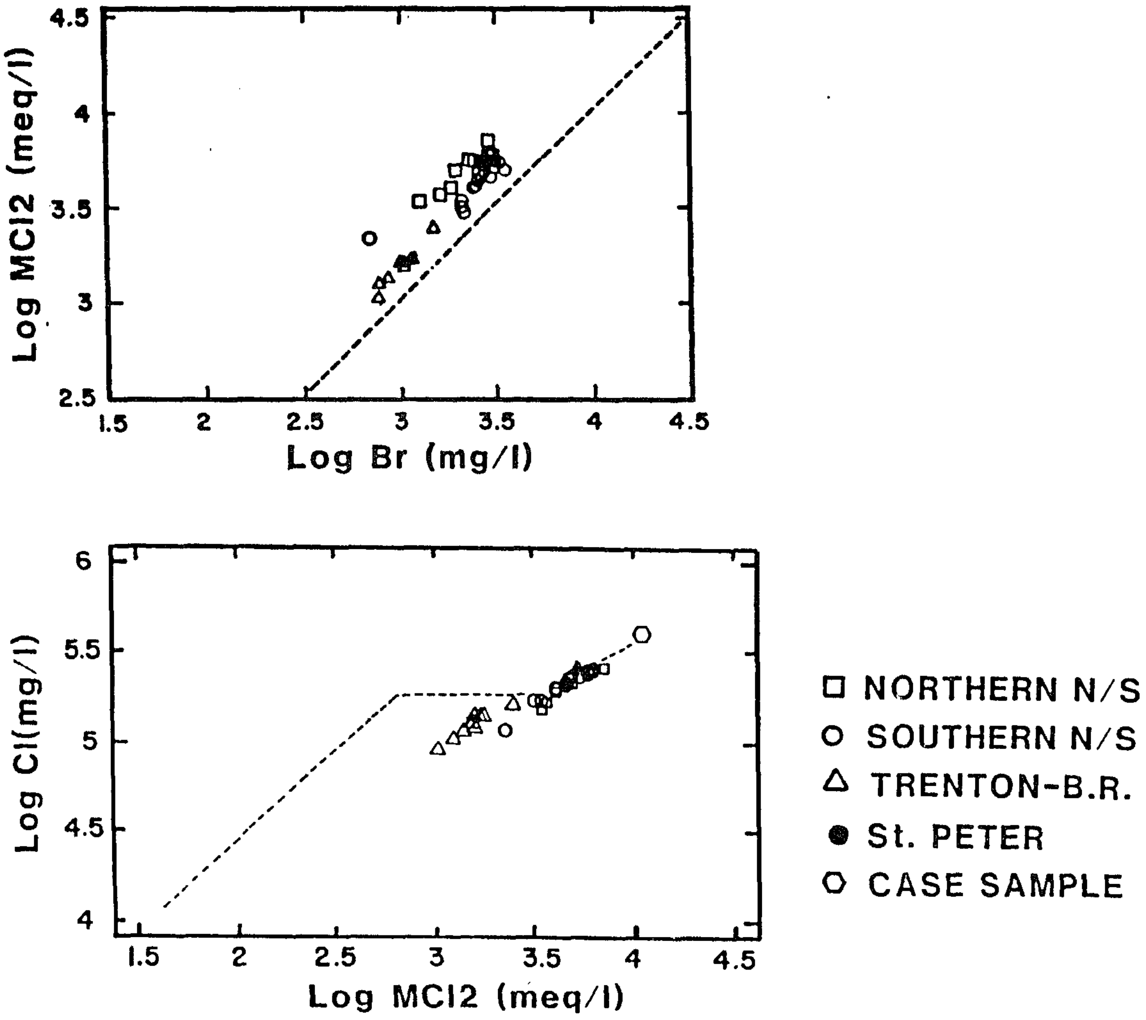


Figure 2-9. Log MCl_2 (meq/l) vs. log br (mg/l) and log MCl_2 (meq/l) vs. log Cl (mg/l) in the Niagara/Salina and Ordovician formation waters, compared with evapo-concentrated seawater (dased line, data from McCaffrey et al., 1988; and Carpenter, 1978)

Figure 2-10. Trenton-Black River and St. Peter Sandstone formation water (log mg/l) compared with evapo-concentrating seawater (dashed lines, data from McCaffrey et al. 1988; and Carpenter, 1978). A: Log Cl-log Br, B: Log Na-Br, C: Log K-Br, D: Log Ca-Br, E: Log Mg-Br, F: Log Sr-Br.

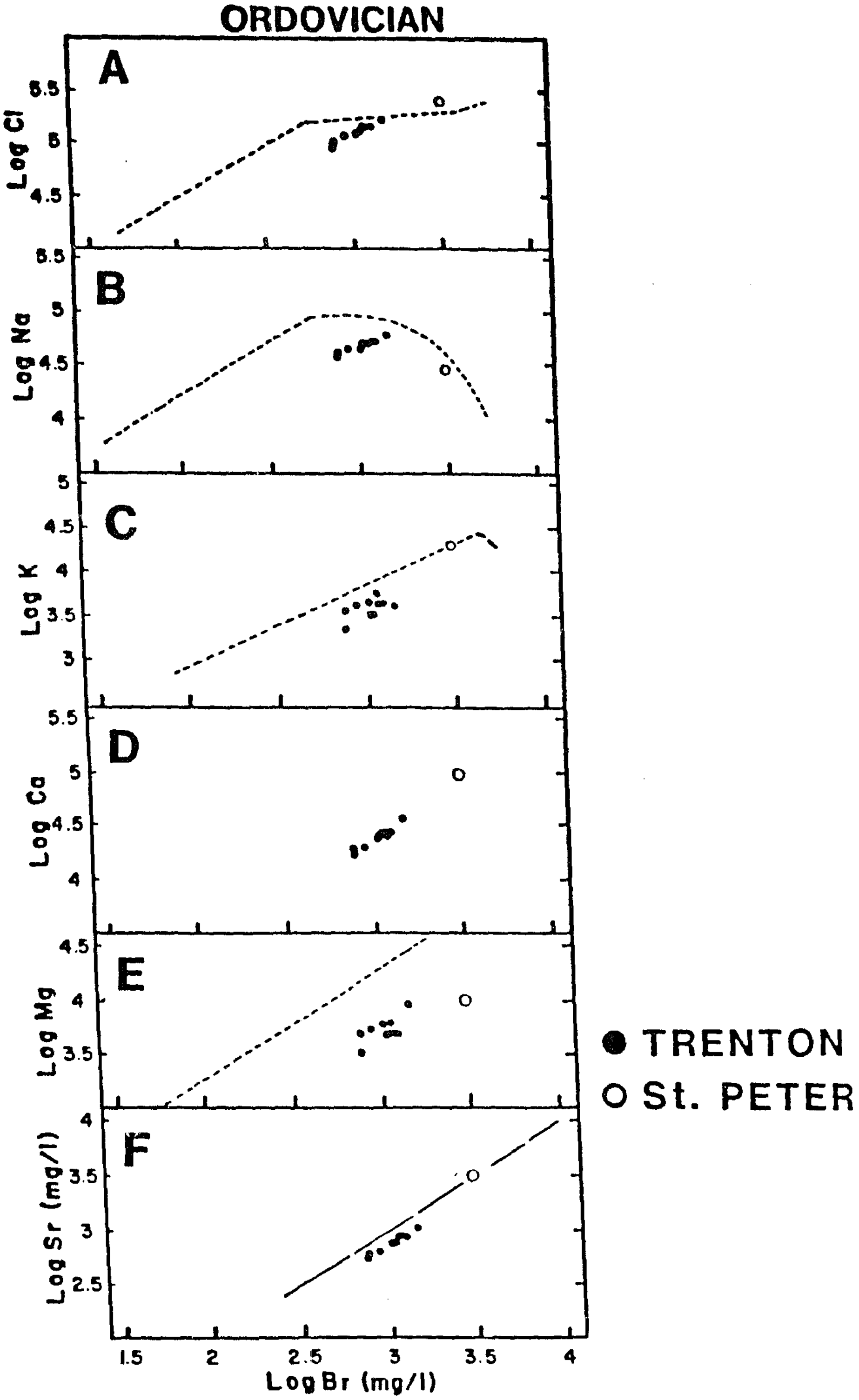

ORDOVICIAN
A
Log Cl
5.5
5
4.5
B
Log Na
5.5
5
4.5
4
C
Log K
5
4.5
4
3.5
3
D
Log Ca
5.5
5
4.5
4
E
Log Mg
4.5
4
3.5
F
Log Sr (mg/l)
4
3.5
3
2.5
1.5
2
2.5
3
3.5
4
Log Br (mg/l)
● TRENTON
○ St. PETER

Figure 2-10.

other cations are plotted versus Br, and in the MCL_2-Cl plot (Figure 2-9b). The TBR are the only samples collected in this study to plot consistently in this manner. The St. Peter brine does not plot with the Trenton-Black River samples, but rather it resembles many of the N/S brine samples by closely resembling seawater at high Br content.

ISOTOPIC RESULTS

As a part of this study, the stable isotopic ratios $^{18}O/^{16}O$ and D/H in 7 Niagara/Salina samples and 5 Ordovician formation samples were measured. The results are listed in Appendix C, and are plotted on Figure 2-11. Also shown is the global-meteoric water line (GMWL) from Craig (1961), and the best fit line for all Michigan basin formation waters from this study (Chapter 1). The N/S brine data plot below and to the right of the meteoric water line, with most samples plotting towards the enriched (positive $\delta^{18}O$ values) end of the Michigan basin best-fit line, similar to water from the lower Devonian formations (Richfield and Detroit River formations, Chapter 1). The Trenton-Black River water and the St. Peter sample (#8040) plot in a tight cluster intermediate between the best fit line and the global meteoric water line.

GEOCHEMICAL EVOLUTION OF NIAGARA/SALINA BRINES

The Cl/Br agree well with the seawater concentration lines, suggesting that the Niagara/Salina formation brine originated from evapo-concentrated seawater. As noted previously, the N/S samples appear to plot as clusters on

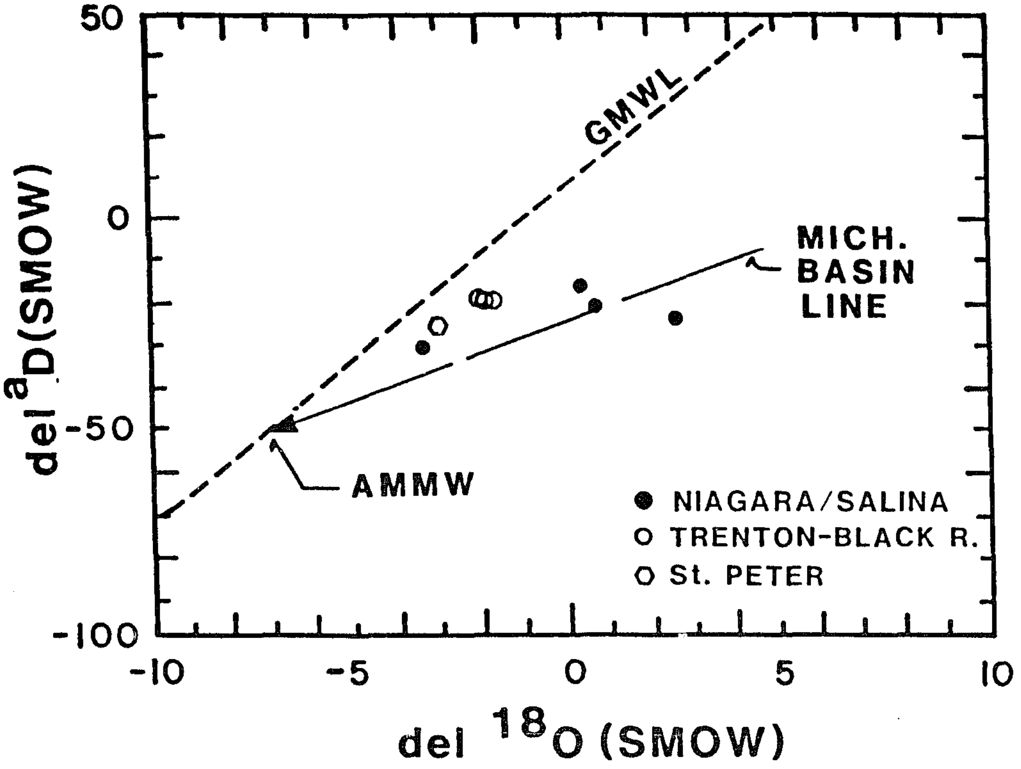


Figure 2-11. del D^{o}/oo SMOW (activity scale) vs. del ^{18}O ^{o}/oo SMOW in the Niagara/Salina and Ordovician formation waters, Michigan basin. Also shown is the global meteoric water line (GMWL) from Craig (1969), and the best-fit line to all Michigan basin formation waters collected in this study.

log concentration plots, perhaps suggesting that this formation contains water with a more homogeneous chemistry than observed in the Devonian formations (Chapter 1). However, differences in chemistry are observed between northern reef and southern reef Niagara/Salina samples, suggesting that the homogeneity reflects the limited distribution of sampling locations for the N/S water compared with the wide distribution for the Devonian.

Although the Cl/Br suggest an evaporative seawater origin, differences exist between Ca, Mg, Sr, K and MCl_2 in the samples when compared with seawater. These differences reflect the geochemical evolution of the water resulting from water-rock reactions or mixing.

Ca-Mg-Sr

Dolomitization appears to be one of the more important reactions in the evolution of Michigan brine, as it explains the Ca and Mg in these waters. The N/S brine is highly enriched in Ca (8d), while Mg is depleted from equivalently concentrated seawater (Figure 2-8e). The model for dolomitization presented in Chapter 1 can be used to demonstrate that the deficiency in Mg from concentrated seawater can explain most of the measured Ca, based on a 1 to 1 mole replacement during dolomitization. The Ca concentrations predicted by this model are compared with the measured values in Figure 2-12. The predicted Ca values, for the most part, agree with the measured Ca supporting that dolomitization by seawater explains the Ca and Mg in

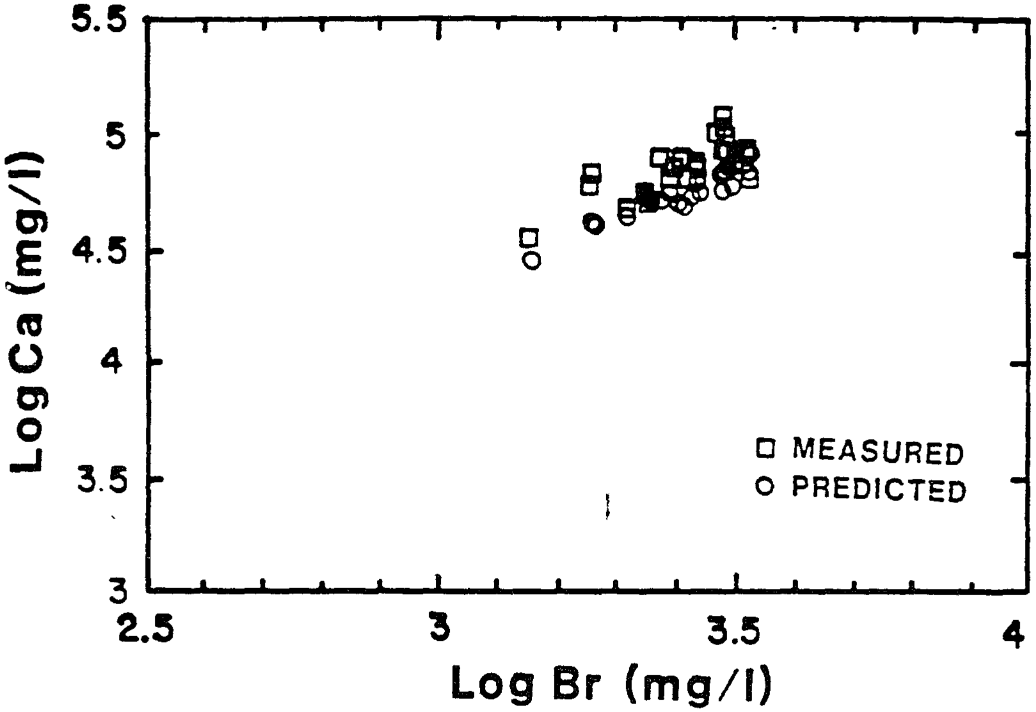


Figure 2-12. Result of dolomitization model (log Ca vs. log Br, mg/l) for Niagara/Salina formation waters. Square symbols are measured Ca values, circles are predicted Ca.

this water. For the Case (1945) analysis as well as for a few lesser concentrated brines, an excess of Ca exists over predicted values. A similar excess is observed in other Michigan formation water (Chapter 1), and is interpreted to show that non-stoichiometric replacement of Mg for Ca during dolomitization has occurred, or that other sources of Ca or Mg must be considered. Other Ca sources might include a Ca enriched parent seawater or the addition of Mg by exchange or clay diagenesis.

Strontium is highly enriched in N/S brines over what is expected for evaporating seawater (Figure 2-8f), and values plot in a cluster very near the 1:1 line. Sass and Starinsky (1979) suggested that the dissolved Sr/Ca might be used to indicate the type of carbonate mineral or reaction that supply Sr to brines. The Sr/Ca (molar) range from 0.009 to 0.022, which according to the model of Sass and Starinsky (1979) suggested that dolomitization of aragonite and solution-reprecipitation of calcite have supplied Sr to these waters.

Thermodynamic calculations also support that the waters are in equilibrium with dolomite, along with anhydrite, halite, and in some cases, sylvite. Histograms of saturation indices (log IAP/Ksp) for these minerals, calculated only for the N/S samples collected and analyzed in this study, are shown in Figure 2-13. Mineral saturation indices were computed using the PHRQPITZ computer routine, which uses Pitzer's equations for activity coefficients

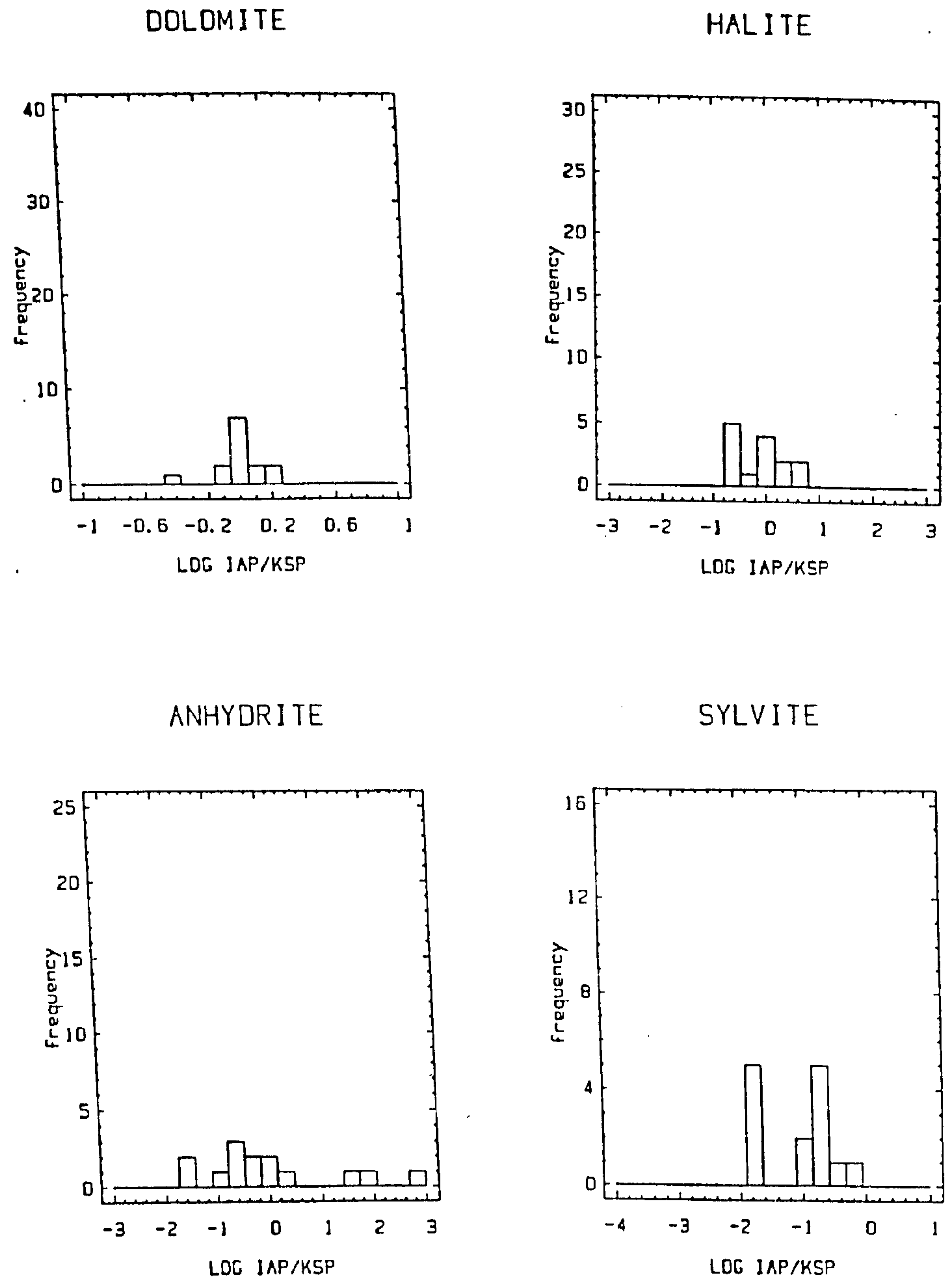


Figure 2-13. Histograms of saturation indices (log IAP/Ksp) for the Niagara/Salina waters and Trenton-Black River samples.

(Plummer et al., 1989). Estimated formation temperatures were based on 10^{o}C at 30m, and a gradient of 23^{o}C/km thereafter (Chapter 1; Vugranovich, 1986). The program makes no adjustment for pressure. The measured pH-alkalinity data were first used in the modeling, and then the modeling was repeated assuming that calcite equilibrium controls pH and alkalinity. A similar range of saturation indices are calculated under both conditions, although the average dolomite saturation indice is reduced slightly, from 0.49 to 0.06, when calcite saturation is assumed.

Potassium

Potassium values plot below the seawater concentration trend line for many of the samples (Figure 2-8c), which is similar to how many of the other Michigan basin formation waters plot (Chapter 1). The K depletion is less severe in the N/S brines however, and does not occur in all samples. The depletion of K from formation water is often interpreted to represent illitization of clay minerals upon deep burial. However, depletion may start early in the history of a seawater brine. For example, Figure 2-14 shows the K-Br concentrations in a seawater sabkha brine from Laguna Madre, Texas (Long and Gudramovics, 1983). This water was collected from the upper few meters of the sabkha sediments, and exhibits a depletion of K from seawater values, perhaps the result of reactions with clay minerals. This data illustrates that the chemistry of a seawater brine may start to evolve soon after entering sediments, and that seawater

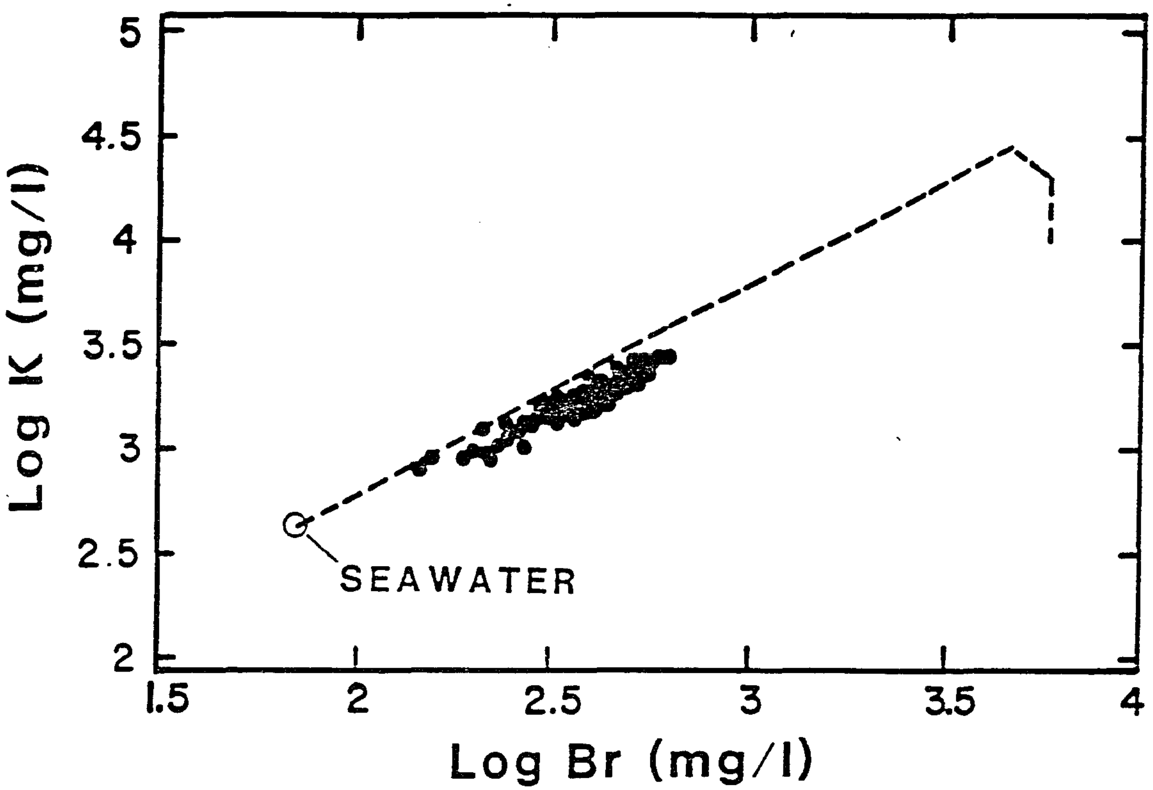


Figure 2-14. Log K vs. log Br (mg/l) in seawater brines from Laguna Madre, Texas (Long and Gudramovics, 1983)

in natural settings may quickly deviate from the evapo-concentrated seawater chemistry measured in salt pans.

The depletion of K from the Niagara/Salina brine might be due to illitization and authigenic feldspar diagenesis. The Niagaran rocks and the Salina salts contain illite and chlorite in shale partings and as thin, black shale layers in the lower Salina rocks (Lounsbury, 1963; Nowak, 1978; Nurmi and Friedman, 1977). Authigenic feldspar has been observed in the Trenton formations, (Sibley, personal communication), and may be present in the Niagaran rocks as well.

MASS BALANCE MODEL

The extent to which these mineralogical reactions can explain the brine chemistry can be evaluated using a mass balance model (Collins, 1975; Carpenter, 1978). The model starts with seawater and attempts to derive the composition of average N/S brine and a southern reef trend (#2098) sample (Table 2-6a) from seawater concentrated to equal degrees (based on Br) by considering dolomitization, recrystallization of aragonite, aluminosilicate diagenesis, Ca removal by $CaCO_3$ precipitation resulting from sulfate reduction (or equally, by $CaSO_4$ mineral precipitation resulting from dolomitization), and halite dissolution-precipitation. Although the "average" brine composition will be used, it is important that an evolution be calculated for an actual sample. Sample #2098 was chosen because its Br content is similar to the average N/S composition.

Many assumptions go into mass balance models of this type, the most important being that seawater is the only source of bromide, and that Br acts conservatively. Other sources for Br might include clay exchange, organic breakdown, halite recrystallization (Stoessell and Carpenter, 1987) and the interaction of halite with saturated brine (Wilson and Long, 1984). To correctly apply such a model the analytical error must be taken into account. The two analyses were corrected for charge balance by distributing the error proportionally among components relative to their concentrations (corrected compositions are also listed in Table 2-2). Finally, it is assumed that the initial seawater composition represents the actual parent solution of the brines. The seawater compositions used in this example are taken directly from data in McCaffrey et al. (1988).

The mass balance results (Table 2-2) show that each liter of average N/S brine might have evolved from seawater by the formation of 192g of dolomite, the recrystallization or dolomitization of 213g of aragonite (containing 10,000ppm Sr), and the formation of 56g of illite. Na and Cl may have followed either of two evolutions. In order to explain Na, the precipitation of 59g of halite is required, removing 35,840mg of Cl. Alternatively, the dissolution of 51g of halite can be used to explain Cl, but in this case, 43,300mg

TABLE 2-2
EVOLUTION OF NIAGARA/SALINA BRINE

A.

Component	Average N/S brine	Average corrected	#2098	#2098 corrected
Br	2400	2420	2560	2650
Cl	210,000	215,900	230,000	247,800
Ca	74,000	72,000	79,600	77,200
Mg	11,500	11,200	16,700	16,200
Na	31,400	30,560	40,200	39,000
K	92,500	9000	8780	8500
Sr	2190	2130	2300	2230
SO_4	50	50	35	35
HCO_3	90	90	350	350
MCl_2	4720	4562	5393	5233

Corrected: corrected for charge imbalance, all values in mg/l, except MCl_2 (meq/l).

B.

Evolution of average Niagara/Salina brine (values in mg/l)

	Ca	Mg	Sr	K	Na	Cl	SO4	MCl2/
Seawater (Br=2440)		48,200		14,500	53,800	185,000	64,400	1.1
Dolomitization (192g)	61,010	-37,000						
Recrystalization of Aragonite	-970		2130					
(*)Illite diagenesis (56g)	2820			5500				
(**)CO_3 precipitation resulting from SO_4 reduction	-26,870						-64,350	
Halite (59g)					-23,240	-35,840		
Predicted Brine a)..	36,000	11,200	2130	9000	30,560	149,200	50	1.1
b)..	62,900							1.7
Average... brine	72,000	11,200	2130	9000	30,560	215,960	50	1.9
Excess a)	36,200					66,800		
b)	9120					66,800		

TABLE 2-2 (Cont'd.)

C.
Evolution of Sample #2098 (values in mg/l)

	Ca	Mg	Sr	K	Na	Cl	SO4	MCl2/Br
Seawater (Br=2630)		52,600		15,500	46,900	185,500	70,300	1.0
Dolomitization (189g)	60,025	-36,400						
Recrystalization of aragonite	-1020		2230					
(*)Illite diagenesis (71g)	3590			7000				
(**)CO_3 precipitation resulting from SO_4 reduction	-29,340						-70,300	
Halite (20g)					-7900	-12,200		
Predicted brine a).....	33,300	16,200	2230	8500	39,000	173,300	35	1.2
b)......	62,600							1.8
Measured ..... brine	77,200	16,200	2230	8500	39,000	247,800	35	2.0
Excess a)....	43,900					74,500		
b)....	14,600					74,500		

Key: Seawater: Composition of seawater based on measured Br.
Predicted brine is sum of reactions.
MCl2/Br: MCl_2 (meq/l)/Br (mg/l), where $MCl_2 = Ca + Mg + Sr - SO4 - 0.5HCO_3$

(*) : The aluminosilicate reaction used is:

$$2K^+ + 3Al_2Si_2O_5(OH)_4 + CaCO_3 = Ca^{2+} + 2KAl_2(AlSi_3)O_{10}(OH)_2 + CO_2 + 4H_2O$$

(**) : Amount of Ca removed by $CaCO_3$ precipitation resulting from SO_4 reduction.

Predicted Ca values:
a): concentration when Ca is removed by $CaCO_3$ precipitation resulting from SO_4 reduction.
b): concentration when Ca is not removed by $CaCO_3$ precipitation resulting from SO_4 reduction.

Excess: measured amount minus predicted amount for case a and b.

(1.88m) of Na must be removed from solution to account for the measured Na. This later evolutionary scheme is not listed in Table 2-2, for reasons discussed below.

A similar evolution is calculated for sample #2098, dolomitization of 189g of carbonate rocks, recrystallizing 223g of aragonite, and the formation of 71.3g of illite, which is about 1.5 times the amount required by the average sample. The Na chemistry might be explained by the precipitation of 20g of halite, or alternatively, if dissolution of 103g of halite is used on to balance Cl, then 48,300mg of Na must be removed to account for the measured Na (this not listed in Table 2-2).

These reactions appear to account for most components in the brine, however, a large excess of Ca and Cl need to be explained, and the role of halite <u>precipitation</u> versus <u>dissolution</u> must be established. The average N/S sample has a Ca excess of 36,000mg/l (0.9m/l) over the model predictions (line a), when Ca is removed with SO_4 (either during sulfate reduction, $CH_2O + SO_4^{=} + Ca^{2+} = CaCO_3 + H_2S$; or by $CaSO_4$ mineralization during dolomitization, $Mg^{2+} + 2CaCO_3 + SO_4^{2-} = CaMg(CO_3)_2 + CaSO_4$). In the evolution by <u>halite precipitation</u> (to balance Na), Cl is in excess by 66,800mg/l (1.88m/l), approximately balancing the 0.9 moles/l excess in Ca. Thus, a significant amount of $CaCl_2$ is not accounted for in the evolution scheme where concentrated seawater has been involved in dolomitization, illitization, sulfate removal, and halite precipitation .

A decrease in the amount of Ca removed by sulfate might explain some of the extra Ca, but not the extra Cl. A possible source discussed below may be the input of a $CaCl_2$ rich brine, which would have caused the halite precipitation to occur (Holser, 1979; Braitsch, 1971).

The possibility remains that Cl should be balanced in the model by <u>halite dissolution</u>, with removal of the added Na by exchange onto clays for Ca. For the average brine composition, exchange of Na generated from halite dissolution could add 37,800mg of Ca, which when added to the predicted Ca (line a; 36,000mg/l), results in a predicted Ca very near the average brine composition of 72,000mg/l. Thus, it would appear that an evolution by halite dissolution accompanied by cation exchange could explain the brine evolution. This evolution however, would require the dissolution of a large amount of halite, 51g/l of halite for the average brine and 100g/l for sample #2098. Dissolution of halite is unlikely because: (1) a seawater brine saturated with halite was used as the parent solution, and would not be able to dissolve halite, (2) the Cl/Br and Na/Br ratios do not support that halite dissolution has affected the brines, and (3) the stable isotope data do not support that meteoric water or seawater has entered the formation and dissolved salt. The evolution calling on halite dissolution is therefor dismissed and the evolution by dolomitization, SO_4 removal by either reduction or $CaSO_4$ precipitation, aluminosilicate reactions, and halite precipitation associated with an input of $CaCl_2$ is suggested.

ENRICHMENT IN $CaCl_2$

Although evapo-concentration of seawater may explain the origin of these brines, the enrichment in $CaCl_2$ suggests that a more complex evolution must be considered. This enrichment in $CaCl_2$ also represents the enrichment in MCl_2 observed in Figure 2-9. The N/S samples, on average, have a MCl_2(meq/l)/Br(mg/l) of about 2 with values ranging up to 2.7, far from the expected ratio of 1 in evaporating seawater (Carpenter, 1978). One mechanism for increasing MCl_2 (as $CaCl_2$) is by the reaction of aluminosilicate and carbonate minerals: $2KCl_{(aq)} + CaCO_3 + 3Al_2Si_2O_5(OH)_4 = CaCl_{2(aq)} + 2KAl_2(AlSi_3)O_{10}(OH_2) + 4H_2O + CO_2$ (Carpenter, 1978). Similar reactions can be written using Na-feldspars. The maximum $CaCl_2$ enrichment obtainable from these reactions occurs when all K^+ in seawater is replaced with an equivalent amount of Ca^{2+}, and would increase MCl_2/Br to a maximum value of 1.2. Potassium has not been completely removed from the Michigan brine, so the upper limit of MCl_2/Br=1.2 helps illustrate the extreme enrichment of MCl_2 in these waters. Exchange of Na for Ca on clay minerals, non-stoichiometric replacement of Ca for Mg during dolomitization, and lack of complete removal of Ca as $CaSO_4$ minerals are possible explanations for some of the extra Ca balanced by Cl. Three other sources of $CaCl_2$ that can be considered are the diagenesis or dissolution of $MgCl_2$

evaporites, and a pre-existing enrichment in $CaCl_2$ in the seawater parent to the brines.

The diagenesis or dissolution of evaporite minerals such as carnallite might generate $MgCl_2$ solutions that would be subsequently altered to $CaCl_2$ by dolomitization. Although previous work has suggested the potash deposits in Michigan are primary salts (Matthews and Egleson, 1974), the origin may be equivocal. Sylvite is not generally considered a primary seawater evaporite mineral during "dynamo-polythermal precipitation" (Borchert and Muir, 1964; Draitsch, 1971; Garrett, 1970; Sonnenfeld, 1985), although some potash deposits are suggested to be primary in origin (Sonnenfeld, 1985). Recent thermodynamic modeling by Harvie and Weare (1980) supports that sylvite is not primary during normal seawater evaporation conditions, both in equilibrium and fractional crystallization evaporation schemes (both schemes do not consider carbonates, however). In short, the "physical chemistry of evaporating seawater does not favor sylvinite (KCl plus NaCl) being directly precipitated under normal circumstances" (Garrett, 1970).

Sylvite can also form by the thermal breakdown of carnallite during burial: $KMgCl_3 \cdot 6H_2O = KCl_{(s)} + MgCl_{2(aq)} + 6H_2O$, or through the leaching of carnallite by undersaturated seawater (Garrett, 1970). Potash deposits may go through cycles of these reactions during burial before stabilizing as sylvite (Sonnenfeld, personal communication), which liberate large amounts of $MgCl_2$ brine and heat (Garrett, 1970). These $MgCl_2$ solutions would have been quickly altered to $CaCl_2$ upon reacting with carbonates minerals.

Whether the sylvite is a primary or secondary mineral deposit in Michigan is not clear. In the only reported geochemical study of these salts, Matthews and Egleson (1974) suggested the Br content of the salts show the sylvite is primary, but other interpretations of their data are possible. The Br in the sylvite of the one reported core from the mid-basin area in Michigan decreases from 4340 to 2320 ppm over the top 0.5m of the core. In the underlying 13m of the potash core, however, bromide in the potash averages 2100 ppm. These values are similar to those Kuhn (1968) reports for descendent or secondary sylvite, which are listed in Table 2-3. A more detailed examination of these salts is warranted, but the possibility exists that the sylvite in Michigan may have originated from a carnallite precursor.

A second source of $MgCl_2$ fluids would be from the incongruent dissolution of the carnallite. Figure 2-5 shows the stratigraphic relationships of the A-1 sylvinite salts in the basin, which is also shown in cross section. In the northern area of the basin the sylvinite is thinned by erosion and is truncation by an erosional surface of the A-1 Carbonate. Interaction of the carnallite with lesser-concentrated seawater would have dissolved the carnallite and would have altered any remaining carnallite to

Table 2-3
Bromide concentrations characteristic of potash minerals

Genetic Type	Description	Carnallite Br (ppm)	Sylvite Br (ppm)
Primary	Crystallization from seawater	3000-5000	3000-4000
Descendent	Crystallization from second cycle brines	1700-3000	1500-3000
Secondary	Alteration at depth by brines and temperature	1000-2000	1000-2000
Posthumuous	Late alteration by groundwater	1000-1700	Not applicable

From Kuhn (1968)

descendent sylvite (Garrett, 1974; Krauskopf, 1979). Both the dissolution and alteration of carnallite would produce $MgCl_2$-rich brine.

In order to estimate the composition of the fluids derived from the alteration or dissolution of carnallite and involved in dolomitization, the composition of a solution in equilibrium with carnallite, sylvite, halite, anhydrite, dolomite, and calcite was calculated. The PHRQPITZ model (Plummer et al. 1989) was used to make this calculation, using a temperature of $50^{o}C$, the approximate present-day formation temperature. Bromide was estimated based on the carnallite-halite mixture being the only source of Br (please see discussion at the end of this paper), using an initial Br content of 3000 mg/kg in the carnallite, which is within the range for primary carnallite (Kuhn, 1968). PCO_2 was not controlled in these calculations.

The results of this calculation are listed in Table 2-5, and suggest that this hypothetical bittern produced from potash salts is enriched in Ca, Na and Cl over concentrated seawater, characteristics common to many N/S samples. More importantly, the calculated bittern has a MCL_2/Br of approximately 2.5, which is also similar to the values in many of the N/S samples and the Case (1945) sample. Although the MCl_2 value is variable based on the Br concentration chosen for the carnallite, these calculations support that enrichment of $CaCl_2$ (MCl_2) can occur by this mechanism.

TABLE 2-4
Modeled brine derived from potash salt compared with N/S brine and seawater

Component	Modeled	Case-1	Case-2	Seawater
pH	6.18	3.55	3.55	
aH_2O	0.49			
TEMP °C	50	65[a]	65[a]	
Ca	158,800	253,000	212,600	nil
Mg	20,470	8830	10,100	84,200
Na	9400	26	4878	17,100
K	44260	26,200	21,800	21,900
Cl	395,000	494,600	432,900	208,000
SO_4	5	nil	nil	103,000
ALK	36.8	1482[b]	2000[b]	nil
Br	3830[c]	4290	4068	4180
MCl_2	9607	10867	9550	4782
TDS	631,522	642798	579328	438,000
MCl_2/Br	2.7	2.5	2.3	1.14

Key: All values as mg/kg, except MCl_2 (meq/kg).

Modeled brine is a solution saturated with sylvite, carnallite, halite, anhydrite, dolomite, and calcite. Case samples are from the Niagara/Salina formation, from the Gulf Salina-1 well, sec. 34, T. 15N, R. 4E., Michigan, permit # 10551. Case-1 sample was collected from a drill stem test, and the Case-2 sample was collected at the surface from the flowing well. From Case (1945).

a: Estimated temperature based on depth.
b: Reported to include organic acids.
c: Estimated, see appendix.

This example is intended only to point out that the enrichment in MCl_2 (as $CaCl_2$) may be the result of reactions involving potash salts, although it is tempting to suggest that the Niagara/Salina formation water originated solely from these salts. This is most likely not the case because based on present-day sylvinite volumes (Chapter 1), insufficient volumes of brine would be generated. The Salina A-1 salt contains between 510 and 720 km^3 of sylvite (depending on %KCl chosen), representing an average of 2790 km^3 of primary carnallite. The isothermal breakdown of $1m^3$ of carnallite produces $0.22m^3$ of sylvite, and approximately 622 liters of water (Borchert and Muir, 1964), therefore, some $1.7x10^{15}$ liters of water may have been liberated from the present-day A-1 sylvite. This volume represents less than 25% of the total pore volume in the underlying Niagaran formation rocks (estimated volume of $7.9x10^4$ km^3 and assuming a porosity of 10%). If the deep Ordovician formation brine, such as the St. Peter formation brine, originated from Salina seawater (as suggested by their similar chemistries and salinities), then even larger volumes of solution are required. While it does not appear realistic that the Niagara/Salina brine originated only from the breakdown of carnallite, they may have been supplemented by this process.

A third source of $CaCl_2$ (MCl_2) could be enrichment of the parent seawater of the brines, occurring before evapo-concentration. Enrichment before evapo-concentration might explain for example, the strong parallel relationship between MCl_2-Br in Figure 2-9. It is not clear what criteria, if any, in brine chemistry can be used to test the hypothesis that the brines originated from a $CaCl_2$ enriched parent seawater. However, an "anomalous" parent seawater might be consistent with the model of the Silurian A-1 potash salts proposed by Matthews and Egleson (1974). Anomalous is used here to signify a difference in chemistry from the seawater measured in evaporative salt pans, which is used in this study for the reference seawater and was taken from McCaffrey et al. (1988) and Carpenter (1978). Matthews and Egleson (1974) suggested that seawater was deficient in $MgSO_4$ because of the lack of $MgSO_4$ salts associated with the A-1 potash unit. In "normal" seawater evaporation schemes, the evapo-concentration from the halite to KCl facies results in the deposition of large volumes of $MgSO_4$ salts (Garrett, 1970). In fact, if the potash originated from a "normal" seawater, then roughly equal volumes of $MgSO_4$ and KCl salts should be found in the basin. The lack of these salts on either side of the sylvite layers, and the thin or non-existent anhydrite layers which separate the A-1 salts from the Niagaran and the A-1 Carbonate (Matthews and Egleson, 1974; Nurmi and Friedman, 1977), suggest that seawater in the Michigan basin was deficient in $MgSO_4$ during the Silurian (Matthews and Egleson, 1974). One explanation for the lack of SO_4 salts is that dolomitization and sulfate reduction occurred near the basin margins, and perhaps outside of the basin margins to deplete $MgSO_4$ from the seawater that entered the central Michigan basin during the Silurian. While these reactions would not enrich the seawater in absolute amounts of $CaCl_2$, other water-rock reactions, perhaps those involving aluminosilicates, may have increased MCl_2 values before evapo-concentration occurred. If the seawater chemistry was "anomalous" and produced primary sylvite without the $MgSO_4$ salts (carnallite) and the $MgCl_2$ solutions described earlier, then it may have also been enriched in $CaCl_2$. However, an "anomalous" seawater is not required to explain the evaporite salts in the basin. Garrett (1970) for example, proposed a model for the origin of sylvite that calls on the direct precipitation of carnallite from normal seawater, without the associated $MgSO_4$ salt. The evolution of the potash salts in Michigan may have been quite complex, but it is possible that they evolved from a carnallite precursor, or they may have evolved from an "anomalous" seawater source.

ISOTOPIC EVOLUTION

Two general models for the evolution of stable isotopes in sedimentary basin brines have been advanced. Clayton et al. (1966) interpreted the stable isotope composition of basin waters to represent the flushing of meteoric waters through the basin, along with isotopic equilibration with host formation carbonate minerals. An alternative view, presented by Knauth and Beeunas (1986) and others (Degens, 1964), is that the isotopic composition of basin brines represents the dilution of evapo-concentrated seawater by meteoric water. This latter explanation is accepted here, however, it is not possible to correlate isotopic dilution with chemical dilution in these waters. The Niagara/Salina samples do not exhibit either isotopic or chemical evidence of dilution. A conclusion that can be reached is that the N/S waters retain an isotopic composition reflecting evapo-concentrated seawater (Chapter 1).

A number of factors need to be considered when interpreting the isotopic composition of formation waters thought to be derived from seawater (Chapter 1; Knauth and Beeunas, 1986). The isotopic composition of evaporating seawater is controlled by many variables, and as such, seawater may exhibit a wide range of isotopic values during evapo-concentration. This was illustrated by Knauth and Beeunas (1986), who reported values from halite fluid inclusions, Pierre et al. (1984), and Holser (1979), who reported values from sabkhas and lagoon waters concentrated up to halite saturation, and Nadler and Magaritz (1979), who reported values for Mediterranean seawater in evaporation pans concentrated past halite saturation. This later study found that the isotopic composition of seawater after reaching halite saturation is more negative in δD than the seawater source. The Niagara/Salina brine is concentrated far past the start of halite saturation, and therefore, may have evolved from a seawater brine having a composition unlike the examples cited above. Additionally, ancient seawater may have had an isotopic composition different from present seawater. For example, Brand and Veizer (1980) suggest that Ordovician seawater was about $-5.5^{o}/oo$ lighter in ^{18}O than present ocean water. If seawater varied to such an extent then the seawater evaporation path would have shifted towards more negative $\delta^{18}O$, and perhaps δD values. In sum, it is not possible to constrain with any certainty the isotopic composition of the parent seawater of the Niagara/Salina brine.

It is also difficult to imagine that the basin waters have not reacted during their history with the carbonate and evaporite minerals ubiquitous to the basin. Although a function of water-rock ratios, carbonate reactions would enrich the brines in ^{18}O (Land, 1982; Clayton et al., 1966). If isotopic equilibrium can be demonstrated then the isotopic composition of the water can not be entirely primary.

The extent of isotopic equilibrium between the brines and carbonate minerals can be evaluated in a general manner. Such an evaluation was attempted by Clayton et al. (1966) who attempted to demonstrate that Michigan basin formation waters are in isotopic equilibrium with calcite. Clayton et al. (1966), however, made assumptions concerning mineral

^{18}O values and formation temperatures and did not consider that dolomite equilibrium may play a role in altering the isotopic composition of the water. Recent data help constrain the temperature and mineral isotopic compositions in the basin and allow for a more refined re-examination of this question.

Determining if isotopic equilibrium exists with dolomite is of course hindered because of the lack of knowledge on oxygen fractionation during the low temperature diagenesis of dolomite (Land, 1980; Carpenter, 1980). Land (1980) discusses four equations (Table 2-3) thought to describe dolomite-water oxygen isotope fractionation developed by Northrop and Clayton (1966), O'Neil and Epstein (1966), Shepard and Schwarcz (1970), and Fritz and Smith (1970). The following average fractionation factor equation can be calculated from these four equations: $10^3 \ln \mathrm{ALPHA}=3.14 \times 10^6 T^{-2} - 2.00$, where $\mathrm{ALPHA}=(10^3 + \delta^{18}O_{dol})/(10^3 + \delta^{18}O_{water})$. Another limitation is the knowledge of temperatures needed for such a calculation. Paleo-temperatures derived from fluid inclusions and conodont color alterations suggest two paleo-temperatures may have been important in the evolution of these rocks and waters: present-day + 23°C, representing burial 1 km deeper at present-day gradients (Nunn et al., 1984; Hogarth, 1985; Cercone, 1984), and 80°C, a minimum temperature found from fluid inclusions in the late diagenetic dolomites in the

TABLE 2-5
Isotopic fractionation factors for dolomite-water

$10^3 \ln \text{ALPHA}_{(\text{dolomite-water})} =$

$3.20\times10^6T^{-2} - 1.50$	(Northrop and Clayton, 1966)
$3.34\times10^6T^{-2} - 3.34$	(O'Neil and Epstein, 1966)
$3.23\times10^6T^{-2} - 3.29$	(Shepard and Schwarcz, 1970)
$2.78\times10^6T^{-2} + 0.11$	(Fritz and Smith, 1970)

All equations corrected to be consistent with Friedman and O'Neil (1977), from Land, (1988).

Average fractionation factor:

$$10^3 \ln \text{ALPHA}_{(\text{dolomite-water})} = 3.14\times10^6T^{-2} - 2.00$$

For calcite:

$$10^3 \ln \text{ALPHA}_{(\text{calcite-water})} = 2.78\times10^6T^{-2} - 2.89$$

(Friedman and O'Neil, 1977)

Niagaran reefs (Cercone and Lohmann, 1987) and in the Trenton (Shaw, 1975).

The isotopic composition of dolomite and calcite in equilibrium with several of the northern reef water samples was computed using the estimated present-day formation temperature, and the two paleo-temperatures. The resulting rock values are compared in Figure 2-15 with $\delta^{18}O$ values ($^{o}/_{oo}$ P.D.B.) of Niagaran and Salina A-1 formation carbonates reported by Cercone and Lohmann (1987) and Sears and Lucia (1982) for northern reef rock samples. Similar calculations were made for calcite using the fraction factor from O'Neil and Epstein (1966), and the mineral data from Cercone and Lohmann (1987). The rock value calculated using the average fractionation factor and the range of rock values from the four fractionation factor equations are shown for reference by the bracket lines. As indicated in Figure 2-15, the brines do not appear to be in isotopic equilibrium with any of the reported dolomites at present-day temperatures. Whether equilibrium with calcite occurs is not clear however, but some of the samples appear to be in isotopic equilibrium with bulk rock limestone values reported by Sears and Lucia (1980).

With increased temperature, the dolomite values predicted to be in equilibrium with the water increase and approach the measured dolomite values, especially for the bulk Niagaran dolomite. This increase is not unexpected considering that the fractionation factor decreases with

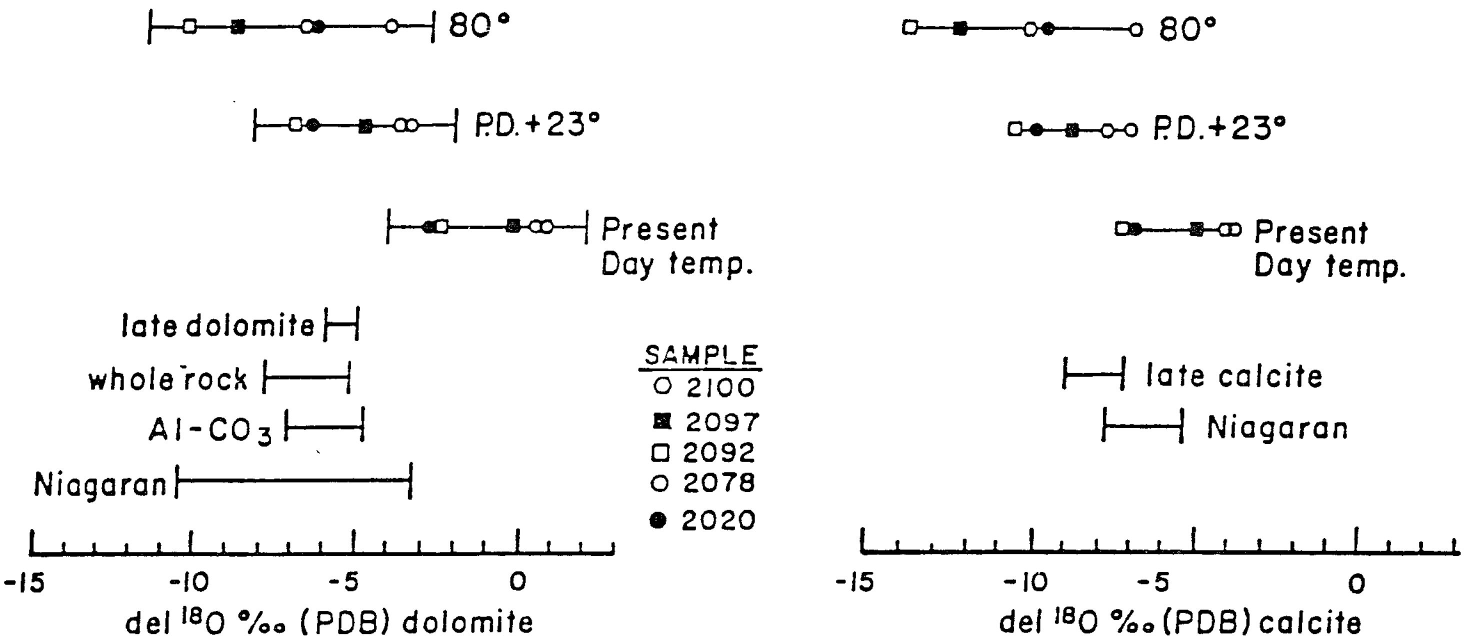


Figure 2-15. Calculated del ^{18}O ^{o}/oo (PDB) values for dolomite and calcite in isotopic equilibrium with Niagara/Salina formation waters at subsurface temperatures of present-day, present-day+23 ^{o}C, and 80 ^{o}C. Bars show range of values from four different dolomite-water fractionation equations discussed in text. Also shown are ranges of del ^{18}O values reported in late diagenetic dolomites and calcites, whole rock (W.R.), A-1 Carbonate dolomites, and Niagaran dolomites and calcites in Michigan, from Cercone and Lohmann (1987) and Sears and Lucia (1982).

increasing temperature. However, the fact that measured values in N/S carbonates are similar to those calculated using independently determined paleo-temperatures might suggest that equilibrium with dolomite at higher paleo-temperatures has affected the isotopic composition of the brines.

Because of the uncertainty in fractionation factors for dolomites and temperatures, the implications of these calculations are somewhat tenuous. Clearly more research is needed to test whether isotopic equilibrium exists between the brine and host rock minerals and cements. If equilibrium can be established, then the simple model of dilution of evapo-concentrated seawater by meteoric water must be refined. The results of these calculations do however, suggest that carbonate equilibrium at warmer paleo-temperatures may have affected the isotopic composition of the brine, and that re-equilibration during basin cooling may not have altered the water $\delta^{18}O$ values. Water-mineral equilibration is not considered in the Knauth and Beeunas (1986) model, and further suggests that the isotopic composition of formation waters may be decoupled from the chemical evolution (Chapter 1).

MODEL FOR THE ORIGIN AND EVOLUTION OF NIAGARA/SALINA FORMATION BRINES

The origin of Michigan basin Ca-Cl brine has been linked, in the past, to geochemical processes such as shale membrane filtration (Graf et al., 1966). The data presented here suggest that the Niagara/Salina formation water originated from evapo-concentrated seawater. The brine appear to have been derived from seawater concentrated far past halite saturation, thus halite saturation has lowered the Na content of the brine. Dolomitization has likewise removed Mg from the parent seawater and replaced it with Ca. Additional reactions involving aluminosilicates and perhaps reactions with evaporitic salts has added $CaCl_2$, and either SO_4 reduction or $CaSO_4$ mineralization have removed SO_4. Dolomitization and halite precipitation appear to be the processes that transformed the original Na-Mg-Cl-SO_4 seawater brine into the Ca-Na-Cl brine now found in the basin.

The high Br levels in the N/S samples suggest that the parent seawater was concentrated to K-salt precipitation. The origin of the brines may, therefore, be linked to the Salina A-1 salts, the only formation containing potash minerals in the basin. During deposition of the A-1 salts, dense seawater bitterns may have entered the Niagaran rocks along the reef margins and may have moved downward through the accumulating halite into the underlying Niagara rocks. During later Salina salt deposition, seawater derived brines may have infiltrated the Niagaran rocks, however it would seem unlikely that brines generated during younger periods of evaporation could reflux through the thickening accumulation of halite. Later compaction of the salts may have been very important in forcing brine into the adjacent formations.

As previously discussed, some of the northern reef samples agree very well with evapo-concentrated seawater. For example, many northern samples are not depleted in K from expected seawater values, a characteristic common to many of the southern reef samples. This may indicate that the northern waters were derived in part directly from the salt during its compaction. This observation may reflect the spatial relationship between the northern reef locations, the A-1 potash salts, and the A-1 Carbonate. Figure 2-5 shows where the N/S waters were sampled in relation to the different salt facies in the Salina A-1 salt and the vertical relationship between the different A-1 salts. The sylvite is thinned and intersects the A-1 Carbonate in close proximity to the northern reefs, while the underlying halite thins below the potash salts in this area. Fluids derived from the A-1 salts during compaction, would have had an easy pathway for migration either through the A-1 Carbonate, or alternatively, downward into the Niagaran carbonates. The short migration would minimize water-rock interactions, explaining for example, the lack of K depletion. In contrast, the southern reefs are not located near the A-1 salts and contain water generally depleted in K, suggestive of water-rock interactions. Any fluids squeezed from the potash salts would have had ample opportunity to react with formation minerals before entering the southern reefs.

ORIGIN OF TRENTON-BLACK RIVER BRINE

The Trenton-Black River formation samples show chemical evidence of mixing between evapo-concentrated seawater and a more dilute water, possibly seawater or freshwater. Whether this mixing represents dilution of a pre-existing brine by dilute water, or enrichment of dilute water by migrating brine is not clear. Figure 2-16 shows the Br values in TBR waters from the Albion-Scipio area. The smooth variation in Br (salinity) argues against localized dilution resulting from production operations. This distribution does not rule out that regional infiltration of dilute water has occurred in this area of the basin. Alternatively, the fact that the deeper Ordovician formation sample (St. Peter Sandstone, #8040) is more saline suggests that an up-dip migration of brine from the deep basin may have also occurred.

If the history of the TBR brines is to be fully explained, then the end member waters must be constrained. Three saline end members are possible considering the geology of the area; seawater (perhaps Ordovician), the present-day Niagara/Salina formation water, and the present-day Devonian formation water. Extrapolation of the Cl-Br data back to the seawater trend line (Figure 2-10a) suggests that the saline end member was concentrated between the start of halite precipitation and the start of $MgSO_4$-salt precipitation. If the TBR brines originated from Ordovician

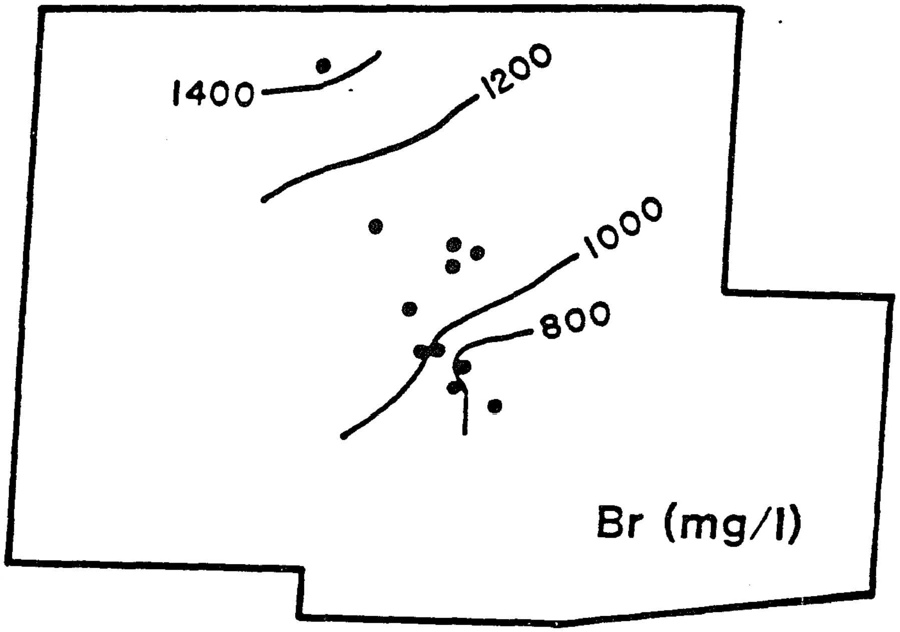


Figure 2-16. Br (mg/l) in Trenton-Black River formation brines from the Albion-Scipio trend.

seawater, then they were concentrated to this degree before dilution occurred. However, this seawater composition is also similar to the present upper Devonian formation brine, both in its salinity and in its Na-Ca-Cl chemistry, suggesting that Devonian formation brine may have migrated down into the TBR formations. Downward migration is possible because the Salina salts do not cover the Ordovician formations in the Albion-Scipio area, the Albion-Scipio fracture system is known to extend up to the Devonian formations (Carpenter, personal communication), and areas of possible basin recharge have been identified in the south-central area of Michigan (Wilson and Long, 1986; Vugranovich, 1986).

The chemistry of the Ordovician formation brine collected from the central basin area (the St. Peter formation sample, #8040) might suggest however, that the previously proposed waters may not be the saline end member water. This sample is a highly concentrated Ca-Cl brine that is similar in many respects to the Niagara/Salina samples (Table 2-1). This suggests that the TBR waters might have had, before dilution, a Ca-Cl chemistry, or alternatively, that Ca-Cl rich waters have migrated into, and mixed with more dilute waters in the Trenton-Black River formations.

Therefore, a third hypothesis is that the TBR formation brines are mixtures of Ca-Na-Cl brine which have been altered to a Na-Ca-Cl composition. The feasibility of this hypothesis can be tested using thermodynamic modeling. Niagaran/Salina sample #2099, a typical N/S brine collected from the southern reef area, was used for the saline end member. Seawater from Nordstrom et al. (1979), concentrated to gypsum saturation (and in equilibrium with calcite) was used for the dilute end member composition. This choice is simply a convenient standard that maximizes the $CaSO_4$ precipitation needed to remove Ca. The results of mixing at several brine/freshwater ratios (1., 0.9, 0.75, 0.5, 0.25, .1, 0) are presented in Table 2-6, and are shown on a log-log plot of Cl-Br and as mole percentages of Ca-Mg-Na in Figure 2-17. The mixing was done using two scenarios, first by equilibrating the end member waters with calcite, dolomite, and anhydrite, and then maintaining equilibrium with these and any other mineral that supersaturates upon mixing. The results of this case are shown as solid symbols. In the second case, the end members were mixed without equilibration (end members plot in slightly different positions from the first case), and mixing was calculated without maintaining equilibrium with any mineral. These results are shown as open symbols on this diagram. In either case anhydrite was predicted to supersaturate in all mixtures.

The results (Figure 2-17) show that Cl/Br ratios are explained by brine/seawater mixing at ratios between 0.25 and 0.5, while the relative percentages of Ca-Mg-Na in these brines suggest a brine/seawater ratio near 0.25. This is

TABLE 2-6
Modeled mixtures of Niagara/Salina brine and seawater

All values mg/kg

Brine/ Seawater ratio	0*:1	.1:.9	.25:75	.5:.5	.75:.25	.9:.1	1**:0
pH	7.33	5.15	4.75	4.35	4.05	3.88	3.77
aH_2O	0.932	0.914	0.882	0.819	0.748	0.703	0.672
Ionic Strength	2.246	2.940	4.025	5.874	7.736	8.851	9.598
TEMP	30	30	30	30	30	30	30
Ca	4581	11136	21590	39888	59026	70845	78853
Mg	1080	2580	4742	7998	10829	12343	13282
Na	39015	39605	40490	41969	43445	44332	44922
K	1446	222	3376	5306	7236	8394	9165
Cl	70122	87275	113000	155900	198800	224500	241600
SO_4	3400	1555	809	338	147	90	65
ALK	16	701	606	378	219	156	124
Br	244	550	1010	1777	2544	3004	3311
Mole percentages							
%Ca	6.2	13.1	21.6	31.6	38.7	42.0	44.0
%Mg	2.4	5.0	7.8	10.4	11.7	42.0	12.2
%Na	88.4	78.9	70.6	58.0	49.6	12.0	43.8

Mineral Balance

Mineral Phase (moles/kg)							
Anhydrite	-0.066	-0.0759	-0.0685	-0.0480	-0.0247	-0.010	-0.0001
Dolomite	-0.146	-.112	-0.0648	-0.0005	0.046	0.067	0.078
Calcite	0.292	0.229	0.134	0.004	-0.092	-.133	-0.155

Key: Composition of various mixtures of seawater evaporated to gypsum saturation and a Niagara/Salina brine from the southern reef trend. Results listed are for the case when equilibrium is maintained with anhydrite, dolomite, and calcite.

* Seawater concentrated to gypsum saturation

**: Niagara/Salina brine sample #2099

Mineral balance: += mineral dissolution, - = mineral precipitation

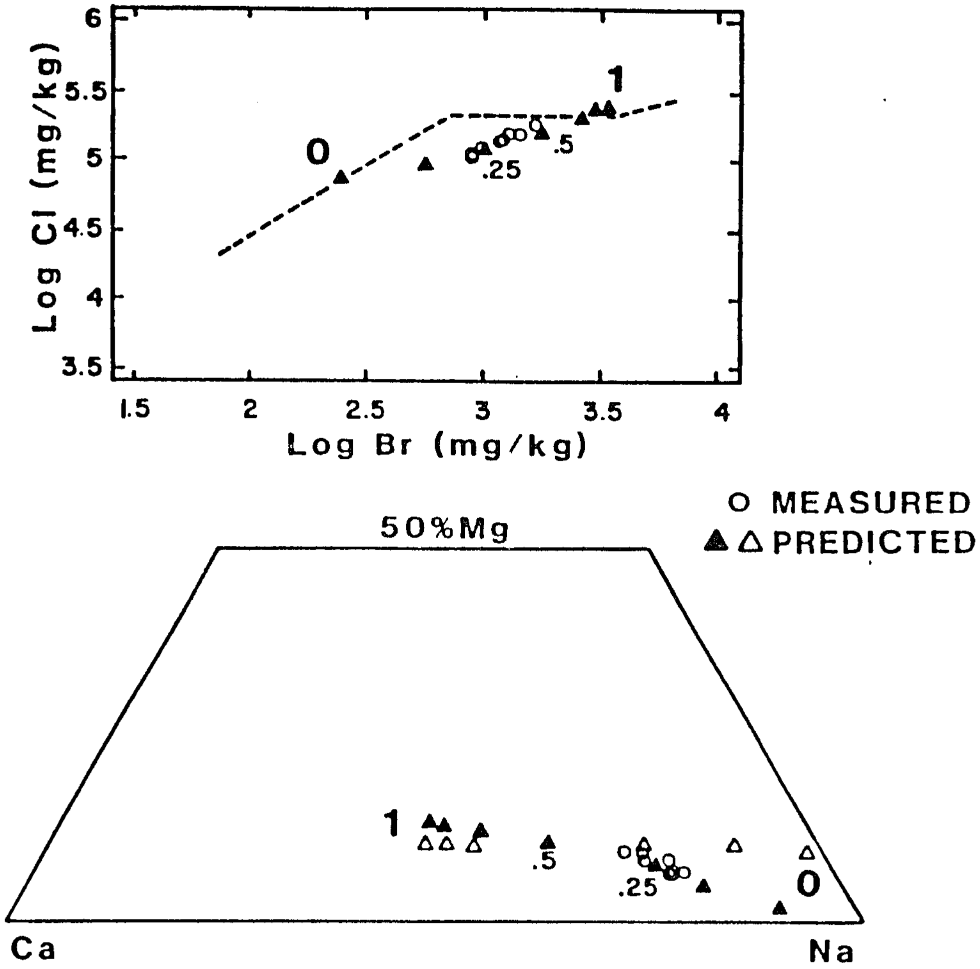


Figure 2-17. Cl-Br (log mg/kg) and relative Ca-Mg-Na composition calculated to result from mixing of N/S sample #2099 (point 1) with seawater concentrated to gypsum saturation (point 0). Numbers indicate seawater/brine mix ratio.

is the case regardless whether mineral equilibrium is reestablished or not. Some of this difference might be explained by a lower Ca/Na ratio in the saline end member or a difference in temperature, or alternatively, that dilute water (seawater) may have dissolved halite (approximately 56g halite/kg) before mixing, or had a lower Ca/Na as the result of evapo-concentration past the start of gypsum precipitation. Nevertheless, the results show that mixing of Ca-Na-Cl brine with seawater is a possible explanation for the TBR formation waters. Mixing with seawater would result in $CaSO_4$, dolomite, and calcite saturation (depending on mix ratio), and if these minerals precipitate, Ca removal would follow. Geologic evidence that some of these reactions have occurred is given by Miller (1988), who reported anhydrite is the last diagenetic mineral to precipitate in the Trenton-Black River rocks in the Albion-Scipio trend.

St. PETER SANDSTONE WATER

The one brine sample collected from the Ordovician St. Peter sandstone formation allows only a limited evaluation of the water chemistry in the deep basin. This sample was collected from a gas well in northern lower Michigan producing from a depth of over 3000m. Although the reliability that can be placed on interpretations made from a single brine analysis is limited, the unique nature of this water deserves some attention. This water is a highly saline (404 g/l TDS) Ca-Na-Cl (Figure 2-7) brine.

Inspection of Figure 2-10 demonstrates that this sample has a Cl, Na, K and Br chemistry that match evapo-concentrated seawater very well, although it plots above the seawater trend line for Cl. Mg is highly depleted and Sr greatly enriched over expected seawater values. Application of the dolomitization model discussed earlier shows that the Mg depletion resulting from stoichiometric dolomitization can explain most the observed Ca. Thus, except for K, the water is interpreted to have evolved from highly concentrated seawater that evolved by dolomitization. The lack of K depletion is curious and somewhat unexpected. This water is produced from a clastic sandstone formation, that has been reported to contain authigenic aluminosilicate minerals (Sibley, personal communication), and brine from other clastic formations in the basin, the Berea for example (Chapter 1), show a depletion in K from seawater values. Many samples from the northern reef trend of the Niagara/Salina formation however, are not depleted in K from their initial seawater content. Indeed, the chemistry in the St. Peter sample is strikingly similar to the chemistry observed in the Niagara/Salina samples (Figure 2-8), including the lack of K depletion and $^{87}Sr/^{86}Sr$ ratios (Chapter 1). This water sample may therefore, be related to the Niagara/Salina water and possibly originated during the deposition of the Niagara/Salina salts and migrated down into the underlying Ordovician formation. Until more samples are recovered and analyzed however, this remains a preliminary interpretation.

ISOTOPIC EVOLUTION

The isotopic data do not support the suggestion that the TBR brine originated from $CaCl_2$ brine source. The stable isotope values in the TBR samples plot as a cluster intermediate of the best-fit line and the SMOW (Figure 2-11). This is not where a water that evolved by mixing of a $CaCl_2$ Niagara/Salina type brine, plotting at the enriched end of the best-fit line would plot when mixed with seawater. The isotopic values of the TBR brine plot intermediate between a dilute formation brine (plotting near the GMWL) and SMOW or seawater at gypsum saturation, supporting this hypothesized origin. The TBR samples also plot intermediate of the St. Peter sandstone sample and SMOW, which might be consistent with an evolution of brine migrating up from deeper areas of the basin and mixing with SMOW. But making this interpretation based on the isotopic composition of a single brine sample is tenuous.

A relationship between δD values and Br (salinity) was found in the Devonian formation water of Michigan (Chapter 1), but as the following list shows, no clear relationship is observed in the TBR samples:

SAMPLE	delD^{o}/oo	del-^{18}O^{o}/oo	Br(mg/l)
6074	-26.40	-1.85	1080
6094	-24.30	-1.99	1160
6095	-26.70	-1.76	1250

The lack of correlation might reflect the small number of analyses available, or that both end member water may have had a similar isotopic composition. Why mixing is not represented in D values remains a question that, given the limited amount of data, does not seem answerable at this time.

It may also be possible that the isotopic values have been masked by reactions with carbonate minerals, at least for ^{18}O. In order to investigate this, the δ^{18}O of dolomite and calcite in equilibrium with the brine was calculated using the same method and temperatures described for Niagara/Salina waters. Figure 2-18 compares the calculated values with the ranges of δ^{18}O in the three types of Ordovician dolomites (Taylor, 1982). Average isotopic values are -6.8^{o}/oo for the regional dolomites, -7.8^{o}/oo for the cap dolomites, and -9.0^{o}/oo for the fracture related dolomites, respectively (Taylor, 1982). The calculated values for minerals in equilibrium with the brines do not agree with any of these minerals at present-day temperatures. However, the brine values are near those in

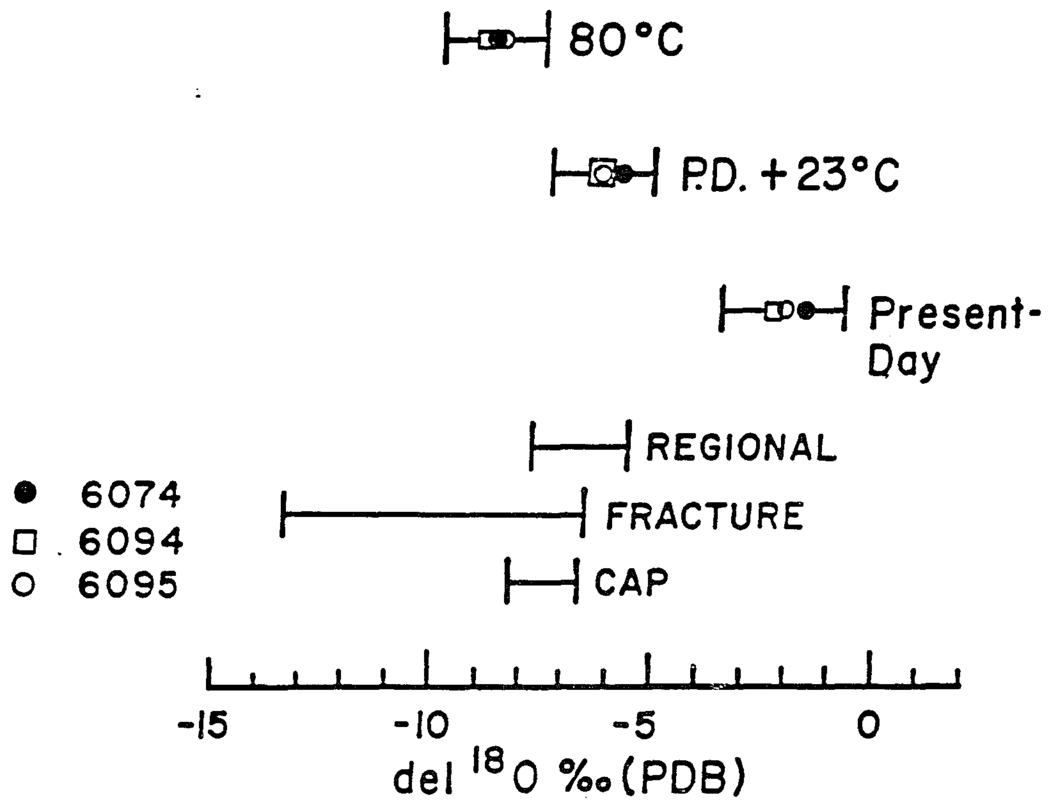


Figure 2-18. Calculated del ^{18}O ^{o}/oo (PDB) values for dolomite in isotopic equilibrium with Trenton-Black River formation waters at subsurface temperatures of present-day, present-day + 23°C, and 80°C. Also shown are ranges of isotopic values for fracture, cap, and regional dolomites in the Trenton-Black River formation, from Taylor (1982).

equilibrium with regional dolomite at temperatures of present-day+23°C, equivalent to burial 1km deeper at the present-day geothermal gradient. The brine also appear to be near isotopic equilibrium with the fracture related dolomite at temperatures near 80°C, but not at higher temperature. Thus the isotopic compoition of the brine may represent equilibrium with formation minerals and not the mixing indicated by the chemical data.

CONCLUSIONS

The following conclusions are made concerning the Niagara/Salina and Trenton-Black River formation brines.

1) The Niagara/Salina formation water originated from evapo-concentrated seawater, concentrated through the halite facies to the $MgSO_4$ facies and in some cases, into the K-salt facies. This suggests that their origin is linked to the Salina evaporitic seas in Michigan, and perhaps to the deposition of the Salina A-1 salts. Dense brine may have refluxed into underlying Niagaran formations during this period. Additional brine may have been squeezed out of these salts during salt compaction.

2) Dolomitization appears to be the most important reaction to have affected the brine, as it explains the Ca-Mg chemistry. Dolomitization in conjunction with extensive halite precipitation were the mechanisms generating the Ca-Na-Cl chemistry from seawater. Reactions such as illitization or K-feldspar diagenesis removed K from the water while carbonate reactions supplied Sr. Reactions

involving aluminosilicates and/or late stage evaporites have apparently increased the $CaCl_2$ content of the brine from seawater values.

3) Although their origin is similar, the Niagara/Salina waters show differences in their chemistry from other formation brines in the basin, reflected in the manner in which they plot on log concentration diagrams. The Niagara/Salina brine may show differences in chemistry within the formation, in samples collected from different areas of the basin.

4) Brine produced from the Ordovician aged Trenton-Black River Formations evolved by mixing of evapo-concentrated seawater with more dilute water. Possible saline end member waters are evapo-concentrated seawater (Ordovician?), Devonian formation brine, or Ca-Cl brine such as found in the Niagara/Salina formations. It is not clear at this time what the true end member waters are. However, thermodynamic modeling suggests that mixing of Ca-Cl brine, such as the Niagara/Salina brine, and seawater can explain the chemistry of the Trenton-Black River water.

5) The isotopic evolution of the formation waters is generally consistent with the model proposed by Knauth and Beeunas (1986) for evaporating seawater, although many questions remain. There is little isotopic evidence for dilution in both sets of formation waters, even though chemical evidence supports it for the Ordovician formation.

The isotopic composition of the Niagara/Salina formation brines might reflect the original seawater composition, however, the isotopic evolution may have been independent from the chemical evolution. One suggestion is that the isotopic composition of the brines has been affected by equilibrium with formation carbonates at higher paleotemperatures. In sum, the isotopic evolution of these deep formation waters may be independent of the chemical evolution.

Estimation of Bromide in salt

The composition of a water in equilibrium with carnallite, sylvite, halite, anhydrite, dolomite, and calcite was calculated using the PHRQPITZ computer routine (Plummer et al., 1989). This calculation was done for a temperature of 50^{o}C, representative of present-day temperatures in the basin. The pCO_2 was not fixed in this example. This computation is rather straight-forward using this computer program, however, Br must be estimated. The only source for Br in this hypothetical brine is the carnallite, and any halite that dissolves during carnallite recrystallization.

The initial carnallite may have had a Br concentration ranging from 3000ppm to 5000ppm (Kuhn, 1968). A 1m^3 volume of carnallite (1.67x10^{3}kg) that converts to sylvite (0.22m^3) releases 36082 moles of H_2O (649.5kg). If the carnallite has a Br content of 3000ppm, then 5.01x10^{6}mg of Br are released into 649.5kg of water, resulting in a Br concentration of 7713mg/kgs (kgs=kg of solution).

This concentration must then be corrected for Br uptake by re-precipitating sylvite and halite. An input of Mg-Ca-K-Cl into solution decreases the solubility of halite dramatically (Holser, 1979), there-by removing Br from solution in addition to that removed by the sylvite. Br uptake by sylvite and halite was considered in this example, although the amount of Br removed by halite is calculated to be negligible. Using a distribution coefficient of d=0.73, (Braitsch, 1971), the reprecipitated sylvite is calculated to contain 5630ppm Br. The total amount of sylvite re-precipitated is 436kg. This removes 2.45x10^{6}mg of Br from solution, leaving a Br concentration in solution of 3930mg/kg.

The calculated sylvite has a Br content higher than the maximum reported value in Michigan potash (4340ppm). However, considering the variability in distribution coefficients and that fact that carnallite may dissolve incongruently, the results are encouraging. If a second generation of sylvite precipitates from the remaining bittern (3800ppm Br), then it is predicted to have a Br content of 2800ppm, near the Br values measured in the Michigan potash by Matthews and Egleson (1974).

APPENDIX A

APPENDIX A

STATISTICAL EVALUATION OF MICHIGAN BASIN BRINES

Natural water can exhibit a wide variation in its chemical makeup. The types and amounts of dissolved components will reflect a water's origin and the geochemical processes involved in its evolution. Processes that control water chemistry are discussed by Stumm and Morgan (1981), Drever (1988), and others, and include mineral equilibria, dissolution-precipitation, ion exchange and adsorption, REDOX reactions, water mixing, evapo-concentration, and biological activity. Often a number of these processes operate, combining to create a structure in the water chemistry reflected by correlations between concentrations of dissolved components. Statistical tests can be a useful tool in elucidating these often complicated relationships, and in doing so, help to demonstrate the processes that control water chemistry.

With a goal of further characterizing the origin and geochemical evolution of the Michigan basin brine, an evaluation of the brine chemistry was undertaken using univariate and multivariate statistical methods. Univariate methods are first used to characterize Michigan basin brine chemistry, compare it with seawater, and then to compare average brine composition between formations. To do this, means and standard deviations are calculated, and the Student's t-test is used to test mean compositions between formations. The multivariate methods of R and Q-mode factor analysis are then used to test data homogeneity, and to attempt to find statistical evidence for processes controlling the brine chemistry. The factor analysis results are compared with results from previous research which used factor analysis to study saline ground waters.

THIS STUDY

The population studied in this investigation is all Michigan basin formation waters. Samples of this population were collected and analyzed for major and minor components as described in Chapter 1 and Chapter 2. The sample population was subdivided by producing formation for statistical testing whenever possible.

Statistical evaluations, especially of natural systems, are often based on several underlying assumptions. The principle assumption made in this study is that the samples are random and representative of the parent population, two assumption typical of ground water studies. Two examples demonstrate the possible short-coming in this assumption. The oil wells from which the samples were collected are not random in the basin, but are located where geologic conditions favor hydrocarbon entrapment. These areas might coincide with, for example, structural features, zones of high porosity or unique mineralogy, or have other characteristics that might make the associated water non-representative of the formation in general. It is also possible that waters are density stratified within formations. Because hydrocarbons reside in up-dip areas of traps, water with non-representative density might be produced by oil wells. Considering this, oil-well samples may not be random or representative of the formation water as a whole.

UNIVARIATE STATISTICS

DATA DISTRIBUTION

Univariate parametric statistical methods are based on a normal distribution of the chemical variables in the samples (Koch and Link, 1971). A number of studies have demonstrated that many geochemical data sets are log-normally distributed (Ahrens, 1954; Koch and Link, 1971, Hitchon et al., 1971, Long et al., 1986). Before statistical test can be correctly applied therefore, the distribution of the sample population must be determined. The chi-squared (X^2) test is used to test for population normality, using both the raw data and log (base 10) transformed data. The results of this test at the 5% significance level or better (TABLE A-1), indicate that the data are lognormally distributed, except for Na and Cl. Histograms (Figure A-1) of Na and Cl show these elements follow a negatively skewed log-normal distribution, and log-probability plots show a break in slope, characteristic of two overlapping populations (Figure A-2). The cause for this distribution is not clear, but because the Na-Cl histograms suggest a lognormal distribution, albeit skewed, all data were log-transformed for use statistical tests.

TABLE A-1
RESULTS OF CHI-SQUARED TEST

COMPONENT	X	SD	X^2	DF	SIGNIFICANCE LEVEL
Br	1550	865	50.5	10	2.18×10^{-17}
a Log Br	3.121	0.262	20.7	7	4.21×10^{-3}
a Cl	18000	39025	12.9	8	0.113
Log Cl	5.241	0.135	33.9	5	2.48×10^{-6}
c Na	55900	21400	21.2	10	0.020
Log Na	4.706	0.210	44.4	9	1.17×10^{-6}
Ca	43900	26900	67.8	10	1.17×10^{-10}
b Log Ca	4.555	0.298	14.4	7	0.044
Mg	7610	3500	30.7	9	3.39×10^{-4}
c Log Mg	3.835	0.210	6.80	7	0.450
K	4860	5250	137.	9	0
c Log K	3.472	0.443	12.8	8	0.120
Sr	1480	1010	38.6	7	2.29×10^{-6}
c Log Sr	3.067	0.321	8.6	8	0.380
Rb	13.0	16.4	89.2	6	0
Log Rb	0.85	0.50	4.753	7	0.690
Cs	2.5	2.4	32.1	5	5.62×10^{-6}
d Log Cs	0.17	0.49	17.811	6	6.72×10^{-3}
d Li	39.6	23.1	25.2	9	2.95×10^{-3}
d Log Li	1.51	0.31	24.8	8	3.22×10^{-3}
B	92.	109.	42.0	5	5.85×10^{-8}
c Log B	1.67	0.58	2.84	5	0.724
NH4N	266.	255.	71.2	6	2.367×10^{-13}
c Log NH4	2.26	0.38	12.2	7	0.093
HCO_3	80.5	96.6	133.	6	0
d Log HCO_3	1.60	0.58	17.9	9	0.035
SO_4	157.	190.	95.5	7	0
Log SO_4	1.72	1.18	85.8	9	1.110×10^{-14}
I	17.2	13.5	62.5	10	1.189×10^{-9}
c Log I	1.12	0.32	7.9	9	0.539
Si	3.2	2.7	36.6	4	2.22×10^{-7}
c Log Si	0.42	0.25	9.9	6	0.128
TDS	294000	65900	16.6	9	0.055
Log TDS	5.452	0.138	34.4	5	2.012×10^{-6}

KEY:

H_0 = no evidence to suggest that sample is not from a normal population

Significance level of acceptance:

a = 2.5% b = 5%
c = 10% d = <1%

X = mean value, SD = standard deviation, X^2 = chi-squared value, DF = degrees of freedom

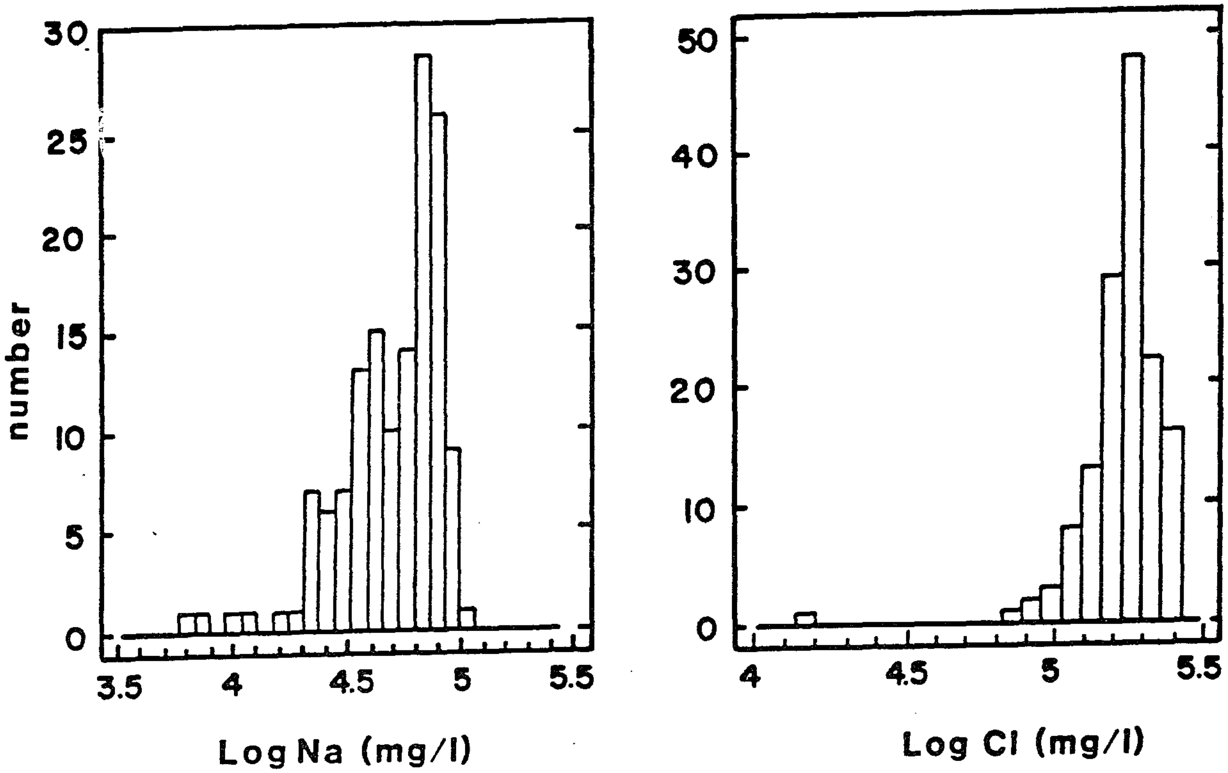


Figure A-1. Histograms of Na and Cl (mg/l) concentrations.

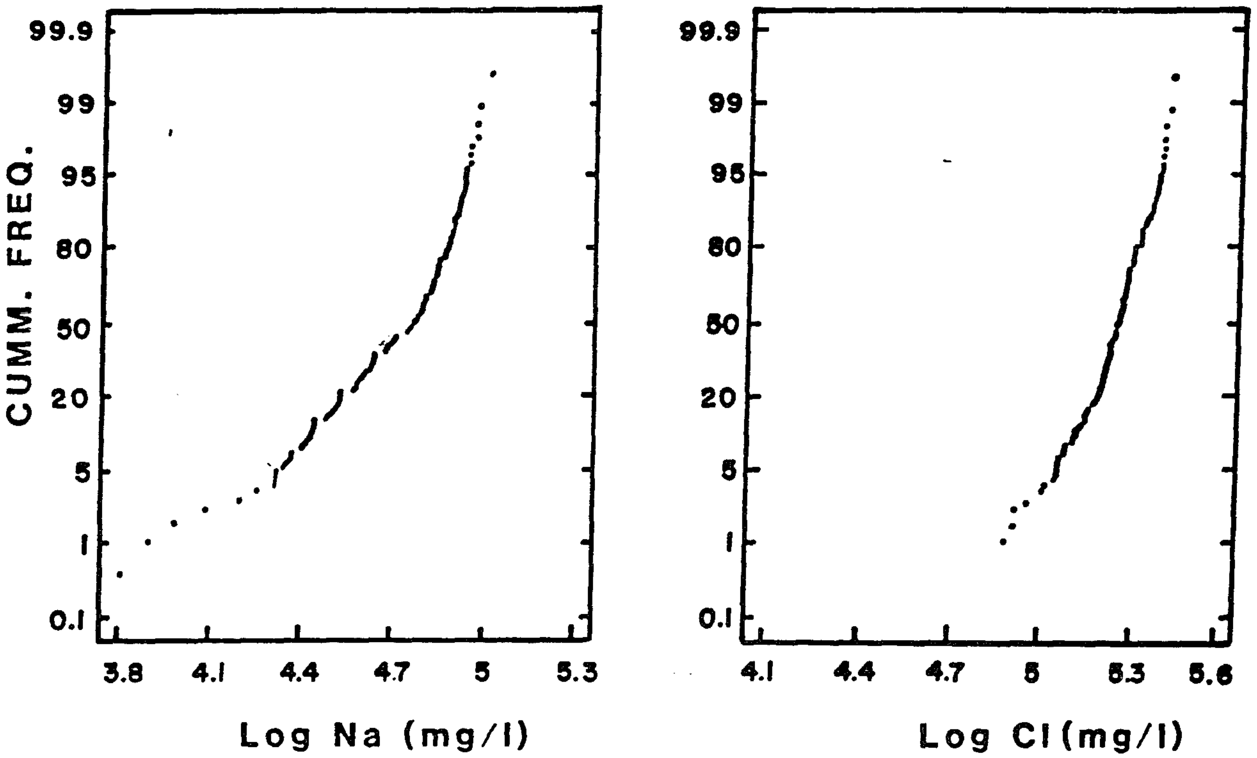


Figure A-2. Log-probability plots of Na and Cl (mg/l) concentrations.

AVERAGE BRINE COMPOSITION

Table A-2 lists the formation water means (geometric means and an unbiased estimator of the mean), maximum and minimum concentrations, variances (unbiased estimator), and sample sizes. Also listed are seawater concentration ratios, defined as: SWR= average brine value/seawater value, and evaporation factors, defined as EF=(concentration ratio of a given constituent/concentration ratio of Br). Seawater values are given in parentheses next to each element, and are from Brewer (1975). Averages and standard deviations calculated from log transformed data represent the geometric means and geometric variances, respectively. The geometric mean may be the preferred estimator of the population means and variance when the coefficient of variation (standard deviation/mean) is less than 1.2, a rule suggested by Koch and Link (1971). However, other estimators of population means and variances exist that are statistically unbiased and have the smallest sampling error variance of all unbiased estimators. These statistics are termed minimum variance unbiased estimators. Generally, unbiased estimators of means are preferred if the lognormal distribution is skewed, as is observed for Na and Cl values (Gilbert, 1987). The unbiased estimates of the population means and variances are calculated using: $m = [\exp (y)]\ X_n({}^1/_2\ S_u^2)$ and $V=\exp(2y)\ [X_n(s_u^2/2)]-X_n[s_u^2(n-2)\ /(n-1)]$ where y=geometric mean, s_u^2= geometric variance, n=number of observations, and the

TABLE A-2
SUMMARY STATISTICS

	BEREA	TRV	DD	RF	DT. R	N/S	TBR
n	(3)	(29)	(40)	(13)	(2)	(26)	(11)
Cl (19,350 mg/kg)							
A	194000	172000	171000	194000	212000	210000	126000
B	195000	175000	173000	194000	212000	214000	128000
C	10000	15600	3430	2070	3720	8180	6219
D	176000	13600	120000	75800	179000	117000	91000
E	209000	196000	212000	242000	251000	265000	163000
SWR	10.0	8.1	8.8	10.0	10.9	10.8	6.5
EF	0.48	0.54	0.59	0.32	0.22	0.33	0.42
Br (67 mg/kg)							
A	1400	1100	1000	2100	3400	2400	1030
B	1460	1240	1090	2300	3400	2400	1050
C	295	164	74.0	308	345	202	63.0
D	940	590	315	1050	3060	690	750
E	1840	2340	2390	4210	3750	3340	1430
SWR	20.8	14.9	14.9	31.3	50.9	32.8	15.7
EF	1	1	1	1	1	1	1
Ca (411 mg/kg)							
A	45100	29000	24500	65200	88000	74000	22800
B	45400	33300	27100	68600	89700	76900	23300
C	3660	4790	2020	6440	17300	4290	1530
D	38400	11600	7390	27800	72400	35200	15800
E	49500	67700	7330	96200	107000	124000	35500
SWR	110.	63.0	59.6	158.	214.	180.	55.5
EF	5.3	4.2	4.0	5.0	4.20	5.5	3.5
Mg (1290 mg/kg)							
A	8250	6600	5100	8700	11800	11500	5130
B	8270	6810	5360	9220	11800	12100	5280
C	355.	630.	284.	939.	1450	763.	410.
D	7600	3840	1820	3370	10400	6080	3200
E	8790	9700	11300	14600	13300	20000	9110
SWR	6.4	4.7	3.9	6.7	9.1	8.9	3.9
EF	0.30	0.31	0.26	0.21	0.18	0.27	0.25
Na (10760 mg/kg)							
A	63000	68200	71000	34200	23100	31400	47300
B	63100	70100	72400	37100	23100	33500	47700
C	2580	6250	2340	4370	900.	2500	1890
D	58200	43000	38800	12400	22200	9820	37200
E	66700	88700	103000	61500	24000	48800	59000
SWR	5.9	5.8	6.6	3.2	2.1	2.9	4.4
EF	0.28	0.39	0.44	0.10	0.04	0.088	0.28

TABLE A-2 (cont'd.).

	BEREA	TRV	DD	RF	DT. R	N/S	TBR
K (399 mg/kg)							
A	640.	1660	1640	7200	13400	9250	3680
B	640.	1910	2010	7930	14300	11000	3780
C	35.0	264.	220.	1035	5020	1400	272.
D	580.	440.	380.	3570	9270	2300	2180
E	700.	4750	8360	13300	19300	24100	5440
SWR	1.6	3.8	4.1	18.	33.6	23.2	9.2
EF	0.075	0.26	0.27	0.58	0.66	0.71	0.59
Sr (8 mg/kg)							
A	2000	1060	780	1970	2680	2190	750.
B	2000	1260	911.	2440	2710	2430	766.
C	114.	195.	86.0	487.	365.	230.	43.0
D	1780	350	170.	290.	2340	800.	540.
E	2140	2920	2350	3980	3070	6030	1040
SWR	250	117	98	246	335	274	94.
EF	12.	7.9	6.5	7.8	6.6	8.4	6.0
Rb (0.12 mg/kg)							
A	3.6	3.7	3.0	12.4	37.3	24.1	7.9
B	3.6	5.6	4.2	13.6	37.5	30.1	8.3
C	0.2	1.7	0.7	1.9	3.7	5.3	1.2
D	3.4	0.4	0.4	6.5	33.8	10.7	4.5
E	3.9	17.2	11.1	23.8	41.2	77.7	11.
SWR	30.	30.8	25.	103	310	200	66.
EF	1.4	2.1	1.7	3.3	6.1	6.1	4.2
Li (0.18 mg/kg)							
A	8.0	29.3	23.9	46.5	92.9	59.2	37.5
B	8.0	33.7	31.8	48.4	96.0	63.9	38.1
C	*	4.6	4.2	3.9	24.0	5.2	2.1
D	8.0	9.2	2.0	24.0	72.0	18.0	26.0
E	8.0	81.0	68.0	76.0	102.	101.	47.0
SWR	44.	150	133	258	516	330	210
EF	2.1	10.	8.9	8.2	10.	10.	13.
B (4.5 mg/kg)							
A	-	28	21	119	226	127	13
B	-	40	43	150	260	170	14
C	-	13	13	37	120	34	2
D	-	18	1	39	134	25	6
E	-	117	85	377	383	498	21
SWR	-	6.4	4.6	27.	50.	28.3	2.9
EF	-	0.43	0.31	0.85	1.0	0.9	0.20

TABLE A-2 (cont'd.).

	BEREA	TRV	DD	RF	DT. R	N/S	TBR
Si (0.5-10 mg/kg)							
A	3.2	2.8	2.6	2.34	1.9	2.2	3.3
B	3.4	3.1	2.9	2.7	1.9	2.5	4.2
C	0.90	0.50	0.30	0.60	0.30	0.30	1.3
D	1.4	1.4	1.2	0.90	1.6	0.90	0.70
E	4.4	5.2	11.6	8.5	2.3	6.3	5.7
SWR	0.61	0.53	0.49	0.46	0.37	0.42	0.63
EF	0.031	0.036	0.033	0.015	.007	0.013	0.040
NH_4N							
A	74	125	107	228	550	547	80
B	77	129	110	230	590	620	80
C	80	130	120	240	570	600	85
D	50	76	29	115	441	235	45
E	126	193	228	400	690	1087	126
HCO_3 (142 mg/kg)							
A	11	85	31	160	180	90	38
B	20	45	51	210	210	150	41
C	6	16	10	43	110	42	6
D	10	0	0	45	100	0	25
E	25.	160	140	390	330	610	90
SWR	0.14	0.32	0.36	1.4	1.5	1.1	0.29
EF	0.007	0.017	0.022	0.042	0.030	0.032	0.018
SO_4 (2710 mg/kg)							
A	45	65	180	1200	10	49	205
B	71	130	300	1200	28	66	250
C	43	35	57	1200	26	11	51
D	10	0	20	0	0	0	100
E	100	610	1130	350	50	150	720
SWR	0.017	0.023	0.66	0.44	0.037	0.018	0.076
EF	0.001	0.001	0.004	0.013	0.0007	0.001	0.005
I (.06 mg/kg)							
A	23	11	11	23	38	25	11
B	23	13	13	28	41	28	12
C	3	2	1	6	16	3	1
D	17	4	0	10	25	7	6
E	28	71	28	68	57	65	26
SWR	380	170	180	380	630	420	180
EF	18	11	12	12	13	13	12
TDS (35,000 mg/kg)							
A	315000	282000	278000	296000	355000	345000	207000
B	316000	289000	280000	315000	360000	352000	210000
C	16400	26100	5570	31900	61400	14000	10100
D	284000	21500	197000	125000	299000	196000	151000
E	335000	326000	349000	395000	421000	444000	273000
SWR	9.0	7.4	7.9	8.5	10.	10.	5.9
EF	0.43	0.50	0.49	0.27	0.20	0.28	0.38

TABLE A-2 (cont'd.).

	BEREA	TRV	DD	RF	DT. R	N/S	TBR
MCl_2 (69.2 meq/kg)							
A	2980	1840	1660	4020	5420	4720	1580
B	2990	2220	1810	4240	5520	4890	1610
C	213.	274.	122.	403.	1010	262.	106.
D	2580	102.	573.	1680	4525	2290	1060
E	3240	4240	4640	6010	6500	7380	2540
SWR	43.	26.6	23.9	58.0	78.3	68.2	23.
EF	2.0	1.7	1.6	1.8	1.6	2.1	1.5

KEY:
All values in mg/l unless noted
A: Geometric mean
B: Minimum variance unbiased estimator of population mean
C: Unbiased estimator of standard eviation
D: Minimum value
E: Maximun value
SWR: Seawater ratio; average brine value(B)/seawater value
EF: SRW/ Br seawater ratio
MCL_2 : Mg + Ca + Sr - 0.5HCO_3 - SO_4 (meq/l)
n: Number of analyses for major components
TRV: Traverse N/S: Niagara/Salina DD: Dundee RF: Richfield
DT. R: Detroit River TBR: Trenton Black River

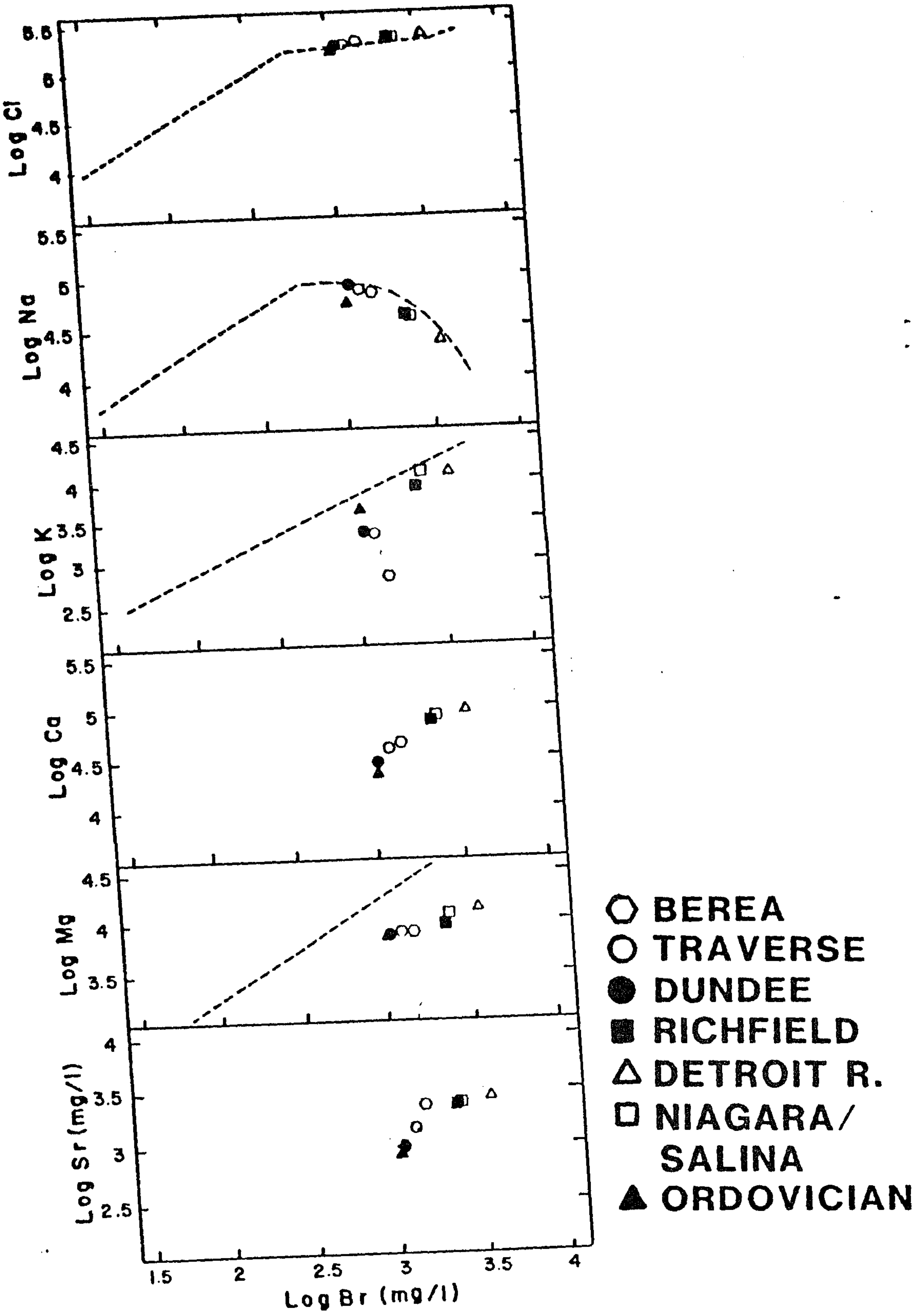
function X_n is from statistical tables or calculated by the following equation from Gilbert (1987):

$$X_n(x) = 1+(n-1)x/n + (n-1)^3x^2/(2!*n^2(n+1))$$
$$+ (n-1)^5x^3/(3!n^3(n+1)(n+3))\ldots ,$$

COMPARISON WITH SEAWATER

The average brine compositions from Table A-2 are compared with the chemistry of evaporating seawater in Figure A-3. The seawater data from McCaffrey et al. (1988) are used in this figure. Inspection of this diagram shows the relative degree of agreement that exists between these brine components and seawater. The brine chemistry can also be compared with seawater by examining the seawater concentration ratios listed in Table A-2. These ratios help to quantitatively illustrate the changes that seawater would have to undergo if it were to evolve into Michigan basin brine. For example, based on brine salinity (TDS), the average brine salinity ranges from 5X to 10X that of seawater depending upon formation, with a maximum of 12.6x. If the brine had originated from seawater and no mineralogic reactions had affected them, then each element concentration ratio (brine value/seawater value) should equal the TDS ratio, at least within individual formations. This is clearly not the case, as some elements are enriched to various degrees (Br, Ca, Mg, Na, K, Sr,Rb, Li, B, I) while other are depleted to various degrees (alkalinity, SO_4, Si). This type of evidence has been used in the past to demonstrate that formation brine is not simply unaltered

Figure A-3. Average Michigan formation brine compostion (log mg/l) compared with seawater (dashed line). Seawater data from McCaffrey et al. (1988).


Log Cl
5.5
5
4.5
4
Log Na
5.5
5
4.5
4
Log K
4.5
4
3.5
3
2.5
Log Ca
5.5
5
4.5
4
Log Mg
4.5
4
3.5
Log Sr (mg/l)
4
3.5
3
2.5
1.5
2
2.5
3
3.5
4
Log Br (mg/l)
BEREA
TRAVERSE
DUNDEE
RICHFIELD
DETROIT R.
NIAGARA/ SALINA
ORDOVICIAN

seawater (Chave, 1960; Collins, 1975). However, salinity is not the best reference to judge the alterations. In order to better judge the magnitude of the enrichments or depletions, a concentration ratio of a conservative element must be used as a reference. In this study, as in others (Collins, 1975), Br is assumed conservative, and its concentration ratio can be used to calculate an excess factor: EF= (concentration ratio of a given constituent/ concentration ratio of Br) (Collins, 1975). Based on the excess factor, elements enriched over seawater include Ca, Sr, Rb, Li, I. Elements depleted from seawater are Cl, Mg, Na, K, alkalinity (HCO_3), SO_4, and TDS. Boron and MCl_2 (Ca + Mg + Sr - $0.5HCO_3$-SO_4 in meq/l) are approximately conservative with, or only slightly enriched, with respect to Br. Both Chapter 1 and chapter 2 explain that these enrichments and depletions generally reflect water-rock reactions.

FORMATION COMPARISON

Univariate statistical methods are used to test equality of water chemistry between different aquifers, from different areas within an aquifer, or from a single well over time (NCASI, 1985). The Student's t-test is used here to test equality of mean brine concentration between formations. This comparison is warranted in light of the similarities found in brine chemistry using graphical methods described earlier (Chapter 1, Chapter 2).

Before applying the Student's t-test, equality of variances must be demonstrated by the F-test, using a null hypothesis Ho: $s_2{}^2=s_1{}^2$, with s^2=variance. For those components meeting the F-test at the 0.01 level of significance or better, the Student's t-test was applied using a null hypothesis $Ho:u_2=u_1$, where u=mean of sample populations. Not rejecting H_o suggests that no statistical evidence exists to suggest the means are different, while rejection of H_o suggests that there is statistical evidence for a difference in means.

For this test, means of the Berea, Traverse, and Dundee were first compared to establish if this group of samples could be combined. Generally, the t-test results showed that means appear similar between each formation. However, several of the major elements in the Traverse samples exhibit a high degree of variance, which caused Br, Cl, Na, Ca, and TDS, to fail the F-test. Because of this, the Dundee samples were used to represent the upper Devonian formation water chemistry for intraformational testing. Table A-3 is a summary of the t-test results for the components and ratios that meet the F-test criteria. Generally, most elements passed at the 0.05 level of significance for the F- and T-test, respectively.

Inspection of Table A-3 shows the following: (1) mean concentrations in the Dundee and Traverse formation samples can be considered statistically similar in the cases where the t-test is applicable. Many of the intraformation

TABLE A-3
STUDENT'S t-TEST RESULTS

FORMATION COMPONENT	DD-TR	DD-RF	DD-NS	DD-TBR	RF-NS	RF-TBR	TBR-NS
Br		R	R	NR	NR		R
Cl		R	R	R	NR	R	R
Na		R	R	R	NR		R
Ca		R		NR	NR	R	R
Mg	NR	R	R	NR	R	R	R
K	NR	R	R	R	NR	R	R
Sr	NR	R	R	NR	NR	R	R
Rb	NR	R	R	R	R	NR	R
Li	NR				NR	R	R
B	NR	R	R	NR	NR	R	R
I	NR	R	R	NR	NR	R	R
Si	NR	NR	NR	NR	NR	NR	NR
NH4N	NR	R	R	NR	R	R	R
SO_4	R	R	R	NR			R
HCO_3	R	R	R		NR	R	R
TDS		NR	R	R			R
D	NR	NR	NR	NR	NR	NR	NR
18O	NR	R	NR		NR		NR

KEY:

H_o = $mean_1$ = $mean_2$

NR, R = not rejected, rejected at the level of significance of at least 0.01 for the F-test, and the 95% to 99% confidence level for the T-test, depending on F-test results

Blank = t-test not applicable due to rejection by F-test at the 0.01 level of significance

FORMATION CODES:

DD= Dundee, TR = Traverse-Berea, RF = Richfield-Detroit River,
NS = Niagara-Salina, TBR = Trenton-Black River

comparisons made using the Dundee samples were found to apply for Traverse samples as well, (2) Mean concentrations in the Richfield-Detroit River brine and Niagara/Salina brine can be considered similar, (3) Mean concentrations in the Richfield, Detroit River, and Niagara/Salina samples are statistically different from the Traverse-Dundee samples; and (4) Mean silica (Si) and deuterium (D) concentrations are statistically similar between all formation samples.

These results suggests that two groups of brine exists, the lesser concentrated water from the Berea, Traverse, and Dundee water and the more highly concentrated Richfield, Detroit River and Niagara/Salina formation waters

CORRELATION COEFFICIENTS

Correlation coefficients measure the degree of relationship between variables. A high degree of correlation, either positive or negative, between elements might be suggestive of a common control. For example, Na and Cl concentrations would correlate positively when both are supplied only by the dissolution of halite. Alternatively, strong inverse correlations might suggest mineral equilibrium. For example, Ca^{2+} and $SO_4{}^{2=}$ would correlate inversely when controlled only by $CaSO_4$ mineral equilibria, as Ca cannot increase without a concomitant decrease in sulfate. Although correlation coefficients are helpful in reducing geochemical data, elemental correlation is not evidence of causation (Egleson and Querio, 1969).

Table A-4 is a correlation matrix generated for the logtransformed data by the SAS program. The closer a correlation coefficient is to ±1, the more the variables are related. The following is a summary of significant correlations from Table A-4.

COMPONENT	+ CORRELATION	- CORRELATION
pH	Cl, SO_4	Mg
Br	Rb, Ca, K	Na, SO_4
Cl	TDS, Mg	SO_4, pH
Ca	Sr, K, Rb,Mg	SO_4, Na
HCO_3	NONE	SO_4
I	Ca, Sr, Rb	Na, SO_4
K	Ca, Rb, B, Sr	Na, SO_4
Li	B, K, Br, Rb	Na, SO_4
Mg	Ca, Sr, K, Br	SO_4, pH
Na	SO_4	Cs, Rb, K
SO_4	Na	Sr, Ca
Sr	Ca, K, Mg	SO_4, Na
Rb	K, Ca, Cs, Sr,Br	Na
Cs	Rb, K, Br	Na
B	K, Rb, Li	Na
Si	NONE	HCO_3
TDS	Cl	pH, SO_4

Several correlations are noted in this table. A reoccurring inverse correlation exists between (Na,SO_4) and many of the other elements. The meaning of this is not clear, but may reflect that the lowest SO_4 and Na concentrations are found in the most highly concentrated samples. Two other notable correlations are between Si-HCO_3, and TDS-Cl, which might represent "basic" pairs, that is, each are more highly correlated with each other than any

TABLE A-4
Correlation matrix
log-transformed data.

	PH	BR	CL	CA	HCO3	I	K	LI	MG
PH	1.00000	-0.29745	-0.51536	-0.36438	0.35092	-0.24382	-0.28416	-0.06310	-0.57018
BR	-0.29745	1.00000	0.42713	0.78716	-0.25514	0.38306	0.78060	0.71279	0.74984
CL	-0.51636	0.42713	1.00000	0.56032	-0.37858	0.47153	0.42915	0.39587	0.68504
CA	-0.36438	0.78716	0.56032	1.00000	-0.24165	0.63511	0.94591	0.71114	0.89698
HCO3	0.35092	-0.25514	-0.37858	-0.24165	1.00000	-0.10242	-0.23808	-0.00214	-0.32052
I	-0.24382	0.38306	0.47153	0.63511	-0.10242	1.00000	0.57760	0.49148	0.59988
K	-0.29416	0.78060	0.42915	0.94591	-0.23808	0.57760	1.00000	0.76103	0.76860
LI	-0.06310	0.71279	0.39587	0.71114	-0.00214	0.49148	0.76103	1.00000	0.48781
MG	-0.57018	0.74984	0.68504	0.89698	-0.32052	0.59988	0.76860	0.48781	1.00000
NA	0.09390	-0.46562	0.18757	-0.65677	0.04931	-0.38150	-0.71112	-0.35199	-0.46548
SO4	0.47277	-0.44378	-0.52414	-0.69076	0.33815	-0.35450	-0.62208	-0.29753	-0.69666
SR	-0.29159	0.70307	0.51537	0.95165	-0.20803	0.62891	0.88565	0.65719	0.86333
RB	-0.31923	0.83875	0.39805	0.90696	-0.22176	0.61593	0.94146	0.70070	0.77237
CS	-0.13211	0.75704	0.04288	0.70614	-0.11275	0.40263	0.77362	0.54224	0.53042
B	-0.17142	0.70147	0.21127	0.78612	0.03337	0.53619	0.87924	0.81678	0.55488
SI	-0.16636	0.27602	-0.05950	0.29576	-0.51067	0.01758	0.43457	0.02962	0.17223
TDS	-0.49935	0.27669	0.77501	0.39155	-0.36476	0.46821	0.32191	0.23469	0.53576

	NA	SO4	SR	RB	CS	B	SI	TDS
PH	0.09390	0.47277	-0.28159	-0.31923	-0.13211	-0.17142	-0.16636	-0.49935
BR	-0.46562	-0.44378	0.70307	0.83875	0.75704	0.70147	0.27602	0.27669
CL	0.18757	-0.52414	0.51537	0.39805	0.04288	0.21127	-0.05950	0.77501
CA	-0.65677	-0.69076	0.95165	0.90696	0.70614	0.78612	0.29576	0.39155
HCO3	0.04931	0.33815	-0.20803	-0.22176	-0.11275	0.03337	-0.51067	-0.36476
I	-0.38150	-0.35450	0.62891	0.61593	0.40263	0.53619	0.01758	0.46821
K	-0.71112	-0.62208	0.88565	0.94146	0.77362	0.87924	0.43457	0.32191
LI	-0.35199	-0.29753	0.65719	0.70070	0.54224	0.81678	0.02962	0.23469
MG	-0.46548	-0.69666	0.86333	0.77237	0.53042	0.55488	0.17223	0.53576
NA	1.00000	0.50096	-0.66066	-0.71604	-0.76989	-0.64378	-0.48192	0.14074
SO4	0.50096	1.00000	-0.70406	-0.54016	-0.33165	-0.33838	-0.26296	-0.48709
SR	-0.66066	-0.70406	1.00000	0.84562	0.67953	0.69476	0.29097	0.36432
RB	-0.71604	-0.54016	0.84562	1.00000	0.89802	0.84393	0.41108	0.29640
CS	-0.76989	-0.33165	0.67953	0.89802	1.00000	0.74608	0.48577	-0.01327
B	-0.64379	-0.33838	0.69476	0.84393	0.74608	1.00000	0.23841	0.12971
SI	-0.49192	-0.26276	0.29097	0.41108	0.48577	0.23841	1.00000	-0.03510
TDS	0.14074	-0.48709	0.36432	0.29640	-0.01327	0.12871	-0.03510	1.00000

of the remaining variables. The meaning of these relationships are explored further using the R-mode analysis discussed below. It is also interesting to note that Egleson and Querio (1969) report KCl-B and Br-I are basic pairs in the Sylvania Formation brine from Michigan, a correlation not found in the present study. Finally, elements with similar geochemical behaviors are observed to correlate together, for example, Ca-Mg-Sr and K-Rb-Cs.

MULTIVARIATE STATISTICS

Multivariate statistical tests of Q-mode and R-mode factor analysis were conducted on the data set in order to evaluate population homogeneity and to help elucidate possible geochemical controls. Factor analysis attempts to reduce the measured variables to a fewer number of interpretable variables, called factors. The goal is to determine the best-fit factors by grouping variables together that describe as much of the data variance as possible. In other words, factor analysis combines the set of m variables (chemical components or wells) into the p number of best fit, mutually uncorrelated factors, with $p<m$. This is accomplished in two fashions, R and Q mode factor analysis.

R-mode factor analysis determines relationships between variables by extracting eigenvectors and eigenvalues from a correlation or covariance matrix generated from the chemical data. The resulting R-mode factors describe the maximum amount of variance in the chemical data. Variables (chemical components) are assigned factor loadings, or scores, which show their importance in describing each factor. Because the variables are grouped into factors according to their intercorrelations, the factors may, or may not, be interpretable to reflect geochemical processes. Principal component analysis (principal factors) is similar to R-mode factor analysis, but is strictly a mathematical manipulation involving the calculation of the eigenvectors of a variance-covariance or correlation matrix (Davis, 1986).

Q-mode factor analysis is concerned with relationships between individual samples. That is, it attempts to discover patterns within a group of objects. This test is used to determine if a sample population is a mixture of various end-members, thereby testing data homogeneity. Q-mode extracts eigenvectors and eigenvalues from a similarity matrix between all possible pairs of samples. Q-mode analysis also generates factors describing interrelationships between samples, based on their similar chemical characteristics. These factors then can be used to help deduce end member water compositions. If Q-mode results show the data set is homogeneous, that is, if only 1 factor describes the relationships between samples, then R-mode can be applied to the entire data set.

Excellent reviews of R and Q-mode factor analysis are found in Klovan (1975), Joreskog et al. (1976), Davis (1986) and Long et al. (1986). No attempt will be made here to present further detailed explanation of these procedures.

INTERPRETING FACTORS

The factors generated in R-mode analysis may, or may not, be interpretable to reflect geochemical processes. Factor makeup can change due to choice of data, the number of factors extracted, and the methods used to rotate the data to get the "best fit" to the variance. Davis (1986) discusses some of the difficulties in selecting number of factors, and the philosophy in choosing rotation methods. The changes on the R-mode factors generated in this study as the result of several different rotation methods and choice of data are evaluated below. Additionally, because interpretations of factors may be subjective, it is instructive to determine if similarities exist in the factor loading patterns generated in other ground water studies. The past work of Kramer (1969), Egleson and Querio (1969) (Figure A-4), Hitchon et al. (1971) (Figure A-5), and Long et al. (1986) (Figure A-6) are summarized next.

PAST WORK

Kramer (1969) applied R-mode factor analysis to over 2400 brine samples, separated by formation rock type and region. The analysis used the squared multiple correlations of the data and the varimax rotation method. The goal of Kramer's study was to use factor analysis to illustrate common characteristics of formation waters, which are discussed below.

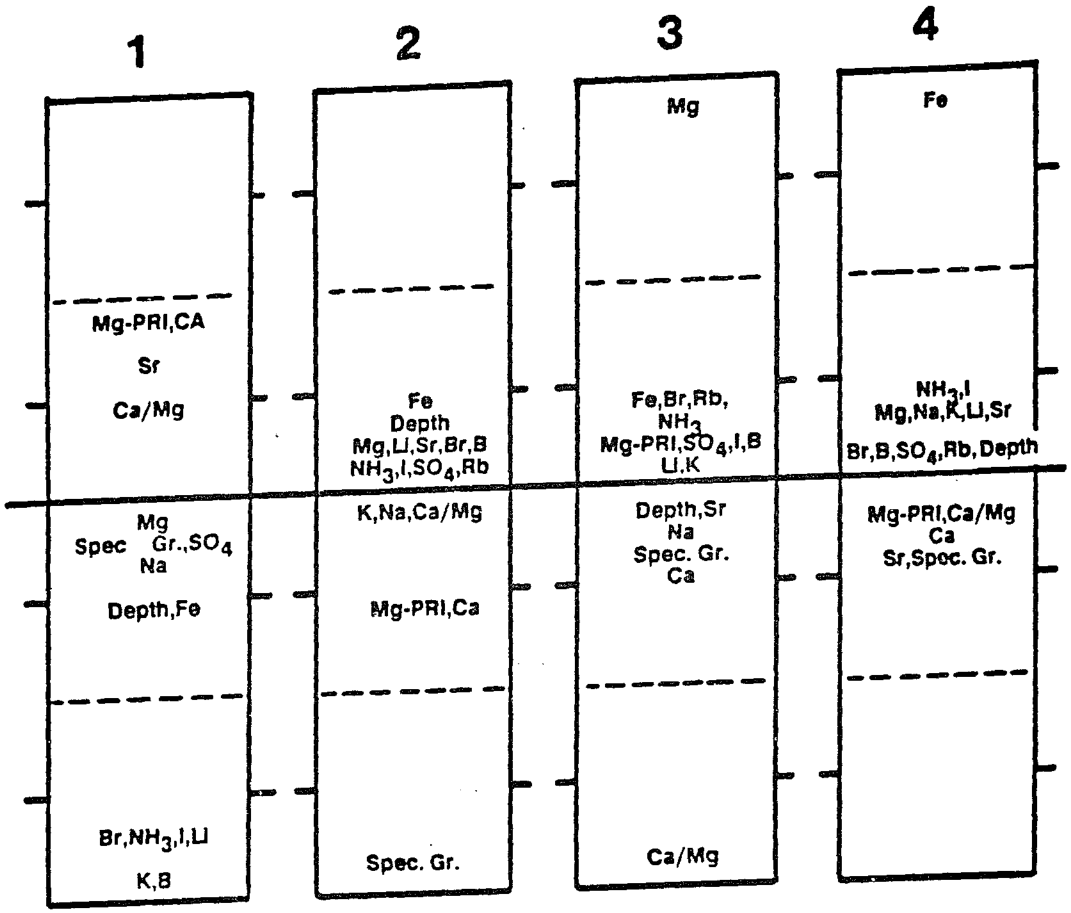
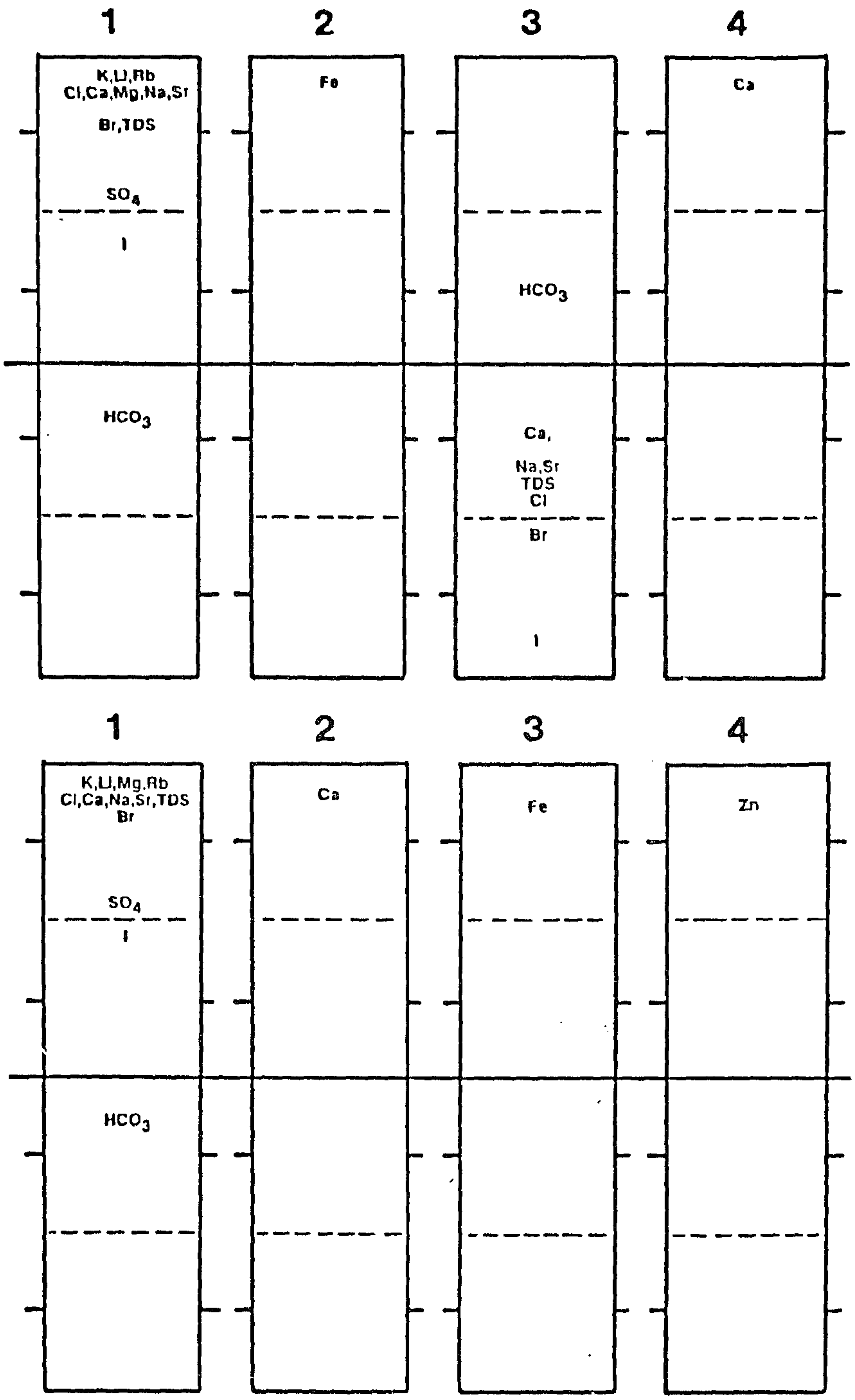


Figure A-4. R-mode factor analysis results (Varimax rotation) from Egleson and Querio (1969) for Sylvania Sandstone formation waters, Michigan Basin.

Figure A-5. R-mode factor analysis results from Hitchon et al. (1971), for West Canada basin waters. TOP: varimax rotation, BOTTOM: bi-quartum oblique rotation.

Hitchon et al. (1971) R-MODE VARIMAX ROTATION

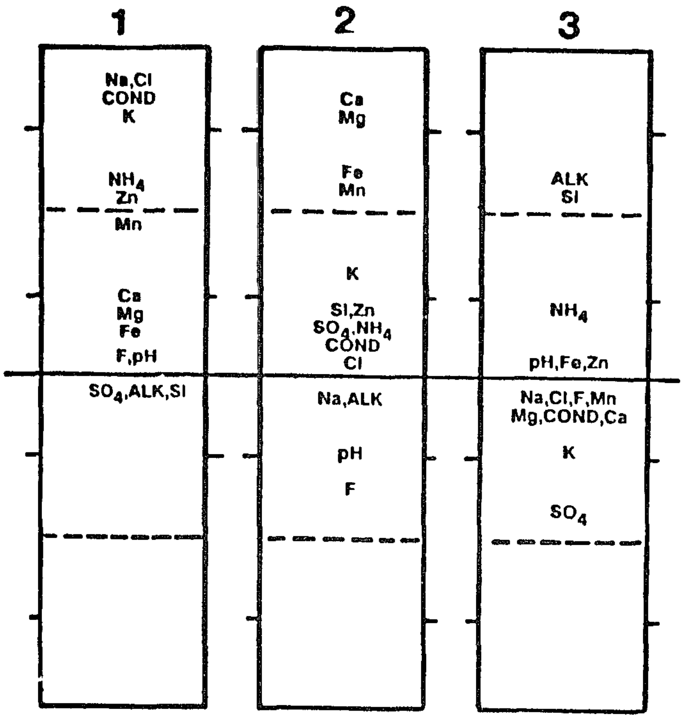


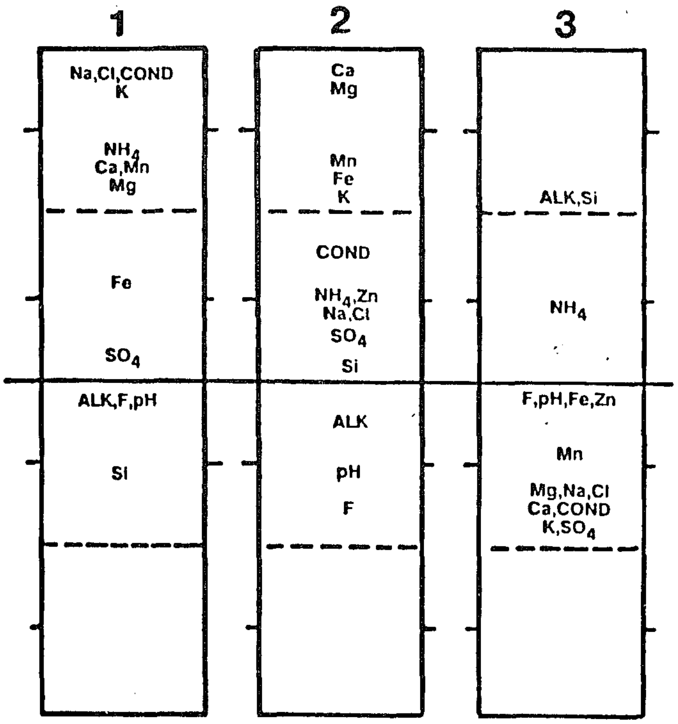
Hitchon et al. (1971) R-MODE BIQUARTIMIN
OBLIQUE ROTATION.

Figure A-5

Figure A-6. R-mode factor analysis results from Long et al. (1986) for near-surface saline groundwaters in Michigan.

Long et al. (1986) R-MODE VARIMAX ROTATION





Long et al. (1986) R-MODE PROMAX ROTATION

Figure A-6

Egleson and Querio (1969) conducted R-mode factor analysis (varimax rotation) on the Sylvania Formation waters from the Michigan basin. Both chemical and physical data were used, but it is not clear if their data were first log-transformed before analysis. Although ten factors were found to account for 100% of the data variance, only the first factor had interpretable loadings; the remaining factors had high loadings on only a single element. Their first factor showed high loadings for the minor elements and production depth, interpreted to reflect a common source related to paleotopography.

Hitchon et al. (1971) used R and Q-mode factor analysis to study West Canada sedimentary basin formation waters. Q-mode factor analysis showed their data are homogeneous. The variation in the Q-mode results were combined with flow direction and depth and used as evidence for shale membrane filtration. R-mode factor analysis was preformed both without the partialling out of salinity, using varimax and oblique rotation methods. A second R-mode factor analysis was conducted combining the results from the first R-mode test with physical parameters and stable isotopic data. The R-mode results were interpreted as evidence that the brine originated from seawater modified by shale membrane filtration.

Long et al. (1986) used both Q and R-mode factor analysis to study saline, near-surface groundwaters in the mid-Michigan area. Although the Q-mode results demonstrated a single population of water exists, the extracted Q-mode scores suggested two types of waters, a normal background (regional) water and localized saline water. Q-mode scores were contoured to delineate areas of saline water infiltration. Four different R-mode rotation methods were used, with similar factors produced by each method. Factors were interpreted to show: (1) a saline water factor, indicating brine input, (2) a water-rock factor, reflecting carbonate, oxide, and clay mineral reactions, (3) a non-halogen factor reflecting sulfate reduction and silicate interactions.

FACTOR PATTERNS

These studies provide a good illustrations of how factor loadings can be interpreted in light of geologic processes. Kramer (1969) outlined several general patterns and the processes they might represent: (1) an inverse loading between anions and cations of common minerals suggests mineral equilibria, (2) a direct loading between anion-anion or cation-cation might represent ion-exchange reactions, and (3) several variables loading highly in a single factor suggests a common source or origin. In addition to these patterns, the other studies have suggested the following interpretations of factor pattern .

A common source: Hitchon et al. (1971) interpreted the high loadings on Li, Rb, K, TDS, Mg, Ca, Na, Cl, Sr, Br, and SO_4 in their first R-mode factor (Figure A-5) as showing a common origin for these elements, seawater. A similar interpretation of many elements loading together in a single factor was made by Egleson and Querio (1969) (Figure A-4).

Mixing of waters: The correlation between the first Q-mode factor with decreasing salinity was used by Hitchon et al. (1971) to support dilution by freshwater. Long et al. (1986) interpreted an R-mode factor showing high loadings on Na, Cl, K, conductivity, Ca, Mg, and NH_3 to reflect the input and mixing of saline water (Figure A-6). Contour maps of their first Q-mode factor, having a high loading on alkalinity, revealed the location of brine inputs.

Membrane filtration: The increasing importance of the second Q-mode factor in a down-dip flow direction was interpreted by Hitchon et al. (1971) to reflect shale membrane filtration. High loadings of Mn, Rb, Sr, and Zn, and high negative loadings on Cu, Na, Cl, HCO_3, and TDS in this factor for downflow samples suggested that metal rich, lower salinity ground waters exit the outflow side of shale layers. In their R-mode analysis combining chemical and physical data, high positive loadings on the seawater factor (factor 1, Figure A-5) of temperature, depth, pressure, and ŠD, opposed by high negative loadings on pH, was thought to reflect increased membrane efficiency with depth, pressure, and temperature, as well as the isotope mixing hypothesis of Hitchon and Friedman (1969).

Dissolution of halite or other minerals: In addition to other data, Hitchon et al. (1971) thought that a weak positive loading on both Na and Cl suggested halite dissolution (Figure A-5). This pattern is in contrast to factors interpreted to show mineral equilibria, which show inverse loadings of common mineral components (Kramer, 1969; Long et al., 1986).

Dolomitization: Hitchon et al. (1971) found little evidence in their results to suggest dolomitization, but thought that high positive loadings of Ca and Mg in the seawater factor with TDS partialled out may reflect dolomitization. This is consistent with the findings of Kramer (1969), who interpreted high positive loadings on Ca and Mg coupled with a negative loading on HCO_3 as reflecting dolomitization. Similar bipolar factor loadings of Ca, Mg, and HCO_3 are also reported by Collins (1969a), Dawdy and Feth (1967), and Long et al. (1986). Although this typical Ca-Mg pattern is associated with dolomitization, several studies have not found this result, even though other data in these studies supported dolomitization (Collins, 1969; Lee, 1969; Egleson and Querio, 1969).

Sulfate reduction: Bacterial reduction of sulfate to alkalinity and sulfide was thought to be represented by bipolar loadings on pH_2S and SO_4 by Hitchon et al. (1971). Long et al (1986) interpreted a strong bipolar loading between alkalinity and sulfate to represent sulfate reduction (Figure A-6).

Formation of chlorite: An inverse loadings of Mg and Fe was interpreted by Hitchon et al. (1971) to represent chlorite formation (Figure A-5).

Cation exchange: The bipolar loadings of Ca and Na in the R-mode results with salinity partialled out was thought by Hitchon et al. (1971) to reflect cation exchange (Figure A-5). Also, decreasing factor loadings in the order Rb>K>Sr>Li>Mg were thought to represent cation exchange, because this is exactly the order of "replacing" power of cations on clays (decreasing non-hydrated ionic radius, increasing hydrated ionic radius, and polarizability).

Contribution from organic matter: Hitchon et al. (1971) concluded that similar factor scores for Br and I might represent an organic material source (Figure A-5). Highly negative loadings of I, Br, and NH_3, and the correlation between I, Br, and production depth in a single factor were interpreted by Egleson and Querio (1969) to reflect a halogen source from organic debris in topographically low areas of the Sylvania Formation (Figure A-4).

Mineral equilibria control: Both Kramer (1969) and Hitchon et al. (1971) interpreted high loadings of HCO_3 and SO_4 along with high negative loadings of Ca, Mg, and Sr (with salinity partialled out) to reflect dolomite, calcite, and celestite equilibrium. Kramer (1969) suggested inverse loadings of Ba and SO_4 reflect barite equilibrium. An inverse loadings on Sr and SO_4 was also found by Egleson and Querio (1969) (Figure A-4). Long et al. (1986) interpreted inverse loadings of Si and K to represent silicate interactions (Figure A-6). Equilibrium was also supported by chemical model calculations. Kramer (1969) interpreted both the inverse loading of Si and Cl (thought to represent cations), and positive pH-SiO_2 loadings to represent aluminosilicate equilibrium.

Q-MODE METHODS AND RESULTS

Q-mode factor analysis was preformed in this study using the SAS statistical program on the IBM 4381 computer at Michigan State University. A non-standardized log-transformed similarity matrix was used, constructed using the cosine theta coefficient of proportional similarity suggested by Davis (1986).

The principal factor solution for the first five Q-mode factors, their eigenvalues, total variance, and the cumulative percentages of variance are listed below.

Factor	1	2	3	4	5
Eigenvalue	140.7	0.558	0.354	0.202	0.714
Difference	140.2	0.204	0.151	0.132	0.033
Proportions	0.991	0.004	0.003	0.001	0.001
Cumulative %	0.991	0.995	0.998	0.999	0.999

The first eigenvector accounts for over 99% of the variance of the data, strongly suggesting that the data are from a single homogeneous population, and that R-mode analysis can be conducted using the entire data set. A single eigenvector explaining such a large percentage of the data variance implies that a single gradient characterizes the samples. This is interpreted as a salinity gradient, similar to the interpretations of Hitchon et al. (1971) and Long et al. (1986).

Davis (1986) suggests that a dominant first factor is often obtained in Q-mode analysis, such as is the case here. Such a dominant factor reveals little about the structure of the data, and is considered a "nuisance" factor". The second and third eigenvectors, although much smaller in magnitude and accounting for small proportions of the variance, may reveal more useful information (Davis, 1986). This was the case for Hitchon et al. (1971), whose first factor accounted for 55% of the variance, and for Long et al. (1986) whose first Q-mode factor accounted for 95% of the variance. The extreme amount of variance (>99%) explained by the first factor in the present study, however, suggests that further Q-mode factoring may not be warranted.

R-MODE FACTOR METHODS

R-mode factor analysis was preformed on the log-transformed data set, using the SAS statistical package available on the IBM 4381 computer at Michigan State University. The review of other factor analysis studies demonstrated three problems that might be encountered in the R-mode factor analysis of brines, which were considered in this study. Firstly, salinity might dominant the factors, as was suggested by the Q-mode analysis and by the results of Hitchon et al. (1971). In order evaluate the effects of salinity in the present study, TDS was partialled out of the R-mode analysis. A comparison of the effects of this are discussed below. Secondly, missing or erroneous variables might bias factors, especially if the variable represents an important species such as pH. Many of the samples obtained from outside this study (M.D.N.R. and oil company open file data) did not report minor components measured in this study. To address this concern, two subsets of the data were evaluated, (1) the entire data set was used including samples with missing data, and (2) only those samples having complete data. No difference were found in the makeup of the resulting factors using either data set (compare Table A-5, case 1a, and A-5 case 1b). In a similar fashion, because the pH measurements are suspect in these highly concentrated waters, the R-mode analysis was run both with and without including the pH data. Slight differences in the makeup of the extracted factors were found when pH was included, which is discussed below.

R-MODE RESULTS

Table A-5 reports the eigenvectors, eigenvalues, communalities, and factor scores for each of the different combinations of data. The results are displayed diagrammatically in Figures A-7 to A-10. Components plotting towards either end of these diagrams have loading approaching ±1. The principal component, varimax, and promax rotation results of the following four trials are shown;

Case 1 (results shown in Figure A-7): only those samples having pH (generally only samples collected in this study) are used, pH variable is included, and TDS is not partialled out.

Case 1b (not shown): all samples are used, pH variable is included, and TDS is not partialled out. Results are listed in Table A-5 for comparison with case 1.

Case 2 (Figure A-8): All samples are used, pH variable is included, and TDS is partialled out.

Case 3 (Figure A-9): All samples are used, pH variable is not included, and TDS is partialled out.

Case 4 (Figure A-10): All samples are used, pH variable is not included, TDS is not partialled out.

The eigenvalues, representing the variance in the data that has been extracted onto each factor, show that 4 factors account for 90 to 92% of the variance in the data (Table A-5). After the fourth factor, the amount of variance explained be each factor drops to less than 3% of the variance, well below the estimated experimental error for the components. Communalities (Table A-5), a measure of the efficiency that each variable is explained, are >0.75 and show the factors are efficient in explaining the variability in the data. Exceptions are pH, alkalinity, and I, having communalities near 0.5. This could signify that additional factors need to be extracted in order to better explain these later variables.

TABLE A-5
R-MODE FACTOR ANALYSIS RESULTS

Case 1) Only samples with pH are used
pH variable included
TDS not partialled out

Factor	1	2	3	4	5
Eigenvalue	9.117	2.5206	1.4524	0.74145	0.4757
Difference	6.597	1.0682	0.7109	0.2657	0.4570
Proportion	0.5960	0.1648	0.0949	0.0485	0.0311
Cummlative	0.5960	0.7608	0.8557	0.9042	0.9353

COMMUNALITIES

PH	.5177	BR	.8189	CL	.9469	CA	.9640
Alk	.5372	I	.5404	K	.9520	LI	.8583
MG	.8931	NA	.9797	SO4	.7611	SR	.9001
RB	.9598	CS	.8789	B	.8604	SI	.7831
TDS	.6799						
TOTAL	13.8118						

A) PRINCIPAL FACTORS

FACTOR 1		FACTOR 2		FACTOR 3		FACTOR 4	
CA	.9761	PH	.9636	Alk	.5173	NA	.3747
K	.9636	CS	.4976	LI	.4984	SO4	.3548
RB	.9582	B	.3463	PH	.2892	BR	.3328
SR	.9279	Alk	.3335	SO4	.2765	SI	.2605
MG	.8810	SO4	.3018	B	.2737	LI	.2527
BR	.8352	SI	.2571	NA	.2656	CL	.1460
B	.8118	RB	.1848	I	.2580	CS	.1303
CS	.7759	K	.1476	CL	.1573	RB	.0864
LI	.7254	LI	.1405	BR	.0678	B	.0811
I	.6451	BR	.07602	CA	.0539	K	.0408
CL	.5455	SR	-.0022	TDS	.0456	PH	.0316
TDS	.4224	CA	-.0171	SR	.0366	TDS	.0300
SI	.3652	I	-.1473	K	.0075	CA	-.0900
Alk	-.2861	MG	-.3128	RB	-.0014	MG	-.1358
PH	-.4216	NA	-.5646	MG	-.0249	I	-.1897
NA	-.6708	TDS	-.7060	CS	-.1103	SR	-.1941
SO4	-.6839	CL	-.7767	SI	-.7181	Alk	-.2765

TABLE A-5 (Continued)

Case 1 (continued)

B) VARIMAX Rotation

FACTOR 1		FACTOR 2		FACTOR 3		FACTOR 4	
B	.9063	CL	.9271	NA	.7551	SI	.8366
LI	.8919	TDS	.8160	SO4	.5831	CS	.3545
RB	.8682	MG	.6562	PH	.1753	BR	.2545
K	.8496	CA	.4251	CL	.1273	RB	.2399
BR	.8232	I	.3988	LI	.0946	I	.2087
CS	.8054	SR	.3930	TDS	.0222	CA	.0942
CA	.7808	BR	.2762	BR	-.0087	MG	.0917
SR	.7117	K	.2704	Alk	-.0220	SR	.0554
MG	.5555	RB	.2341	SI	-.1986	B	-.0109
I	.5118	NA	.2176	B	-.1986	TDS	-.0252
CL	.2611	LI	.1591	I	-.2789	CL	-.0552
SI	.1999	B	.0177	CS	-.2988	LI	-.1685
TDS	.1136	SI	-.0606	SR	-.3062	SO4	-.1768
Alk	-.0007	CS	-.1233	K	-.3369	I	-.2039
PH	-.0360	ALk	-.4355	MG	-.3814	NA	-.2519
SO4	-.2465	SO4	-.5736	CA	-.4059	PH	-.2576
NA	-.5465	PH	-.6475	SR	-.4858	Alk	-.5892

C) PROMAX Rotation

FACTOR 1		FACTOR 2		FACTOR 3		FACTOR 4	
RB	.9455	CL	.9548	NA	.9182	SI	.8684
K	.9362	TDS	.8225	SO4	.7093	CS	.4515
B	.9113	MG	.7484	PH	.2914	RB	.3245
CA	.8988	CA	.5568	Alk	.1577	BR	.2998
LI	.8686	SR	.5174	CL	-.0648	K	.2939
BR	.8666	I	.4858	TDS	-.0974	CA	.1749
SR	.8353	K	.4117	LI	-.2366	SR	.1422
CS	.8287	BR	.4010	BR	-.4100	MG	.1404
MG	.7168	RB	.3775	I	-.4372	B	.0784
I	.5939	LI	.2954	SI	-.4390	TDS	-.0626
CL	.3936	B	.1677	B	-.5231	CL	-.0991
SI	.2700	NA	.1028	MG	-.6377	LI	-.1190
TDS	.2484	CS	.0139	CS	-.6451	I	-.1531
Alk	-.1141	SI	-.0266	RB	-.6843	SO4	-.2288
PH	-.1918	Alk	-.4251	K	-.7008	PH	-.2428
SO4	-.4377	SO4	-.6249	CA	-.7245	NA	-.3874
NA	-.6208	PH	-.6493	SR	-.7659	Alk	-.5571

TABLE A-5 (Continued)

Case 1-b) Same as case 1 except all samples are used.

Factor	1	2	3	4	5
Eigenvalue	9.1174	2.5206	1.4524	0.7414	0.4757
Difference	6.5968	1.0681	0.7109	0.2658	0.6457
Proportion	0.5960	0.1648	0.0949	0.0485	0.0311
Cummlative	0.5960	0.7608	0.8557	0.9042	0.9353

COMMUNALITIES

pH	.5176	BR	.8189	CL	.9469	CA	.9641
Alk	.5372	I	.5404	K	.9520	LI	.8583
MG	.8931	NA	.9797	SO4	.7611	SR	.9000
RB	.9598	CS	.8788	B	.8605	SI	.7831
TDS	.6799						
TOTAL	13.832						

A) PRICIPAL FACTORS

FACTOR 1		FACTOR 2		FACTOR 3		FACTOR 4	
CA	.9761	PH	.5126	ALK	.5173	NA	.3747
K	.9636	CS	.4976	LI	.4984	SO4	.3548
RB	.9582	B	.3463	PH	.2892	BR	.3329
SR	.9279	ALK	.3335	SO4	.2765	SI	.2605
MG	.8810	SO4	.3018	B	.2737	LI	.2528
BR	.8353	SI	.2571	NA	.2655	CL	.1460
B	.8118	RB	.1848	I	.2580	CS	.1303
CS	.7759	K	.1476	CL	.1573	RB	.0864
LI	.7254	LI	.1405	BR	.0678	B	.0811
I	.6451	BR	.0760	CA	.0539	K	.0408
CL	.5455	CA	-.0171	TDS	.0455	PH	.0316
TDS	.4224	SR	-.0022	SR	.0366	TDS	.0300
SI	.3652	I	-.1473	K	.0075	ALK	-.0900
ALK	-.2862	MG	-.3128	RB	-.0014	MG	-.1358
PH	-.4126	NA	-.5646	MG	-.0249	I	-.1897
NA	-.6708	TDS	-.7060	CS	-.1103	SR	-.1941
SO4	-.6839	CL	-.7767	SI	-.7181	HCO3	-.2765

TABLE A-5 (Continued)

Case 1b (continued)

B) VARIMAX Rotation

FACTOR 1		FACTOR 2		FACTOR 3		FACTOR 4	
B	.9063	CL	.9271	NA	.7552	SI	.8366
LI	.8919	TDS	.8160	SO4	.5832	CS	.3544
RB	.8682	MG	.6562	PH	.1753	BR	.2545
K	.8496	CA	.4251	CL	.1273	RB	.2399
BR	.8233	I	.3988	LI	.0947	K	.2087
CS	.8054	SR	.3930	TDS	.0222	CA	.0942
CA	.7808	BR	.2762	ALK	-.0221	MG	.0917
SR	.7117	K	.2704	BR	-.0087	SR	.0555
MG	.5555	NA	.2176	B	-.1964	B	-.0109
I	.5118	RB	.2341	SI	-.1986	TDS	-.0252
CL	.2612	LI	.1591	I	-.2789	CL	-.0553
SI	.1999	B	.0177	CS	-.2988	LI	-.1685
TDS	.1136	SI	-.0606	RB	-.3062	SO4	-.1768
ALK	-.0008	CS	-.1233	K	-.3369	I	-.2039
PH	-.0360	ALK	-.4355	MG	-.3814	NA	-.2519
SO4	-.2465	SO4	-.5736	CA	-.4059	PH	-.2576
NA	-.54654	PH	-.6475	SR	-.4858	ALK	-.5892

C) PROMAX Rotation

FACTOR 1		FACTOR 2		FACTOR 3		FACTOR 4	
RB	.9455	CL	.9518	NA	.9182	SI	.8684
K	.9362	TDS	.8225	SO4	.7093	CS	.4515
B	.9114	MG	.7484	PH	.2914	RB	.3245
CA	.8988	CA	.5568	ALK	.1577	BR	.2998
LI	.8686	SR	.5174	CL	-.0648	K	.2939
BR	.8666	I	.4858	TDS	-.0974	CA	.1749
SR	.8353	K	.4117	LI	-.2366	SR	.1422
CS	.8287	BR	.4010	BR	-.4100	MG	.1405
MG	.7168	RB	.3775	I	-.4372	B	.0785
I	.5939	LI	.2954	SI	-.4390	TDS	-.0626
CL	.3936	B	.1677	B	-.5231	CL	-.0991
SI	.2700	NA	.1028	MG	-.6377	LI	-.1190
TDS	.2484	CS	.0139	CS	-.6451	I	-.1531
ALK	-.1141	SI	-.0266	RB	-.6842	SO4	-.2288
PH	-.1918	ALK	-.4251	K	-.7008	PH	-.2428
SO4	-.4377	SO4	-.6249	CA	-.7245	NA	-.3874
NA	-.6208	PH	-.6493	SR	-.7569	ALK	-.5571

TABLE A-5 (Contined)

Case 2) All samples are used,
pH variable included
TDS partialled out.

Factor	1	2	3	4	5
Eigenvalue	8.775	1.6290	1.4041	0.8579	0.5884
Difference	7.1462	0.2249	0.5441	0.2715	0.1331
Proportion	0.6141	0.1140	0.0983	0.0602	0.0412
Cummlative	0.6141	0.7281	0.8263	0.8865	0.9277

COMMUNALITIES

PH	.3776	BR	.8018	CL	.8955	CA	.9690
ALK	.4500	I	.4500	K	.9481	LI	.8401
MG	.8876	NA	.9889	SO4	.6978	SR	.8927
RB	.9579	CS	.8727	B	.8552	SI	.7837

TOTAL 12.66

A) PRINCIPAL FACTORS

FACTOR 1		FACTOR 2		FACTOR 3		FACTOR 4	
CA	.9724	ALK	.5664	CL	.8568	SO4	.3980
K	.9671	LI	.5240	NA	.3913	BR	.3343
RB	.9652	PH	.5240	MG	.3484	NA	.3320
SR	.9197	SO4	.3956	CA	.1187	SI	.3303
CS	.8713	B	.3156	SR	.0892	LI	.2394
B	.8487	I	.2953	BR	.0887	CL	.1742
MG	.8484	NA	.2046	LI	.0347	CS	.1644
BR	.8236	CL	.0746	I	-.0561	RB	.1085
LI	.7121	BR	.0624	ALK	-.0799	B	.0824
I	.5581	CA	.0355	K	-.0896	PH	.0731
SI	.4191	K	.0308	RB	-.1166	K	.0626
CL	.3540	RB	.0296	SO4	-.1570	CA	-.0900
ALK	-.1447	SR	.0248	B	-.1700	MG	-.1786
PH	-.2390	CS	-.0345	CS	-.2919	SR	-.1943
SO4	-.5985	MG	-.1209	SI	-.2973	I	-.2177
NA	-.8268	SI	-.6408	PH	-.3253	ALK	-.3192

TABLE A-5 (Continued)

Case 2 (continued)

B) VARIMAX Rotation

FACTOR 1		FACTOR 2		FACTOR 3		FACTOR 4	
B	.9165	SO4	.7701	SI	.8019	CL	.9086
RB	.9083	NA	.6064	CS	.3015	NA	.3911
K	.8949	PH	.4422	BR	.2732	MG	.3634
LI	.8627	LI	.1101	RB	.2166	BR	.2812
CS	.8511	ALK	.1062	K	.1871	LI	.2393
CA	.8249	BR	-.0940	MG	.1056	CA	.2027
BR	.7996	B	-.1159	CA	.0761	SR	.1376
SR	.7586	SI	-.1648	SR	.0198	K	.0482
MG	.5905	CL	-.1795	CL	.0123	RB	.0355
I	.5655	CS	-.2000	B	-.0405	B	-.0056
SI	.2661	I	-.2512	NA	-.1577	I	-.0199
CL	.1935	RB	-.2911	LI	-.1628	SO4	-.0616
PH	.0426	K	-.3314	SO4	-.1768	ALK	-.1232
ALK	.0307	CA	-.4947	I	-.2584	CS	-.1320
SO4	-.2641	SR	-.5452	PH	-.3313	SI	-.2065
NA	-.6659	MG	-.6289	ALK	-.6501	PH	-.2655

C) PROMAX Rotation

FACTOR 1		FACTOR 2		FACTOR 3		FACTOR 4	
RB	.9642	SO4	.8334	SI	.8471	CL	.9082
K	.9582	NA	.7999	CS	.4149	NA	.3936
CA	.9239	PH	.4589	BR	.3514	MG	.3615
B	.9124	ALK	.2018	RB	.3405	BR	.2758
CS	.8866	LI	-.1582	K	.3141	LI	.2589
SR	.8629	CL	-.2522	MG	.2230	CA	.2062
BR	.8345	SI	-.3722	CA	.2092	SR	.1432
LI	.8158	I	-.3744	SR	.1558	K	.0477
MG	.7365	B	-.4013	B	.0690	RB	.0339
I	.5819	BR	-.4021	CL	.0138	B	.0075
SI	.3455	CS	-.5133	LI	-.0942	I	-.0003
CL	.2776	RB	-.6059	I	-.1661	SO4	-.0516
ALK	-.0508	K	-.6343	SO4	-.2887	ALK	-.0875
PH	-.0936	CA	-.7447	NA	-.3123	CS	-.1382
SO4	-.4381	SR	-.7616	PH	-.3625	PH	-.2448
NA	-.7674	MG	-.8039	ALK	-.6454	SI	-.2463

TABLE A-5 (Contined)

Case 3) All samples are used,
pH variable not included
TDS partialled out

Factor	1	2	3	4	5
Eigenvalue	8.7132	1.5118	1.2784	0.8432	0.4375
Difference	7.2014	0.2333	0.4353	0.4057	0.0403
Proportion	0.6513	0.1130	0.0956	0.0630	0.0327
Cummulative	0.6413	0.7643	0.8599	0.9229	0.9556

Communalities

Br	.7983	CL	.9167	CA	.9755	ALK	.4789
I	.4440	K	.9479	LI	.8138	MG	.8474
NA	.9898	SO4	.7365	SR	.9097	RB	.9624
CS	.8827	B	.8822	SI	.7611		

TOTAL=12.3466

A) PRINCIPAL FACTORS

FACTOR 1		FACTOR 2		FACTOR 3		FACTOR 4	
CA	.9730	ALK	.4809	ALK	.3747	SO4	.4286
K	.9696	LI	.4636	SO4	.3395	BR	.3327
RB	.9663	CL	.4534	B	.3198	NA	.3225
SR	.9209	NA	.3669	CS	.2421	SI	.3043
CS	.8729	SO4	.2924	I	.1858	LI	.2336
B	.8508	I	.2323	LI	.1711	CS	.1849
MG	.8399	B	.2119	RB	.1449	CL	.1344
BR	.8219	BR	.0918	K	.0597	RB	.1207
LI	.7177	CA	.0740	BR	-.0592	B	.1051
I	.5604	MG	.0625	SI	-.0742	K	.0579
SI	.4131	SR	.0364	CA	-.1139	CA	-.1011
CL	.3491	K	-.0283	SR	-.1216	MG	-.1769
ALK	-.1389	RB	-.0291	NA	-.2588	I	-.2035
SO4	-.5933	CS	-.1670	MG	-.3261	SR	-.2132
NA	-.8271	SI	-.7017	CL	-.7557	ALK	-.2966

TABLE A-5 (Continued)

Case 3 (continued)

B) VARIMAX Rotation

FACTOR 1		FACTOR 2		FACTOR 3		FACTOR 4	
B	.9077	SR	.6731	SI	.7988	CL	.9314
RB	.8650	MG	.6473	CS	.3057	MG	.3877
LI	.8531	CA	.6035	BR	.2685	NA	.3441
K	.8249	K	.4648	RB	.2237	BR	.2782
CS	.8238	RB	.4016	K	.2089	CA	.2517
BR	.7863	I	.3421	MG	.1179	LI	.2413
CA	.7328	CS	.3086	CA	.1042	SR	.2097
SR	.6386	B	.2338	SR	.0687	K	.0867
I	.5180	SI	.2001	CL	.0237	RB	.0524
MG	.5137	BR	.1747	B	-.0576	I	.0044
SI	.2288	CL	.1513	LI	-.1631	B	-.0150
CL	.1604	LI	.0341	NA	-.1858	CS	-.1236
ALK	.0543	ALK	-.0757	SO4	-.2227	SO4	-.1349
SO4	-.1269	NA	-.7202	I	-.2421	ALK	-.1448
NA	-.5641	SO4	-.8078	ALK	-.6703	SI	-.1748

C) PROMAX Rotation

FACTOR 1		FACTOR 2		FACTOR 3		FACTOR 4	
RB	.9600	SR	.8671	SI	.8506	CL	.9388
K	.9411	CA	.8454	CS	.4594	MG	.4203
B	.9247	MG	.8176	RB	.3913	NA	.3089
CA	.8967	K	.7609	K	.3806	BR	.3052
CS	.8876	RB	.7179	BR	.3775	CA	.2948
BR	.8422	CS	.6231	CA	.2814	LI	.2907
LI	.8276	B	.5251	MG	.2676	SR	.2519
SR	.8204	BR	.5028	SR	.2482	K	.1259
MG	.7120	I	.4534	B	.0975	RB	.0914
I	.5703	SI	.3584	CL	.0245	I	.0498
SI	.3271	LI	.3184	LI	-.0571	B	.0369
CL	.2699	CL	.2514	I	-.1153	CS	-.0926
ALK	-.0366	ALK	-.1786	SO4	-.3594	ALK	-.1086
SO4	-.3779	SO4	-.8324	NA	-.3869	SO4	-.1480
NA	-.7293	NA	-.8741	ALK	-.6538	SI	-.2004

TABLE A-5 (Contined)

```
Case 4) All samples are used,
        pH variable not included
        TDS not partialled out.

Eigenvalue      8.9521     2.2999     1.3506     0.7291     0.421
6
Difference      6.6522     0.9493     0.6215     0.3075     0.067
5
Proportion      0.6246     0.1605     0.0942     0.0509     0.023
4
Cummlative      0.6246     0.7850     0.8793     0.9302     0.959
6

Communality
BR    .8152     CL    .9594     CA    .9676     ALK  .5646
I     .5377     K     .9536     LI    .8355     MG   .8722
NA    .9814     SO4   .7765     RB    .9617     CS   .8864
           B    .8768      SI    .7595      TDS  .6761      SR    .
9085
TOTAL=13.33

A) PRINCIPAL FACTORS
FACTOR 1        FACTOR 2        FACTOR 3        FACTOR 4
CA    .9773     CL    .8135     ALK   .5786     NA    .3694
K     .9694     TDS   .7152     LI    .4831     SO4   .3642
RB    .9626     NA    .5824     SO4   .3321     BR    .3308
SR    .9308     MG    .3144     B     .3227     SI    .2474
MG    .8675     I     .1990     I     .2198     LI    .2416
BR    .8359     CA    .0554     NA    .2004     CS    .1422
B     .8209     SR    .0502     BR    .0687     CL    .1355
CS    .7873     LI    -.0458    CL    .0416     RB    .0923
LI    .7359     BR    -.0474    CA    .0280     B     .0864
I     .6439     K     -.1117    RB    .0124     K     .0384
CL    .5268     RB    -.1623    K     .0001     TDS   .0225
TDS   .4023     SO4   -.2856    SR    -.0047    CA    -.0932
SI    .3630     ALK   -.2860    TDS   -.0479    MG    -.1311
ALK   -.2722    B     -.3020    CS    -.0512    I     -.1877
SO4   -.6723    SI    -.3194    MG    -.0599    SR    -.1987
NA    -.6824    CS    -.4935    SI    -.6808    ALK   -.2717
```

TABLE A-5 (Continued)

Case 4 (continued)

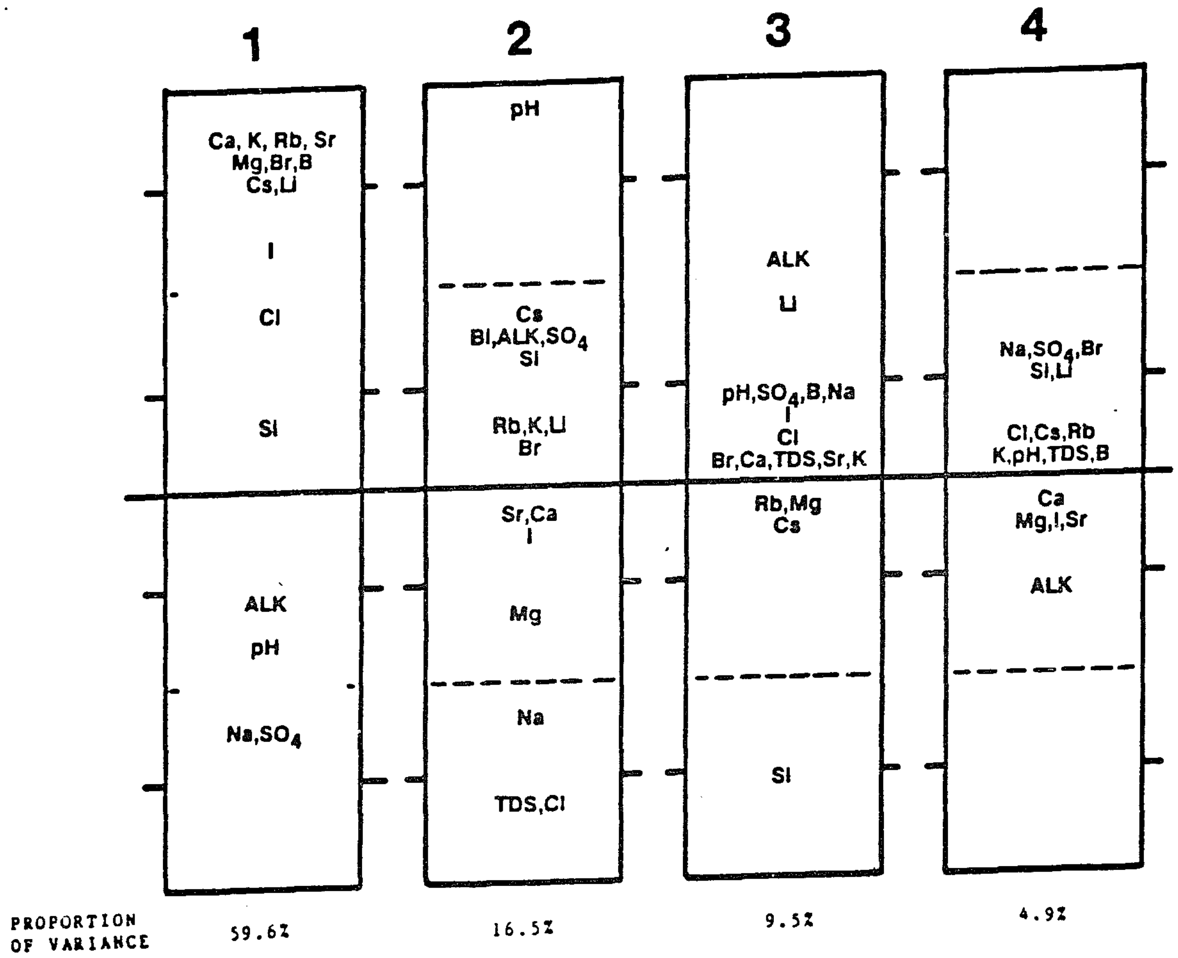
B) VARIMAX Rotation

FACTOR 1		FACTOR 2		FACTOR 3		FACTOR 4	
B	.9037	CL	.9546	NA	.7449	SI	.8107
LI	.8695	TDS	.8119	SO4	.6721	CS	.3237
RB	.8498	MG	.5947	ALK	.0331	BR	.2588
K	.8158	I	.4009	LI	.0039	RB	.2435
BR	.8151	CA	.3943	CL	-.0177	K	.2263
CS	.8098	SR	.3662	BR	-.0889	MG	.1344
CA	.7348	NA	.3213	TDS	-.0933	CA	.1269
SR	.6512	BR	.2753	SI	-.1961	SR	.1008
MG	.5167	K	.2446	B	-.2414	TDS	.0493
I	.4687	LI	.2314	CS	-.3119	CL	.0342
CL	.2161	RB	.1984	I	-.3604	B	-.0415
SI	.2043	B	.0144	RB	-.3753	LI	-.1610
TDS	.0759	SI	-.1453	K	-.4208	I	-.1659
ALK	.0144	CS	-.1689	MG	-.4832	NA	-.2208
SO4	-.1854	ALK	-.3370	CA	-.5062	SO4	-.2341
NA	-.5240	SO4	-.4854	SR	-.5832	ALK	-.6431

C) PROMAX Rotation

FACTOR 1		FACTOR 2		FACTOR 3		FACTOR 4	
RB	.9478	CL	.9709	NA	.8789	SI	.8522
K	.9299	TDS	.8183	SO4	.7738	CS	.4534
B	.9201	MG	.6632	ALK	.2075	RB	.3707
CA	.8833	CA	.4870	TDS	-.2172	K	.3541
BR	.8619	I	.4632	CL	-.2204	BR	.3406
LI	.8549	SR	.4544	LI	-.3395	CA	.2523
CS	.8502	BR	.3573	SI	-.4145	SR	.2292
SR	.8133	K	.3417	BR	-.4956	MG	.2245
MG	.6976	LI	.3188	I	-.5172	B	.0863
I	.5717	RB	.2971	B	-.5704	TDS	.0326
CL	.3506	NA	.2356	CS	-.6528	CL	.0161
SI	.2877	B	.1164	MG	-.7322	LI	-.0772
TDS	.2129	CS	-.0755	RB	-.7497	I	-.0833
ALK	-.1036	SI	-.1226	K	-.7777	SO4	-.3174
SO4	-.4126	ALK	-.3788	CA	-.8158	NA	-.3861
NA	-.6382	SO4	-.5286	SR	-.8411	ALK	-.6186

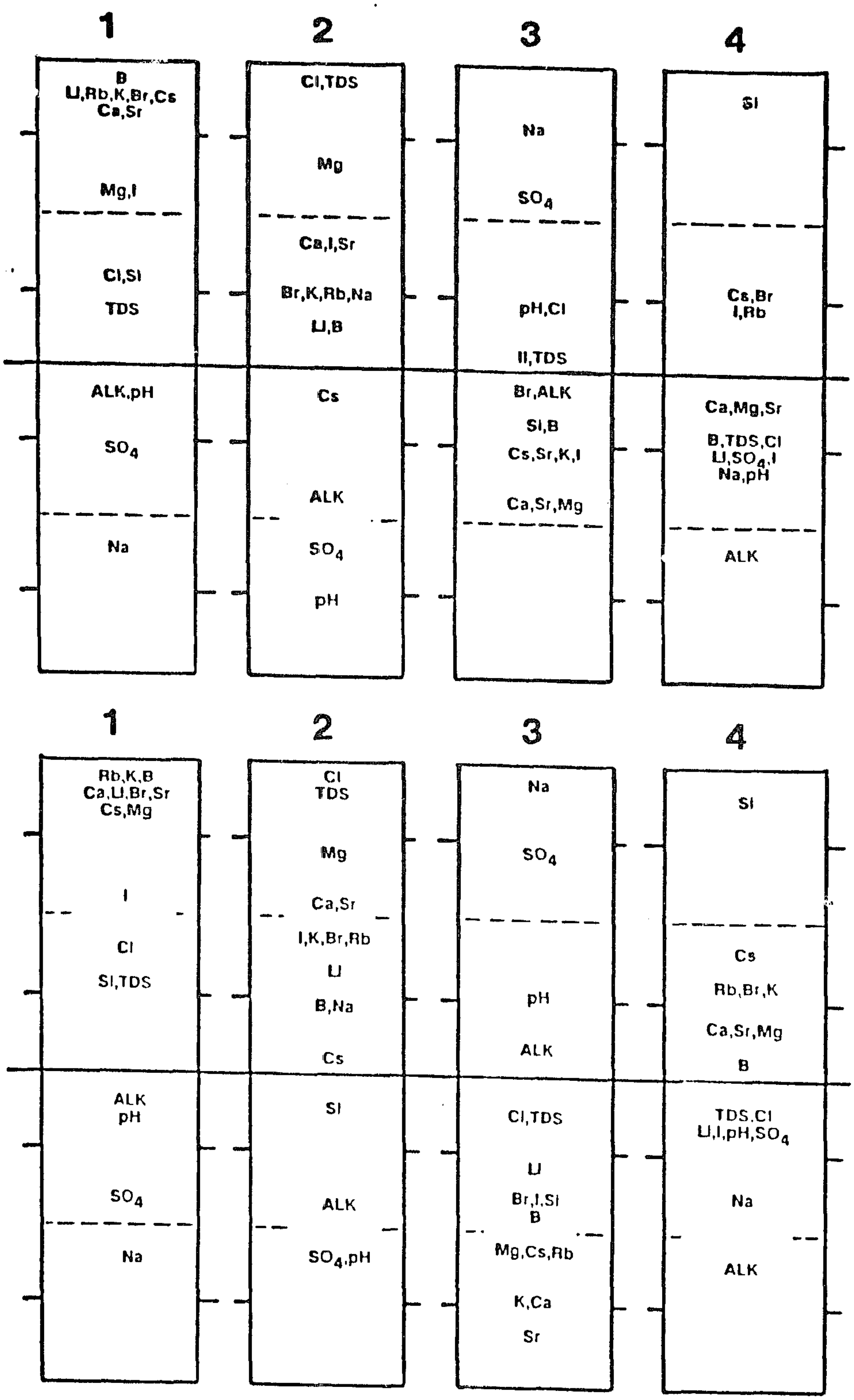
Figure A-7 . R-mode factor analysis results, case 1. Only samples with pH variable are used, pH variable included, TDS not partialled out.



CASE 1 - PRINCIPAL COMPONENTS

Figure A-7

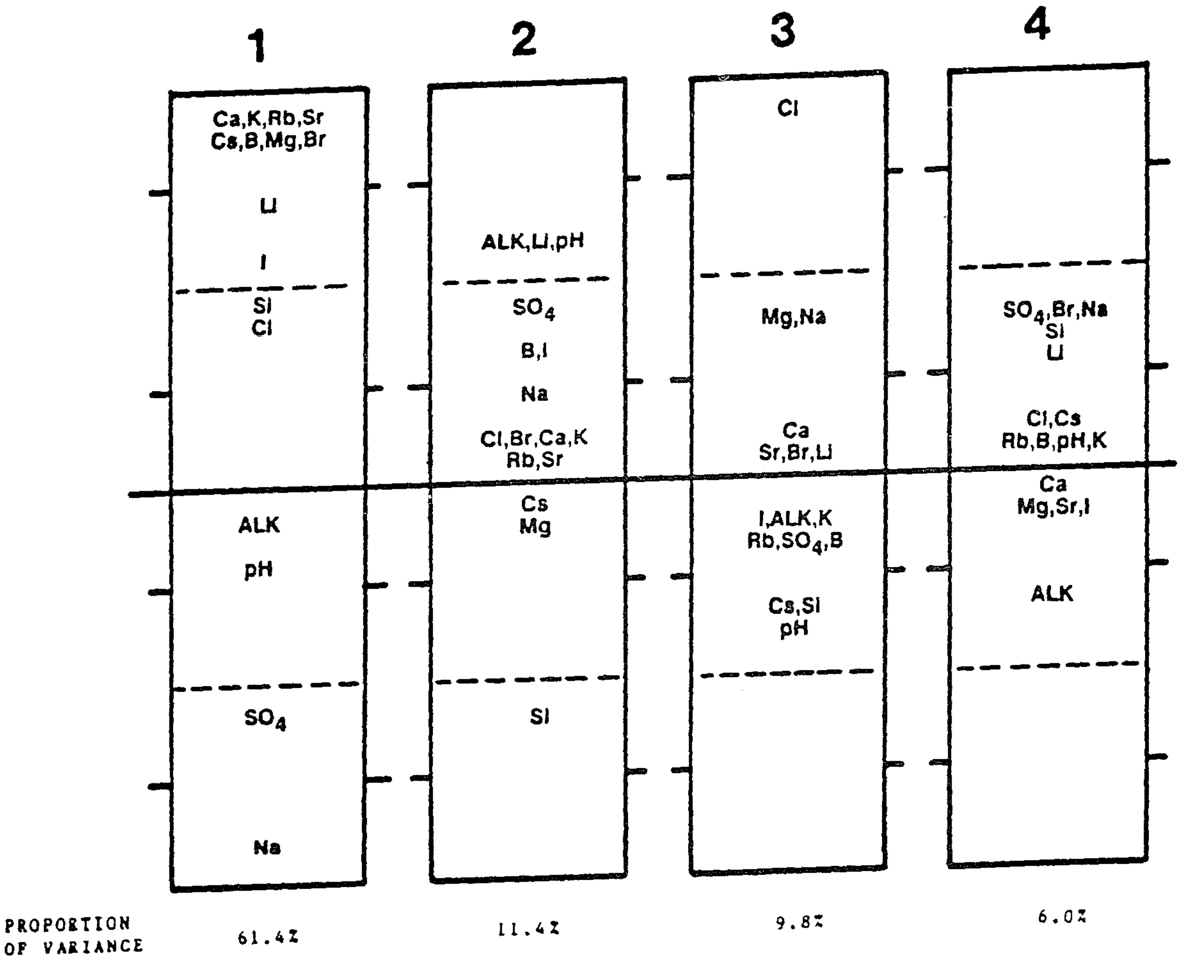
CASE 1 - VARIMAX ROTATION



CASE 1 - PROMAX ROTATION

Figure A-7

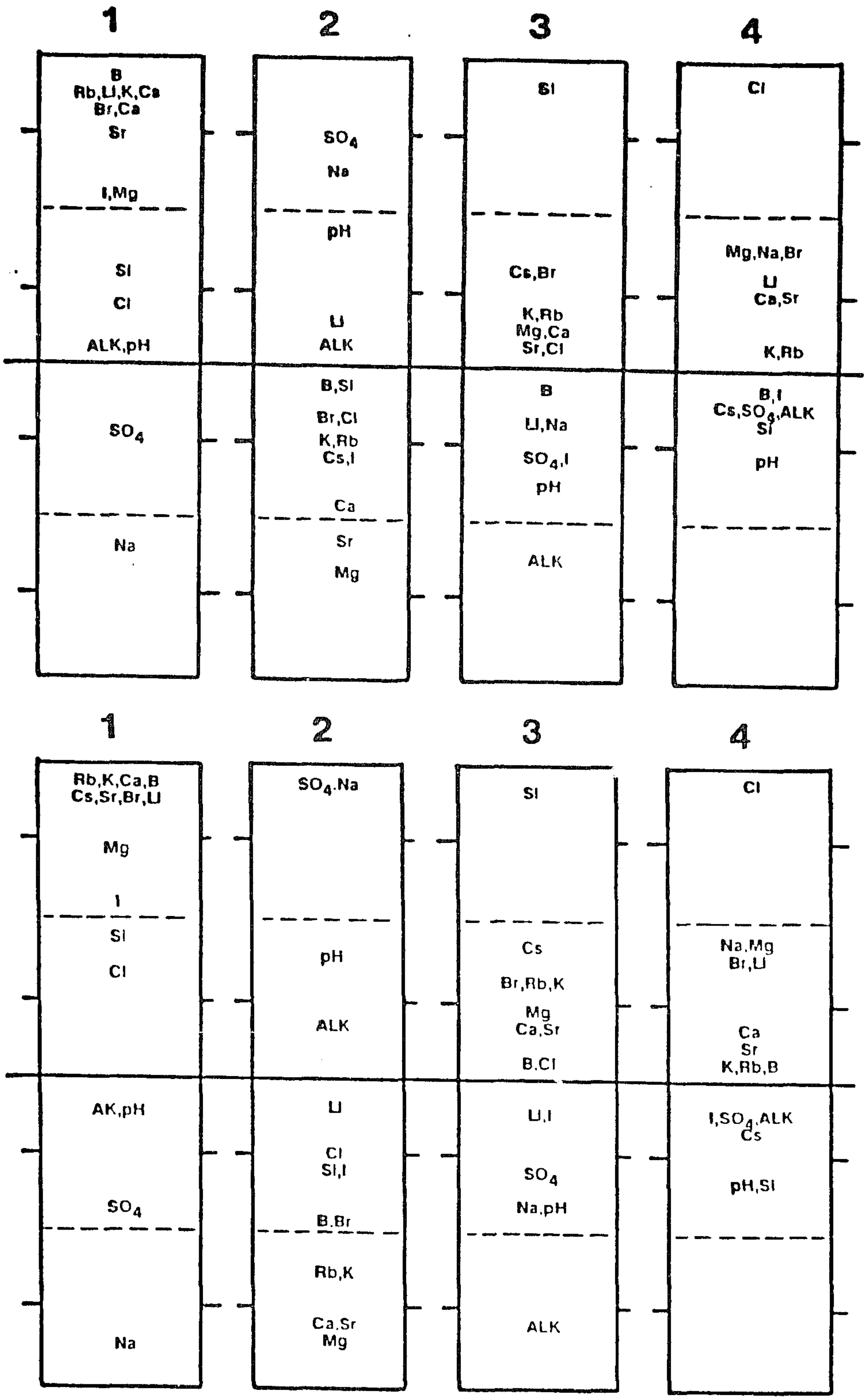
Figure A-8. R-mode factor analysis results, case 2. All samples are used, pH variable included, TDS partialled out.



CASE 2 - PRINCIPAL COMPONENTS

Figure A-8

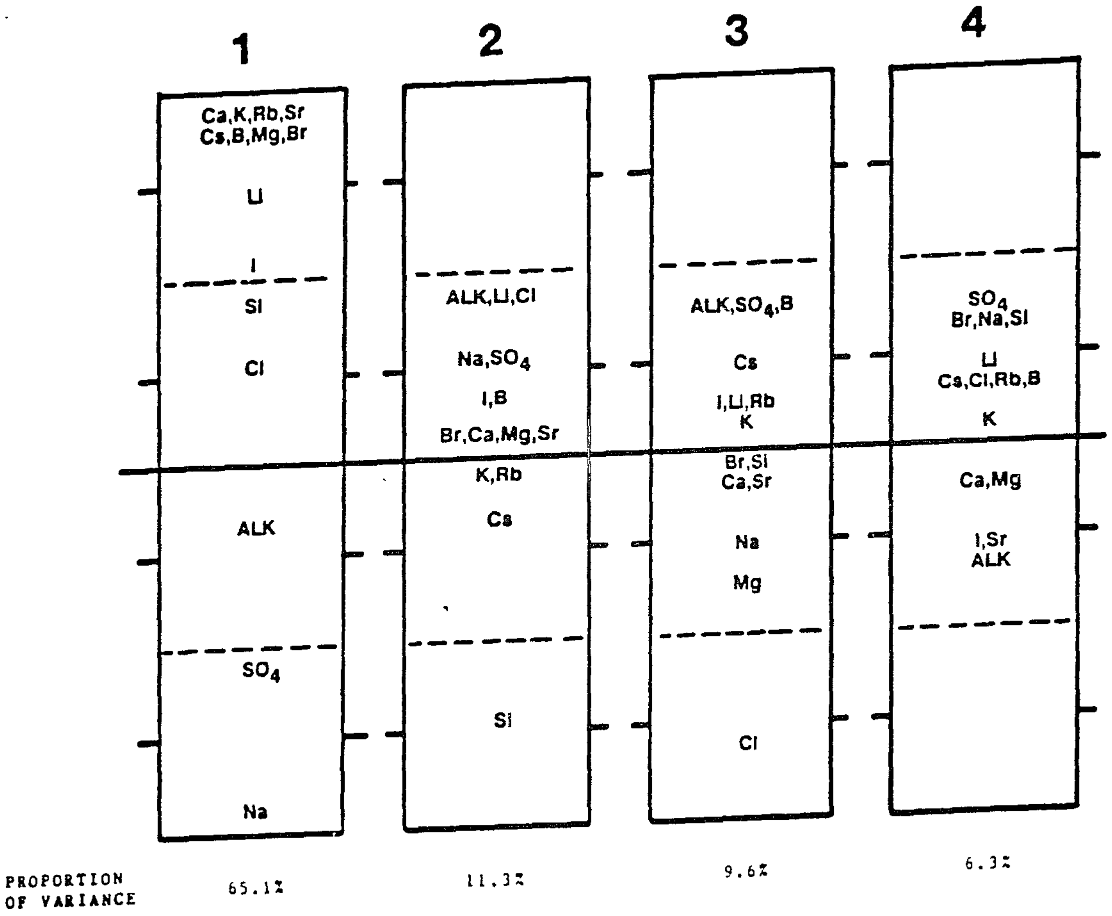
CASE 2 - VARIMAX ROTATION



CASE 2 - PROMAX ROTATION

Figure A-8

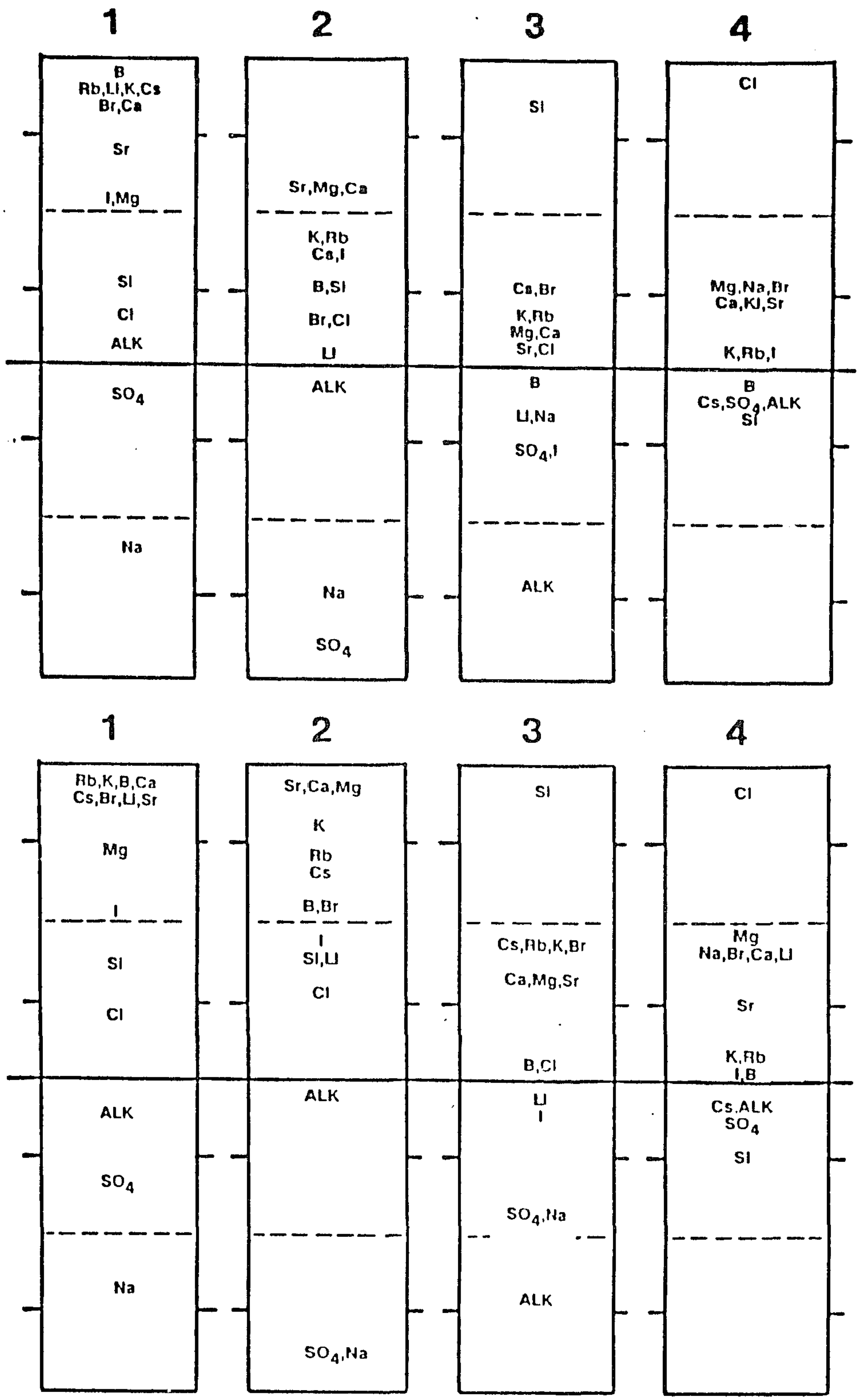
Figure A-9. R-mode factor analysis results, case 3. All samples are used, pH variable not included, TDS partialled out.



CASE 3 - PRINCIPAL COMPONENTS

Figure A-9

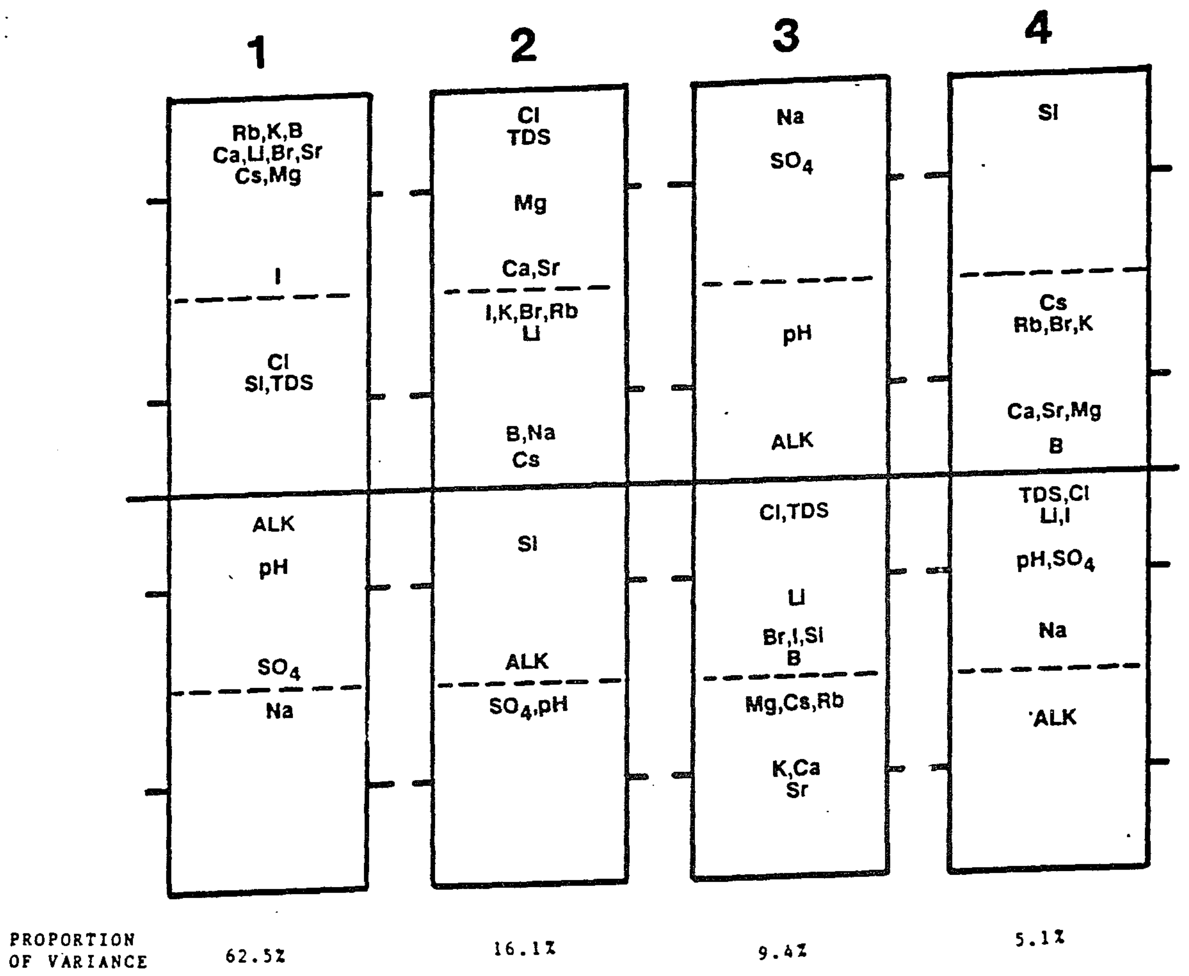
CASE 3 - VARIMAX ROTATION



CASE 3 - PROMAX ROTATION

Figure A-9

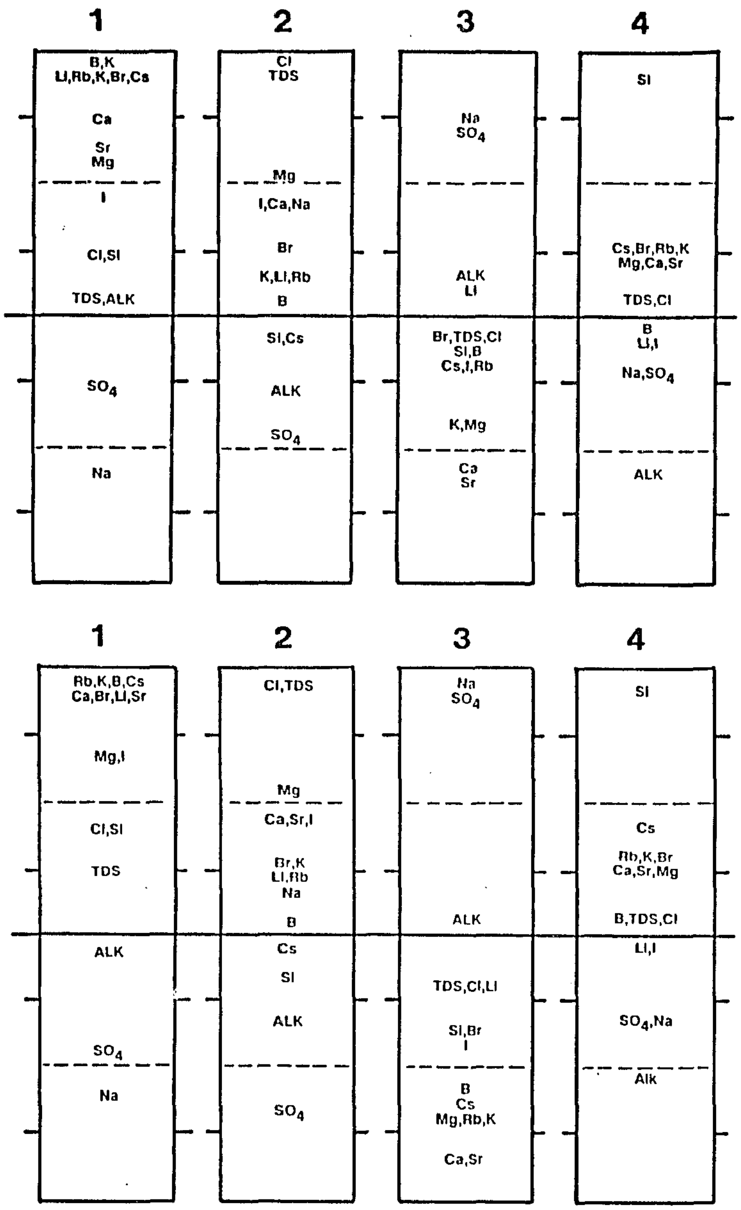
Figure A-10. R-mode factor analysis results, case 4. All samples are used, pH variable not included, TDS not partialled out.



CASE 4 - PRINCIPAL COMPONENTS

Figure A-10

CASE 4 - VARIMAX ROTATION



CASE 4 - PROMAX ROTATION

Figure A-10

EFFECT OF pH VARIABLE

Figures A-7 and A-10 shows the effect of including pH in the data set on factor makeup when TDS is partialled out. No significant changes in the makeup of the 4 factors occurs with the varimax rotation when pH is not included. Likewise, no significant changes are observed in the promax rotation, although slight changes in the loadings of Ca, Mg, and Sr in factor 2 occur when pH is removed. In both rotations, pH loads in the factors near ALK and SO_4.

Removing pH also does not change the results when TDS is partialled out (compare Figure A-7 and A-10). However, factor 2 is found to invert upon removal of pH, although the relative factor loadings of the variables remains constant. Also, including pH apparently reduces the loading of Ca, Mg, and Sr in factor 3, but the relative positioning of these elements remains constant. In sum, pH apparently does not significantly alter the factor makeup or relative factor loadings.

EFFECT OF PARTIALLING OUT SALINITY

As discussed above, variations in sample salinity may mask identification of other processes affecting the brine chemistry. In order to remove the influence, salinity (the TDS variable) is partialled out by using a partial correlation matrix in the R-mode calculations. It is important to determine the effect of salinity, for example, because most elements (except SO_4 and Na) increase with the brine salinity, and therefore, variables may intercorrelate with salinity in this respect. The R-mode analysis results preformed with and without TDS partialled out, are compared in Figures A-7 and A-10, and A-8 and A-9, respectively.

The most apparent change resulting from partially out of salinity is found in the relative makeup and importance of factors 2, 3, and 4:

Factor	1	2	3	4
% variance with TDS not partialled out	59.6	16.5	9.5	4.9
% variance with TDS partialled out	61.4	11.4	9.8	6.0

While the amount of variance explained by each factor does not dramatically change the partialling out of salinity affects the make-up of factors 2 to 4. In essence, the factors switch in their importance upon partially out of TDS. Factors that might represent water-rock interactions (factor 2 and 3) increase in their relative importance over a factor that might represent salinity (factor 4) .

EFFECT OF ROTATION METHOD

Both varimax and promax rotations were used in this study. Varimax is an orthogonal rotation, while promax is an oblique rotation method. In the varimax solution, factor axes are kept orthogonal during rotation until the best fit is obtained, maximizing the variance each factor explains

(Hitchon et al., 1971). Promax differs in that the axes are not constrained to be orthogonal. Comparing the results of the cases demonstrates that the rotation method chosen, for this example, generally does not alter the makeup of the factors. However, the variables appear to be better separated using the promax oblique rotation. A similar result was found by Long et al. (1986) and Hitchon et al. (1971).

A problem with oblique rotation methods is the possible correlation between factors, which by design, should be uncorrelated (Davis, 1986). When factors correlate, the relationships between the variables and the factors may be highly complex, and the true controlling processes may remain hidden. A correlation between the first and second factor occurred using the promax rotation ($r^2 = -.53$), regardless of the test case (if salinity was partialled out or if pH was included). The meaning of this correlation is not clear, but the observation that both orthogonal and oblique rotations produce nearly identical factors suggests that factor correlation does not effect factor makeup.

INTERPRETATION OF R-MODE RESULTS

The varimax and promax rotations with salinity partialled out and pH not included (case 2, Figure A-9) best illustrate the factor analysis results, although similar interpretations can be made from each case presented. Factor loadings between ±0.25 were not considered significant when making the interpretations.

Factor 1 is characterized by very high positive loadings on B, Rb, Li, K, Cs, Br, Ca, Sr, Mg, and I, and a highly negative loading of Na. It is interpreted as a common source factor, eg., a seawater source for the elements, especially for minor elements such as Rb and B. It is not clear why Na loads so strongly inverse to the other elements, but this may reflect the behavior of Na during seawater evaporation. Alternatively, the inverse relationship between Na and Cl in this factor may represent halite equilibrium.

This first factor is similar to the first factor of Hitchon et al. (1971) (Figure A-5), as both have high (+) loadings on minor elements, alkaline metals, and alkaline earth elements. The negative loading of Na in factor 1 with salinity partialled out is also similar to each study. Egleson and Querio (1969) interpreted the high loading of minor elements (B, K, Li, I, Br, and NH_3) in their first R-mode factor as showing a common mechanism affecting these elements.

Factor 2 is characterized by high (+) loadings on Sr, Mg, and Ca, intermediate (+) loadings on K, Rb, I, and Cs, and high negative loadings Na and SO_4. This factor is interpreted as representing a carbonate mineral factor, perhaps also indicating $CaSO_4$ mineral equilibrium. A characteristic of this factor, found in each of the different trials studied, is the strong co-loading of Na and SO_4. A possible explanation is that this loading represents the decrease in Na in evapo-concentrating seawater (due to halite precipitation) and the fact that more highly saline samples contain little or no SO_4. Other explanations that are possible include: (1) $CaSO_4$ and NaCl equilibrium, both common minerals in the basin, (2) $NaSO_4$ mineral dissolution, or (3) strong Na-SO_4 ion pairing suggested by Hitchon et al. (1971). $NaSO_4$ minerals have not been reported in basin, and the ion-pairing explanation is not supported by theoretical considerations. Pitzer (1973) reports that single ion electrolyte interaction parameters between Na and SO_4 are quite small, thus ion-pairing between these components is not expected to be significant.

Factor 3 is characterized by high (+) loading on a single ion, Si, intermediate (+) loadings on Cs, Rb, K, and Br, and a significant (-) loading on alkalinity. This factor might represent silicate-carbonate buffering or equilibrium, in essence, the balance between aluminosilicate and carbonate mineral reactions. Such a processes might represent the illite-carbonate reactions suggested by Carpenter (1978): $2K^+ + CaCO_3 + 3Al_2Si_2O_5(OH)_4 + 4SiO_2 = Ca^{2+} + 2KAl_2(AlSi_3)O_{10}(OH)_2 + H_2O + CO_2$ alkalinity). This is further supported by the positive loadings of K and Rb in this factor, particularly in the promax rotation.

Factor 4 is characterized by a single high positive loading on Cl, and intermediate (+) loadings on Na, Mg, Br, Li, Ca, and Sr, and no variable showing a strong negative loading. This is interpreted to be a salinity factor, or alternatively, because a similar factor is found when TDS is partialled out, it might represent that Cl is the dominant anion in the brine samples.

DISCUSSION

The R-mode results appear consistent with interpretations made using graphical and chemical modeling techniques in Chapter 1 and Chapter 2. Most important, factor analysis supports a seawater origin for the Michigan basin brine, as a common source is suggested for many of the elements, especially the minor elements. This is reasonable because once the minor elements, such as Br, B and Rb, are enriched by evaporation, very few reactions will significantly reduce their concentrations. Q-mode results suggest that this characteristic, and origin, is reflected throughout the entire Michigan basin sample population. Furthermore, the Student's t-test results suggesting differences between the upper Devonian formation waters (Berea, Traverse, and Dundee) and the Richfield-Detroit River-Niagara/Salina samples, might be in interpreted to represent the different degrees of evapo-concentration reached by these waters in the basin.

The importance of carbonate reactions (Chapter 1) may be supported by the combined loading of Ca-Mg-Sr in a single factor. The third factor which is interpreted to represent silicate-alkalinity buffering, although somewhat more tenuous, is also consistent with proposed reactions affecting K (Chapter 1).

One notable difference from previous studies is the lack of a halogen factor where Br,I, and Cl load together (Hitchon et al., 1971; Egleson and Querio, 1969; and Kramer, 1969). It is not apparent why this factor is not found, but it may reflect that the I enrichment occurs by processes not related to evapo-concentration, such as from organic matter decomposition (Egleson and Querio, 1969).

CONCLUSIONS

(1) Q-mode factor analysis demonstrates that the Michigan basin brine data are characteristic of a homogeneous population, described by a single factor interpreted as a salinity gradient. R-mode factor analysis of the entire data set is therefore, justified.

(2) R-mode factor analysis was run using varimax orthogonal and promax oblique rotation methods. Different trial cases to determine, for example, what the effect of including pH and the partialling out of salinity on the resulting factor makeup, was evaluated. In generally, similar interpretations can be made from all cases. Four factors were found to account for 90 to 92% of the variance in the data. Communalities were high (>.75) for most variables.

(3) The factors are interpreted as follows:

Factor 1: common source for most elements including minor elements, suggested to be a seawater source.

Factor 2: A carbonate-sulfate mineral factor.

Factor 3: Silicate-carbonate buffering or equilibrium.

Factor 4: A salinity or dominant anion (Cl) factor.

(4) The multivariate statistical methods support the interpretations made from graphical and chemical modeling results, and suggest a seawater origin modified by water-rock reactions.

APPENDIX B

APPENDIX B

METHODS

BRINE SAMPLING

The brine samples used in this study were collected directly from the well head whenever possible, although several Niagara/Salina samples were collected from distribution lines or the bottom of separator tanks. At each site, sampling valves at the well head were opened and the brine-hydrocarbon mixture was collected in a 5 gallon pre-rinsed, plastic carboy. The mixture was allowed to stand and separate for several minutes, after which clean brine was withdrawn through the bottom spigot. The brine was passed through glass-fiber wool, filtered through Watman #1 filter paper, and collected in a plastic beaker. Some samples would not separate in-field because of hydrocarbon viscosity and in these instances, the combined hydrocarbon-brine mix was collected in sealed plastic bottles and allowed to separate in the laboratory over several days to several weeks. The brine was withdrawn from the bottom of the bottle and filtered in the same manner as above. The following splits were taken from each sample:

1) 25ml were pipeted in to a capped widemouth plastic bottle for pH, Eh, and alkalinity analysis.

2) 125ml were carefully pipeted into plastic bottles containing 125ml of 5% HNO_3 acid for cation analysis.

3) 125ml were preserved with 1ml of reagent grade formaldehyde for SO_4 analysis.

4) 500ml were collected in boro-silicate glass bottles with teflon sealed caps for stable isotope analysis. Often it was necessary to open these bottles to release accumulating gas pressure.

5) 500ml were collected for Cl and strontium isotope analysis. If salt precipitation was expected, as was the case for Niagara/Salina brines, or if salt crystals were observed in the filtered brine, then this sample was replaced by diluting 125ml of brine with 125ml of double distilled H_2O.

The field dilutions were made using a single set of 100ml and 25ml Class A glass volumetric pipets. All samples collected for chemical analysis were stored in high density polyethelyne bottles. The samples were labeled and transported to the laboratory in a covered plastic pail that was iced on particularly warm days.

FIELD ANALYSIS

Field analysis consisted of measuring temperature, pH, Eh, and when possible, alkalinity. Temperature (^{o}C) was measured using a standard laboratory mercury thermometer. pH was measured using an Orion model 407 pH meter with an Orion 91-05 gel filled combination pH electrode. Standardization of the pH electrode was made using NBS reference standards of pH 4 and 7. Because well head temperature of the brine was normally between 9 to $10^{o}C$, the pH standards were chilled on ice during the summer field work. Electrodes were cleaned between use with Alconox detergent. An Orion model 96-78 combination platinum electrode was used for measuring Eh, which was normally done concurrent with pH. Alkalinity was measured following the procedure in Brown et al. (1970) by titrating 25.0ml samples with standardized H_2SO_4 acid delivered from a 50ml glass buret. The acid was standardized daily using a standardized HCO_3 solution.

DISCUSSION

There are several aspects that differ considerably between sampling brine and normal salinity groundwater. Most importantly is the potential change in pressure-temperature that occurs during brine production. Because brine in Michigan is produced from depths of several thousand feet of depth, brine undergoes considerable changes in temperature and pressure during production. These changes result in the exsolution of gases and in the precipitation of salts and paraffin in the well bore, a common problem faced during Michigan oil production. There is no method for surface sampling that will reduce these changes, short of using down-hole pressurized samplers. The chemical changes in brines that result from pressure-temperature changes are difficult to evaluate and are not well understood at this time.

Several aspects of the pH Eh, and alkalinity measurements also deserve some discussion, because these measurements involve the use of electrodes. Sources of error that become significant in using electrodes to measure high salinity waters include the changes in liquid junction potentials caused by the differences in salinity and composition of standards and samples, and the non-specificity of electrodes. Liquid junction potential errors could be minimized if standards had compositions that match the brines, which is not possible for highly saline brines such as the Michigan basin brines. For example, the $TRISH^+$ standards suggested by Millero (1979) for measuring seawater have a salinity some 9 to 10 times less than the average Michigan brines. The commercial standards used in this study were dilute solutions, therefore, liquid junction error may have been a significant error in this study. pH electrodes may also respond to monovalent ions such as Na and Li when present at high concentrations (Levine, 1978). Similar problems affect Eh measurements as well, with Eh electrodes responding to Fe or S species (Langmuir, 1971; Kharaka et al., 1980). Often the pH and Eh measurements were not stable over short and long periods of time, or could be arbitrary adjusted by slowly stirring the sample. Considering these problems, the pH and Eh measurements are probably not representative of true solution conditions, and the true pH-Eh values of the brines at subsurface conditions remain an unknown at this time.

It was also observed during the alkalinity titrations that the pH would not respond to the addition of acid, even upon the addition of very large amounts of acid. This was observed most often in the more highly concentrated Detroit River, Richfield, and Niagara/Salina formation samples. This pH response may be due, in part, to the electrode phenomenon described above, however, the alkalinity measurement may have been affected by dissolved organic acids present in the brine (Case, 1945; Willey et al., 1975). Attempts at measuring the dissolved organic acid content of these brines using liquid-ion-chromatography were not successful due to salinity interferences (B. Fischer, personal communication). However, evidence suggesting that dissolved organic acids might be present in the brines was found. For example, Figure B-1 shows alkalinity titrations preformed on Richfield and Niagara/Salina samples, and a titration of a typical carbonate buffered, non-saline groundwater sample. Assuming that the pH measurements are accurate in the brines, inflection points are observed for these brines near a pH of 3.5, not near the pH of 4.5 observed in the ground water sample. An inflection at this pH is thought to reflect the presence of acetate, a principal organic acid in brines (Willey et al., 1975).

ANALYTIC METHODS

Cations were measured using atomic adsorption and emission spectroscopy methods, on a Perkin-Elmer 506 A.A.S. instrument. Anion analysis was by titrimetric,

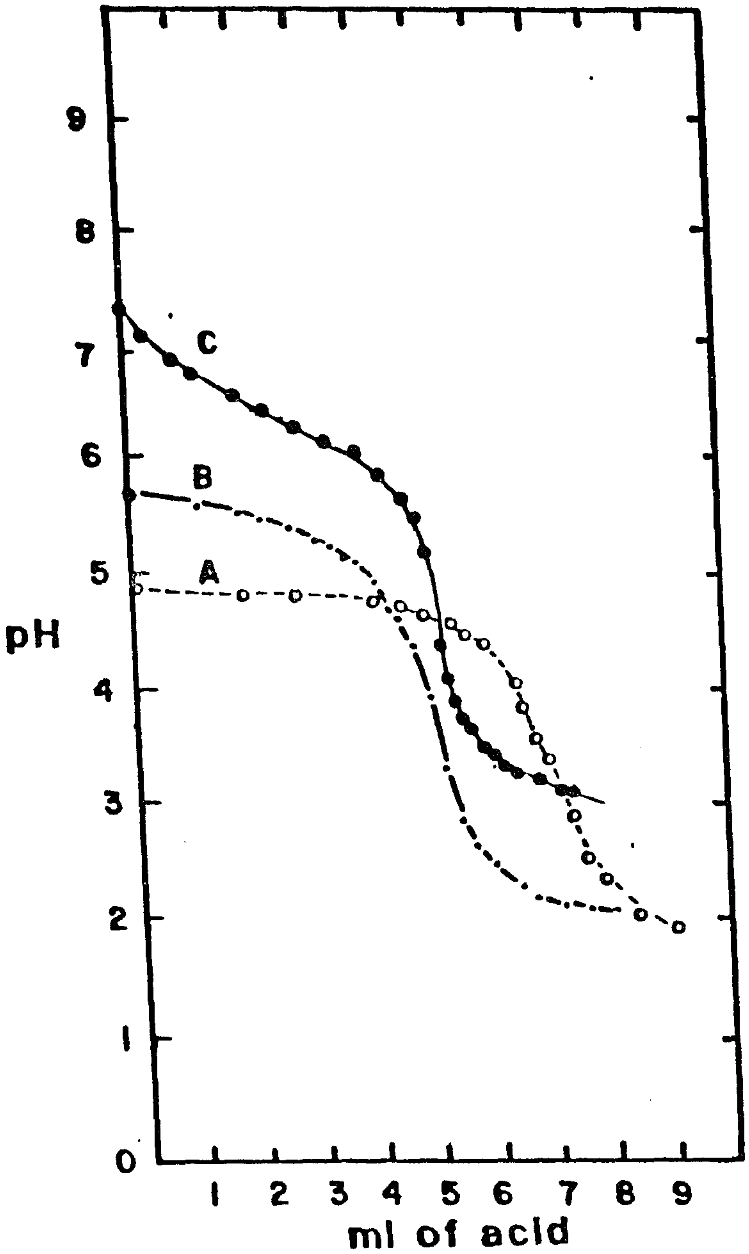


Figure B-1. Alkalinity titration curves, pH vs. volume of acid added (ml). Curve A, Richfield brine sample, curve B, a Niagara/Salina formation brine, curve C, a near-surface ground water from Michigan.

colorimetric, and gravimetric methods. Individual procedures and their references are listed in Table B-1, and selected methods are discussed in detail here.

Sample Preparation

Suitable working dilutions were prepared based on the concentrations of species of interest. For Ca, Mg, Sr, Na, and K analysis, a 1:2000 dilution was prepared by carefully pipeted 1ml of the 50% field dilution into a 1000ml volumetric flask, adding 1ml of concentrated HNO_3, and then bringing the volume up with de-ionized, distilled water. If field diluted samples were found to contain visible hydrocarbons, aliquots of non-diluted brine were withdrawn from the bottom of the sample bottles in the laboratory, filtered, and allowed to sit. This procedure was repeated until clean brine was obtained, which was then handled in a similar fashion to the samples described above. A single Class A pipet (1.0ml) and volumetric flask (1l) were used for all samples in order to minimize error between samples caused by glassware. Although such a large dilution introduces considerable error in the analysis (see discussion below), this dilution was necessary in order to bring concentrations within measurable ranges and to minimize matrix and other interferences in the A.A.S. analysis. All diluted samples were stored in pre-rinsed polyethylene plastic bottles. Similar procedures were followed for other dilutions in this study. Working standards for most components were prepared from commercial

TABLE B-1
Components measured and analytic methods.

COMPONENT	METHOD	DILUTION	REFERENCE
pH	electrometric	none	1
Ca, Mg, Sr	flame emmision w/1:10 of 87g/l $LaCl_2$	1:2000	1
Na,K	flame emmision w/1:10 of 25.4g/l NaCl or KCl	1:2000	1
Rb,Cs	flame emmision w/1:10 of 25.4g/l Na-K-Cl	1:26	1
Li	flame emmision w/1:10 of 25.4g/l Na-K-Cl	1:200	1
Cl	Mohr titration	none	1
Br	colorimetric	1:40	2
I	bromide oxidation	1:2	1
B	colorimetric w/carminic acid	1:10	1
Si	colorimetric following extraction	1:200	3
NH_4N	potentiometric titration	1:2	4
SO_4	gravimetric	none	5
Alkalinity	potentiometric titration	none	1
Density	pyconometer @25°C and by calculation $SPG = \log TDS * 7.102\mathrm{x}10^{-7} + 0.996$	none	5
TDS	calculation		

References:

1: Brown et al., (1979) *Methods for Determination of Inorganic Substances in Water and Fluvial Sediments*, U.S.G.S. Water Resources Investigation Book 5, Chapter A-1, Washington, D.C.

2: Presely, B.J. (1971), Part I: Determination of selected minor and major inorganic constituents, in: Ewing, J.I. and others, Initial Report of the Deep Sea Drilling Project, Volume VII, Part 2: Washington, D.C., U.S. Govt. Printing Office, p. 1749-1755.

3: Schrink, D.R., (1965) Determination of silica in sea water using solvent extraction, Anal. Chem., 37, 764-765.

4: Collins, A.G., Cassaggno, J.L., and Macy, V.W. (1969) Potentiometric determination of ammonium nitrogen in oil-field brines, Environmental Science and Technology, 3, 274-275.

5: A.P.I. (1968) *Recommended Practice for Analysis of Oil-field Waters*, American Petroleum Institute, Washington, D.C., 2nd edition, 58p..

1000mg/l stock standards. Stock standards of Rb, Cs, B, I, Br, and SO_4, were prepared from reagent grade salts that were oven-dried overnight and cooled in a desiccator before weighing. All standards were made in reagent grade Na-K-Cl solutions having Cl concentrations similar to the diluted sample.

Ca, Mg, and Sr

The alkaline earth elements were measured on a single aliquot of the 1:2000 dilution. In order to suppress ionization, 1ml of 87g/l $LaCl_2$ was added to each 10ml of sample and standard. Flame emission was used for the analysis, following Brown et al. (1970).

Na, and K

The alkali metals were also measured on the 1:2000 dilution. In order to reduce ionization effects, 1 ml of 25.4 g/l NaCl or KCl was added to each 10ml of sample and standard for K and Na analysis, respectively. A red filter was used for K analysis, and flame emission was used for analysis, following Brown et al. (1970).

Rb, Cs, and Li

These metals were particularly difficult to analyze due to their low concentrations compared with the alkali metals. For Rb and Cs, 3ml of the 50% field diluted sample were diluted with 10ml of distilled water, while Li was measured in a 1:100 dilution of the field diluted sample. Na-K-Cl was not added to these samples, but was added to the standards by adding 1 to 2ml of 25.4 g/l Na-K-Cl solution to each 10ml of standard. The Na-K-Cl solution was checked against distilled water and was found not to contain measurable Rb, Cs, or Li at the dilutions used. Analysis was by flame emission using a red filter, following Brown et al. (1970).

Silica

Silica was measured by the method in Schrink (1965) and Collins (1975). The method involves adding 1ml of a mixed ammonium molybdate sulfuric acid solution (100ml of 52g/l ammonium-molybdate mixed with 50ml of 1 molar H_2SO_4) to 50ml of 1:100 dilution of the field diluted sample. The mixture is stirred well and allowed to stand for 20 minutes. 15ml of 1:1 H_2SO_4 acid is then added and the mixture is cooled to room temperature for several minutes on ice. In a 100ml pre-rinsed separatory funnel (pre-rinse with ethyl-acetate and wash down with acetone) 10.0ml of ethyl-acetate is pipeted and the sample-reagent mixture is added. The funnel is shaken vigorously for 1 minute, and the mixture is allowed to separate for 1 minute or until all ester has separated. The aqueous phase is then discarded and the ester phase is collected in a cuvette and its absorbance measured at a wavelength of 335nm using a B&L Spec-20 spectrophotometer. Standards were prepared using 25.6 g/l (1ml/100ml) Na-K-Cl solution and treated in the same manner.

Boron

Boron was measured using the carmine method outlined by Lico et al. (1982). Stock B standard was first prepared using recrystallized $Na_2B_4O \cdot 10H_2O$ (place overnight in distilled water). 0.2ml of the 50% field dilution is mixed with 2ml of distilled H_2O and 2 drops of concentrated HCl, to which 10ml of concentrated H_2SO_4 was slowly added. The mixture is iced for 30 minutes to cool. Then 10ml of carmine solution (0.5g carmine dissolved in 1000ml of concentrated H_2SO_4) is added, mixed very well using a vibrating mixer, and allowed to stand for 1 hour mixing occasionally. The absorbance of blanks, standards, and the samples were measured at a wavelength of 600nm using a B&L Spec-20 spectrophotometer.

NH_4N

The NH_4N analysis followed an adaptation of the procedure in Collins (1975). 10.0ml of the 50% field dilution is pipeted into a 250ml flask, brought up to 100ml with distilled H_2O, and boiled on a hot plate for 5 minutes. The mixture is cooled on ice and the pH adjusted to 7.00 with 1N and 0.1N NaOH. 5.0ml of reagent grade 37 formaldehyde solution is then pipeted into the solution, mixed well, and the mixture heated to 40°C on a hot plate.

The mixture is quickly cooled to room temperature using ice-water bath, and titrated to pH 8.6 using 0.02N NaOH. A blank was carried along with each batch of samples.

Chloride

Chloride was measured on a 50ul non-diluted sample using the Mohr titration method (Brown et al., 1970). This method involved the addition of 50ml of distilled water to the sample, several drops of K_2CrO_4 reagent, and titration with standardize silver-nitrate solution. Standards were prepared from Na A.A.S standard that was check with NaCl salt standard.

Bromide

Bromide was measured using the procedure outlined by Presely (1971) as modified by Long and Gudramovics (1982). For this analysis, 50ul of acidified 50% field diluted sample was added to 950ul of distilled water. To this, 25ml of phenol red-acetate buffer (0.016g phenol red plus 2ml of .1N NaOH brought up to 100ml with distilled water, then mixed 1:4 with acetate buffer (18.1g anhydrous Na-Acetate, 7ml glacial acetic acid brought up to 1000ml with distilled H_2O)) and 4ml of Chloromine-T (.56g/l) are added using adjustable repipets. After mixing for exactly 30 seconds, 10ml of Na-thiosulfate is added (0.955g/1000ml anhydrous Na-thiosulfate), mixed, and the absorbance measured at 592nm using a B&L Spec-20 student grade spectrophotometer. Trials showed that HNO_3 did not affect the development of color, but the method is sensitive to the presence of iodine. However, the I concentration of these waters are generally less than 5% of the Br concentration, with in the estimated error of the analysis. Standards were made from reagent grade KBr, and along with a blank, were measured in an identical fashion.

Iodine

Iodine was measured using an adaptation of the method in Brown et al. (1970). Non-acidified sample was treated overnight with 1g of CaO to remove iron. The sample is filtered and 25.0ml are added to 75ml of distilled H_2O. The pH is adjusted to 6.2 with 1M H_2SO_4 and/or 0.1M NH_4OH. In an iodine flask, 15ml of 273g/l Na-acetate, 5ml of 2.2M glacial acetic acid, and 5ml of saturated Br_2 water are mixed, and the flask is stoppered for 5 minutes. Approximately 6ml of Na-formate solution (50g/100ml) is added until the yellow color disappears, the Br vapors in the flask are blown out with air, and the sides washed down with distilled H_2O. Then 1g of KI and 3ml of 3.6M H_2SO_4 are added, the solution is well stirred, tightly stoppered, and allowed to stand in the dark for 5 minutes. After 5 minutes, 1 to 2ml of starch indicator is added and the solution titrated with standardized 0.01N $Na_2S_2O_3$ until the endpoint is reached. A blank is carried through this procedure.

Sulfate

Sulfate was measured using the gravimetric procedure outlined in A.P.I (1968). 50ml of non-diluted sample were used, to which 50ml of distilled water were added, 1ml of concentrated HCl, and 10ml of BaCl solution (100g/l). The mixture is loosely covered and heated to 30°C for several hours, cooled and allowed to stand overnight. The mixture is washed through Watman #42 filter paper which is then dried for 1 hour at 30°C, placed in a pre-weighed ceramic crucible, and ashed at 850°C in a muffle furnace for 10 minutes. The crucibles were cooled in a desiccator and re-weighed. A blank and a series of standards were measured in a similar fashion, and a calibration curve was prepared. Two calibration curves were required, one below 25mg/l, and one for higher concentrations. The results reported in this study are calculated from the calibration curve.

TDS and Density

TDS values were calculated by summing measured components. This procedure was used because it was found very difficult to get repeatable weights by evaporation and weighing salts directly, most likely the result of the hydroscopic nature of the brine components. Density was determined on 25 samples by weighing in a pyconometer at 25°C. The pyconometer was warmed slightly to remove gas before cooling to 25°C in a water bath. Density was calculated for the remaining samples from the best-fit least squares line relating TDS to density: Density = log TDS * $7.102\text{x}10^{-7}$ + 0.996 (r^2 = 0.9) . Using this relationship, brine analyses obtained from other sources were put on the same density scale. Adjustment to formation temperature and pressure can be made using:

$p^* = p * \exp [B*(P-0.1) - A*(T-25)]$ where p* = density (kg/m3) at temperature T oC and pressure P (MPa), p = density at 25oC and 1 MPa, A = $5\text{x}10^{-4}$ oC^{-1}, B = $4.3\text{x}10^{-4}$ MPa^{-1}.

Oxygen and Hydrogen Isotopes

The oxygen ($^{18}O/^{16}O$) and hydrogen (D/H) stable isotopic ratios were measured at the Environmental Isotope Laboratory, University of Waterloo, Waterloo, Ontario. Several $^{18/16}O$ analyses were made at Teledyne Laboratory, (Princeton, New Jersey), and were checked with several replicate samples measured at Waterloo. Identical results within, analytic error and variance, were obtained from each laboratory. Oxygen isotope analysis utilized 72 hour equilibration with CO_2, and deuterium analysis used complete distillation techniques. All methods are discussed in detail in Fritz et al. (1986). Measured ratios are normalized to SMOW and have a precision of ± $2^{o}/oo$ for D and ± $0.2^{o}/oo$ for oxygen. However, repeat analysis of samples show larger ranges of measured values, up to $1.22^{o}/oo$ for ^{18}O and $3.9^{o}/oo$ for D:

TABLE B-2
Variability in $^{18}O/^{16}O$ and D/H

SAMPLE	$^{18}O/^{16}O$	D/H
3081	-6.19,-5.86	-52.7
3082	-3.50,-4.77	-46.5,-46.1
1085	-2.58,-2.16	-43.6
1086	-5.81,-5.02	-55.8
2092	-3.39	-48.2,-51.4
2097	0.45	-38.6,-41.4
2100	0.23,0.37	-40.8
8040	-2.90,-3.03	-46.5
3042	-2.03	-40.5,-37.9
2020	0.75	-37.4,-39.9
1004	-0.60,-0.80	-31.5
10043	-0.93,-1.17	-32.9,-29.0
3007	-4.51	-53.9,-50.1
3082	-3.50,-4.77	-46.5,-46.1
3086	-5.81,-5.02	-55.8

Deuterium values were corrected for activity following Sofer and Gat (1975):

$$\text{del } {}^{a}D = \text{del } {}^{c}D - [6.1M_{Ca} + 5.1M_{Mg} + 2.4M_{K} + 0.4M_{Na}]$$

and oxygen isotope activities were corrected to concentration using:

$$\text{del } {}^{c18}O = \text{del } {}^{a18}O - 1.11M_{Mg} + 0.47M_{Ca} - 0.16M_{K},$$ from Sofer and Gat (1972).

Strontium Isotopes

Strontium ($^{87}Sr/^{86}Sr$) isotopic ratios were measured using the procedures outlined by Stueber et al. (1984). Throughout this procedure, distilled HCl was used. 1ml of non-diluted sample is first loaded onto a large column containing 100ml of Dowex resin (8x-200). The Sr was then eluted from the column using <u>standardized</u> 2N distilled HCl. A calibration curve prepared for this column showed that Sr was separated from Ca and eluted after passing through 1150ml to 1400ml of acid. The column was standardized by eluting a Ca-Sr standard (having a similar absolute concentration to typical samples), collecting the eluent in 25ml sub-samples, and analyzed for Ca-Sr using A.A.S methods. The 1150-1400ml eluent volume was collected in a new, acid washed, scratch-free beaker, and slowly evaporated overnight on a slightly warm hot plate. The beaker was loosely covered and its sides were washed down periodically with HCl. The residue is then taken up in 5ml of 2N HCl, making certain to dissolve the residue completely, and loaded onto a small column of Dowex resin (8x-200, 50ml volume) along with 10ml of distilled H_2O. The Sr is eluted from this column using 450 to 600ml of standardized 2N HCl. The eluent is collected in an acid-washed, scratch free beaker, and a 5ml aliquot of the eluent is taken and analyzed for Sr and Ca. The remaining eluent was dried slowly on a hotplate overnight, periodically washing down the beaker sides with acid. Once dried and cooled, the residue is taken up in 10ml of 2N HCl and an aliquot containing 10-15ug of Sr is transferred, based on the measured Sr in the eluent, into a 10ml acid washed glass beaker, that is slowly evaporated on a hot plate, washing the beaker sides with HCl. The sample was covered with parafilm for transport to Argonne National Laboratory for $^{87}Sr/^{86}Sr$ analysis. Both columns are regenerated between samples with 50ml of concentrated distilled HCl washed through with at least 5 column volumes of distilled water. Each column is periodically back-flushed with deionized water after several samples. At the laboratory, the Sr residue is taken up in 50ul of distilled HCl and loaded onto the tungsten-rhenium filament and loaded into a VG-Isotopes Inc. MM54R 90° arc mass spectrometer for analysis. The instrument is calibrated to N.B.S. standard #987 having a $^{87}Sr/^{86}Sr$ of 0.710201 ± 0.040/mil

Subsurface Temperature and Pressure

Subsurface temperatures and pressures are very seldom measured in the Michigan basin, therefore, subsurface conditions were estimated using methods outlined in Vugranovich (1986). A geothermal gradient of 23°C/km is used in this study, starting at a temperature of 10°C at 33m. Geophysical logs were obtained for a number of the sampled wells and indicated approximate bottom-hole temperatures for a few locations. These temperatures are suspect however, as there are no means for determining from this data if the geophysical probe had equilibrated before temperature was recorded (Vugranovich, personal communications).

Variations in measured temperature, due either to non-equilibration or real variations in basin temperature gradients are illustrated by Figure B-2. This figure shows formation temperatures that Vugranovich (1986) thought to be reliable, and are plotted versus production depth. As this figure shows, measured temperatures vary considerably around the assumed geothermal gradient.

Subsurface pressures in the basin are thought to be hydrostatic (Wilson and Long, 1985; Vugranovich, 1986). Changes in subsurface pressures are therefore, dependent upon brine salinity as a function of formation depth in the basin. The characteristic of the basin shape, the individual formation brine compositions, and location of production within unique areas of the basin result in a poor correlation between salinity, brine density, and production elevation or depth. The least squares best-fit line relating brine density to production elevation is: density = 1.171 $-4.264\mathrm{x}10^{-4}$ * (production elevation in meters). The poor correlation ($r^2 = -0.367$) of this line suggests that predicting pressure versus depth in the basin based on brine salinity or density would not provide useful information.

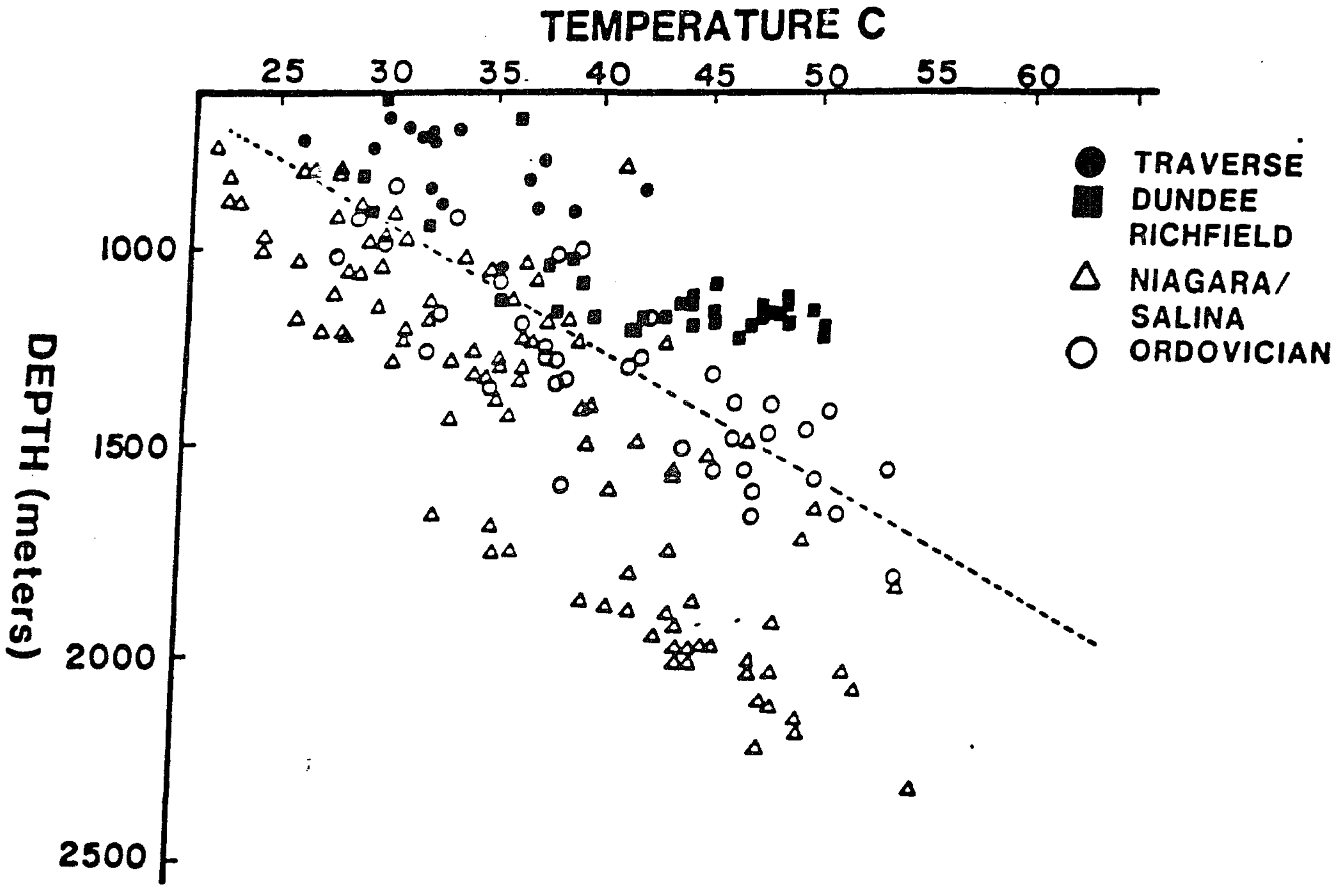


Figure B-2 . Formation temperature vs. production elevation (meters). Also shown is a geothermal gradient of 23°C/km, starting at 10°C at 33m. Data from Vugranovich (1986).

ANALYTIC ERRORS-CHARGE BALANCE

One method available for determining the reliability of chemical water analyses is the calculation of charge balances. In this study, charge balances were calculated as: (CATIONS-ANIONS)*100/(CATIONS+ANIONS), where CATIONS and ANIONS represent the sum of cation and anion equivalences, respectively. Most charge balances were found to be under 5% error. It should be realized that charge balances for highly saline formation waters can be misleading and do not represent the same degree of reliability as for normal salinity waters. This is the result of two phenomenon. First, charge balance calculations include the error associated with determining several cations, offset by a single anion. For example, the dominant anion in these brines is Cl, balanced by Ca, Na, Mg, K, and Sr. Because analytic errors are additive, these calculations really represent the sum of cations and their associated error offset by the concentration and error in Cl. The combined error in the cations may be quite large, however, and may account for some of the charge imbalance. Secondly, charge balance error normally considered acceptable for normal salinity waters, 5% for example, can represent a very large error in a single or in several components at the high salinities of these waters. For example, a +5% error in charge in a typical Michigan basin water with 350,000 mg/l TDS, can represent an error in measurement of about 21,000mg/l SO_4.

ERROR ESTIMATE

An important part of any chemical analysis is an estimation of analytic precision and accuracy. This is particularly important in studying highly concentrated brines requiring large dilutions for analysis. Error in this study results from non-determinate sources, and can be estimated or calculated using propagation of error methods. Precision of the different component analyses was determined by measuring ten replications of a single sample (#2078), and is listed by component in Table B-3 Generally, the analytic precision, as represented by 1 standard deviation of the analysis mean, and compared by the coefficient of variation (SD*100/MEAN) is less than 5% of the measured concentrations. It should be noted that these precision values do not reflect human error in the field dilution of the brines. Also listed in this table are the estimated accuracy in the analyses.

The propagation of error method can be used to estimate the minimum error (maximum accuracy) in the analytic methods employed in this study (see below). The calculated errors were generally less than 5% of the measured concentrations (except for SO_4). However, other considerations must be taken into account. For example, it was the authors experience that the brines were difficult to work with both in the field and laboratory, due to their high salinities, viscosity, and presence of large amounts of species such as iron which are known to interfere with many of the analytic

TABLE B-3
ANALYTIC PRECISION AND SAMPLE COMPARISONS

Zimmerman #19-A
#2078
Niagara/Salina

	Mean mg/l	Stnd. Dev.	Coeff. of variance
* Ca	109160	1160	1.06
* Mg	11000	152	1.38
* Na	27760	135	0.48
* K	24100	260	1.08
* Sr	3586	24	0.67
* Cl	274750	4250	1.60
* Br	3010	80	2.66
HCO3	10	-	-
SO4	22	-	-
* Rb	77.7	0.37	0.48
* Cs	14.3	0.43	3.00
Si	1.32	-	-

Charge
Balance 2.91%
* = average of 10 analyses, other species n=3.
- = Standard deviation out of range.
Coeff. of variance= Stnd. deviation *100/mean.

SAMPLE COMPARISION

	Wm. Schmidt B-1 #1024 Traverse brine This study	Wm. Schmidt B-1 M.D.N.R. Sample (1976)
Ca	30200	31500
Mg	5560	7460
Na	78100	81500
K	928	1760
Sr	1140	1210
Cl	194000	182000
Br	1280	1260
HCO3	5.4	NA
SO4	106	NA
Cs	2.2	2.36
I	12	5
Li	32	33
Rb	3.3	NA
Si	4.28	NA
NH4	106	NA
SPG	1.2263	1.225
Charge balance	-0.73%	+5.97%

methods used. Considering this, the accuracy of the analysis were estimated (Table B-1) to be 10% of the measured concentrations. For some components such as SO_4, alkalinity, and B, error cannot be predicted and is estimated to be much higher (A.P.I, 1968).

Maximum accuracy of the analyses were computed by error propagation methods. Two typical examples are presented here. Propagation of error for procedures following $X=A^aB^bC^c...$ is: $S_X/X = [(S_A/A)^2 + (S_B/B)^2 + (S_C/C)^2 + ...]$, $(a,b,c = -1,0,1)$ when the procedure follows $X=A+B+C$, the error is calculated as: $S^2{}_X = S^2{}_A + S^2{}_B + S^2{}_C$, and when the procedure follows $F = Ax \pm By \pm Cz$, the error is calculated as: $S^2(X) = A^2S^2(x) \pm B^2S^2(y) \pm C^2S^2(z)$. For all cases, S_X, S_A, S_B, and S_C are the variances in the unknown or calculated value (X), and measured values A, B, and C, respectively. Table B- 4 lists the glassware tolerances for the pipets, volumetric, standards, and the balance used in this work.

Example 1) Error in Ca (40,000 mg/l) analysis.

This error is typical of all A.A.S analysis made in this study, and includes error in field dilution, lab dilutions, and in the measurement. Field dilution consisted of making a 50% dilution by adding 125ml of sample to 125ml of acidified water (termed the dilution factor, df=2). This results in the following error: $S_X = [0.08^2 + 0.03^2 + 0.08^2 + 0.03^2]^{1/2} = 0.12$ml, where glassware tolerances from Table B-2 are used as the variance. A 1:1000 dilution of the

TABLE B-4
GLASSWARE TOLERANCES

Class A pipets

Volume ml	Accuracy ml
1	0.006
5	0.01
10	0.02
20	0.03
25	0.03
50	0.05
100	0.08

Volumetrics

Volume ml	Tolerance ml
50	0.05
100	0.08
200	0.10
250	0.12
500	0.20
1000	0.30

Eppendorf pipets

Volume ul	Accuracy ul	Precision ul
10	0.06	0.04
50	0.30	0.10
100	0.60	0.20
200	1.20	0.40
250	1.50	0.50
500	3.00	1.00
1000	6.00	2.00

field dilution is next prepared in the lab, (1ml of field dilution brought up to 1000ml). The error in this mixture is calculated as: $[0.002^2 + 0.30^2]^{1/2} = 0.30$ml, bringing the total error at this point to $[0.12^2\text{ml} + 0.30^2\text{ml}]^{1/2}=0.32$ml. 10ml of the sample (and standards) were added to 1ml of $LaCl_2$ before analysis, with an error to $.02^2 + .002^2 = .02$ ml. The final sample volume error is calculated to be 0.32ml.

The next error to consider is in the concentration of the standards. Stock standards have a concentration of 1000mg/l+10%. Preparing 100ml of 20mg/l standard results in an error of $S_x = 10* [(10/1000)^2 + (0.006/1)^2 + (0.006/1)^2 + (0.08/100)^2]^{1/2} = 0.014 = 0.14$ mg/l. Instrument error was estimated by repeated measurements of standards, and was found to be approximately 5% of the measured concentration, or in this example 0.5mg/l. The resulting error in measuring a 20mg/l concentration is calculated to be $[0.15^2 + 0.5^2]^{1/2} = 0.52$mg/l.

With these calculated errors, the error in measuring a brine having 40,000 mg/l of Ca is:

$N_1 = N_2V_2*df / V_1 = 20*1000*2/1 = 40{,}000$mg/l

$S_{n1}/N_1 = [(S_{N2}/N_2)^2 + (S_{v2}/V_2)^2 + (S_{v1}/V_1)^2]^{1/2}$

$S_{n1} = N_1* [(0.52/20)^2 + (0.32/2000)^2 + (0.006/1)^2]^{1/2}$

$=40{,}000 * 0.03$ mg/l, so $S_{N1} = 1200.$ mg/l, Example 2) Error in bromide measurement.

In this analysis the dilution factor is 40x, which results from adding 50ul of the 50% field diluted sample to 950ul of distilled water. The Br standard was prepared by weighing out 1.4943g (± 0.0005g) of oven dried KBr and dissolving in 1000ml (± 0.30ml) distilled H_2O. The calculated error in the stock standard is S_{Br} = 1000mg/l*[$(0.0005/1.4943)^2 + (0.30/1000)^2]^{1/2}$ = 0.45mg/l.

The standards were prepared by diluting this stock into 100ml of water. The error, for example, in a 30mg/l standard is:

N_1V_1/V_2 = 1000mg/l * 3ml / 100ml = 30mg/l

$S_{30} = 30*[\ (0.45/1000)^2 + 3*(.01/1)^2 + (0.08/100)^2]^{1/2}$

30*0.02 = 0.60 mg/l (0.001mg/ml)

(3-1ml aliquots of stock standard were used)

This error increases to 1.47 mg/l for a 60mg/l standard.

A typical standardization curve for Br is presented below:

mg Br	S_{Br} (mg)	%T	ABS	S_{ABS}
0		100	0	
0.03	0.001	54.0	0.270	0.004
0.04	0.001	42.5	0.375	0.005
0.05	0.001	33.0	0.480	0.006
0.06	0.0015	27.0	0.570	0.008

Repeated measurements of standards would typically vary by 0.5%T, which is converted to the variance in adsorbance (S_{ABS}, listed above) by $S_{ABS}/A = -S_T/(T \ln T)$, where T = decimal form of %T, ABS = absorbance, S_{abs} = variance in absorbance in %T.

For this typical standardization curve the best-fit line is calculated as Br (mg) = 0.0006 + ABS*0.1044 r^2=0.998. Graphical and numerical methods exist for calculating the variance in the Br content when the error in the best-fit line slope and intercept are considered. However, considering the high degree of fit in the standardization curve, the error in the measured absorbance is estimated by the best-fit line to the calculated error in the absorbances listed above:

S_{ABS}= 0.0001 + 0.0134*ABS r^2=0.987

The bromide analysis follows Beer's law up to a concentration of about 60mg/l (Long and Gudramovics, 1982), so that concentrations can be calculated from c=A/eb. The spectrophotometer cell used in this analysis is round and has a path length of 1.00cm ± 0.001. Neglecting the error in the molar absorbtivity (e) and the error in adding reagents, the error in measurement of a 50ul sample containing 1200mg/l Br (a typical Br concentration for Michigan brines equal to 0.06mg of Br) is: 0.06mg = 0.57/e*1.00

with a calculated error of:

$S_{Br} = 0.06 *[(0.008/0.57)^2 + (0.01/1.00)^2]^{1/2} = 0.001$ mg

Thus, the brine concentration and error is:

$(0.06)/(0.05) * 1000ml/l = 1200\ mg/l$

and:

$S_{Br} = 1200 * [(0.001/0.06)^2 + (0.003/0.05)^2]^{1/2} = 74.7mg/l$

or 6.2% error.

APPENDIX C

APPENDIX C

DATA

Key: ID: Identification number
GROUND ELEV.: Ground elevation in feet above sea level
PROD. ELEV.: Production elevation in feet above sea level
TWN: Tier number, + north, - south
RNG: Range number, + west, - east
DEPTH: Depth of well
TDS: Total dissolved solids, in mg/l
SPEC. GRAV: Specific gravity, estimated
TEMP: Estimated down hole temperature, °C
IMBALANCE: Charge balance error, in percent

Chemical data reported in mg/l.
^{18}O, D : del ^{18}O and del D values, in ^{o}/oo vs SMOW
^{87}Sr: ^{87}Sr/^{86}Sr ratio
MCl_2: $MCl_2 = Ca + Mg + Sr - SO_4 - 0.5HCO_3$ (in meq/l)

ID	GROUND ELEV. Ft.	PROD. ELEV. Ft.	TWN	RNG	SEC	FORMATION	DEPTH Ft.	TDS mg/l	SPEC. GRAV.	TEMP °C	SOURCE	IMBALANCE %
BEREA												
7001	643.0	-1778	14	-3	7	7	2421	328650	1.229	26.3	1	4.25
7005	650.0	-1811	15	-2	36	7	2461	284278	1.198	26.6	1	1.43
7006	661.7	-1739	14	-2	1	7	2550	335300	1.230	26.4	1	0.44
TRAVERSE												
1101	694.3	-644	1	13	10	1	1338	273504	1.190	18.7	2	6.21
1102	824.0	-960	3	11	8	1	1784	258184	1.179	21.8	2	3.12
1103	648.0	-823	4	14	34	1	1471	268000	1.186	19.6	2	0.88
1104	670.0	-850	4	15	2	1	1520	268468	1.186	20.0	2	4.99
1105	710.0	-1235	19	-4	21	1	1945	295324	1.206	22.9	2	5.10
1107	640.0	-1586	17	-4	18	1	2226	306690	1.214	24.9	2	5.95
1109	877.4	-1460	9	11	35	1	2337	326440	1.228	25.7	2	6.21
1110	647.3	-2478	15	1	13	1	3125	325110	1.227	31.2	2	6.48
1111	1175.1	-1428	24	5	16	1	2603	286836	1.199	27.5	2	5.51
1112	990.0	-2113	12	6	10	1	3103	315300	1.220	31.1	2	6.52
1113	913.0	-1874	12	10	1	1	2787	308690	1.215	28.8	2	3.66
1114	836.0	-1492	12	13	11	1	2328	278481	1.194	25.6	2	4.03
1115	1042.9	-1737	14	11	8	1	2780	303560	1.211	28.8	2	5.51
1116	835.0	-1265	14	14	5	1	2100	264686	1.184	24.0	2	4.90
1117	1230.0	-1880	18	9	6	1	3110	260692	1.181	31.1	2	3.70
1118	719.0	-1204	7	13	36	1	1923	272433	1.189	22.8	2	4.19
1119	751.3	-484	-1	14	17	1	1235	263852	1.183	18.0	2	-0.51
1008	972.2	-1888	16	10	27	1	2860	254280	1.176	29.3	1	1.22
1009	972.4	-1891	16	10	27	1	2863	249883	1.173	29.4	1	1.13
1011	993.4	-1885	16	10	28	1	2878	301253	1.210	29.5	1	0.59
1014	913.0	-1874	12	10	1	1	2787	316363	1.220	28.8	1	0.74
1017	1221.3	-1879	18	9	6	1	3100	235642	1.163	31.0	1	5.18
1028	718.2	-1296	19	-3	36	1	2014	299466	1.208	23.4	1	-1.13
1024	640.0	-1586	17	-4	18	1	2226	298312	1.208	24.9	1	2.46
1048	1142.0	-1822	22	4	17	1	2964	297052	1.207	30.1	1	0.82
1049	1222.0	-2268	19	10	36	1	3490	294026	1.205	33.8	1	3.78
1085	888.0	-1407	19	13	18	1	2295	282070	1.196	25.4	1	0.02
1068	631.2	-953	16	17	6	1	1584	215250	1.149	20.4	1	-3.16
DUNDEE												
3301	725.3	-2200	19	-3	26	3	2925	273921	1.190	29.8	2	6.22
3302	594.5	-2276	14	-4	2	3	2870	301830	1.210	29.4	2	6.57
3304	1104.0	-2792	19	6	33	3	3896	264050	1.183	36.6	2	3.32
3305	1136.0	-2640	20	6	12	3	3776	291750	1.203	35.8	2	0.71
3306	1132.0	-1778	27	1	28	3	2910	258517	1.179	29.7	2	3.26
3307	723.2	-2797	17	-2	18	3	3520	220063	1.152	34.0	2	6.08
3309	754.5	-2881	16	3	28	3	3635	300650	1.209	34.8	2	-2.92
3311	665.2	-3114	16	1	26	3	3779	348500	1.243	35.8	2	4.22
3312	1185.5	-263	22	6	26	3	381	287310	1.200	36.1	2	3.27
3313	796.0	-2382	10	5	3	3	3178	196796	1.136	31.6	2	2.62
3314	600.0	-1468	16	18	1	3	2068	252806	1.175	23.8	2	3.57
3315	840.3	-1645	21	-3	16	3	2485	271217	1.188	26.7	2	2.63
3002	703.4	-3347	17	-1	30	3	4050	296662	1.206	37.7	1	-1.95
3003	601.6	-2201	15	-4	30	3	2803	251291	1.174	28.9	1	0.70

DUNDEE (Contined)

ID	GROUND ELEV. Ft.	PROD. ELEV. Ft.	TWN	RNG	SEC	FORMATION	DEPTH Ft.	TDS mg/l	SPEC. GRAV.	TEMP °C	SOURCE	IMBALANCE %
3004	597.9	-2220	15	-4	26	3	2818	267592	1.186	29.1	1	0.773007
804.3	-1605	20	-4	3	3	2409	283407	1.197	26.2	1	3.99	
3012						3		298387	1.208		1	0.37
3015	976.5	-2567	13	9	36	3	3543	328379	1.229	34.1	1	1.50
3016	973.0	-2587	13	9	36	3	3560	328880	1.229	34.3	1	1.70
3022	600.0	-2122	14	-8	29	3	2722	286155	1.199	28.4	1	2.81
3029	746.0	-2835	18	1	14	3	3581	298884	1.208	34.4	1	-0.21
3033	787.6	-2768	15	4	2	3	3556	315206	1.220	34.2	1	2.69
3042	1183.0	-2728	21	7	22	3	3911	299414	1.208	36.7	1	2.74
3051	808.6	-1598	20	-4	10	3	2407	283464	1.197	26.2	1	4.13
3052	590.3	-2145	14	-4	12	3	2735	218059	1.151	28.5	1	-9.59
3070	1123.0	-3869	20	6	31	3	4992	298290	1.208	44.3	1	-2.83
3071	1109.0	-2629	20	6	29	3	3738	309790	1.216	35.5	1	-4.18
3027	736.4	-2790	18	1	23	3	3526	313898	1.219	34.0	1	4.94
3034	754.3	-2899	15	4	13	3	3653	301726	1.210	34.9	1	0.35
3025	787.5	-2094	19	-3	22	3	2881	277895	1.193	29.5	1	-0.77
3023	645.5	-2310	17	-4	18	3	2955	240643	1.167	30.0	1	-0.01
3047	1135.8	-2802	21	3	30	3	3938	276568	1.192	36.9	1	2.26
3039	1195.0	-2653	22	7	25	3	3848	269534	1.187	36.3	1	-2.34
3026	781.6	-2104	19	-3	15	3	2886	292162	1.203	29.5	1	0.32
3063	587.7	-2097	14	-8	29	3	2684	269155	1.187	28.1	1	3.50
3070	1123.0	-3869	20	6	31	3	4992	298290	1.208	44.3	1	-2.83
3087	692.3	-1550	17	16	26	3	2242	315100	1.220	25.0	1	0.59
3043			21	7	30	3		298021	1.207		1	0.33
3082	591.3	-1474	16	18	1	3	2065	261758	1.182	23.8	1	0.64
3086	700.0	-1549	17	16	25	3	2249	232360	1.161	25.1	1	-0.32
3081	643.7	-1462	16	17	8	3	2106	213550	1.147	24.1	1	0.67

RICHFIELD

ID	GROUND ELEV. Ft.	PROD. ELEV. Ft.	TWN	RNG	SEC	FORMATION	DEPTH Ft.	TDS mg/l	SPEC. GRAV.	TEMP °C	SOURCE	IMBALANCE %
4010	899.5	-2404	12	10	1	4	3303	326500	1.228	32.5	1	2.23
4013	911.1	-2421	12	10	1	4	3332	327135	1.228	32.7	1	0.51
4018	912.2	-2393	12	10	12	4	3305	146374	1.100	32.5	1	1.52
4035	1395.5	-2747	24	-2	33	4	4142	320218	1.223	38.3	1	0.55
4036	772.1	-3871	15	4	11	4	4643	125260	1.085	41.8	1	3.62
4037	786.5	-3993	16	4	35	4	4779	294832	1.205	42.8	1	1.97
4068	1135.8	-2802	20	6	30	4	3938	379680	1.265	36.9	1	-0.66
4069	1138.0	-3918	19	6	19	4	5056	386780	1.270	44.7	1	0.93
4046	1142.0	-3975	22	4	8	4	5117	334670	1.233	45.2	1	1.31
4050	1259.7	-3004	24	-1	26	4	4264	317460	1.221	39.2	1	5.04
4403	1111.8	-3840	20	5	8	4	4952	315240	1.220	44.0	2	7.40
4406	1010.0	-3037	22	-2	18	4	4047	395297	1.277	37.7	2	7.27
4407	1252.0	-2928	24	-1	14	4	4180	375940	1.263	38.6	2	5.58

DETROIT RIVER

ID	GROUND ELEV. Ft.	PROD. ELEV. Ft.	TWN	RNG	SEC	FORMATION	DEPTH Ft.	TDS mg/l	SPEC. GRAV.	TEMP °C	SOURCE	IMBALANCE %
5019	647.0	-3245	14	-8	36	5	3892	298670	1.208	36.6	1	5.84
5030	735.5	-3777	18	1	36	5	4512	421420	1.295	40.9	1	6.01

ID	GROUND ELEV. Ft.	PROD. ELEV. Ft.	TWN	RNG	SEC	FORMATION	DEPTH Ft.	TDS mg/1	SPEC. GRAV.	TEMP °C	SOURCE	IMBALANCE %
NIAGARA/SALINA												
2206	1233.0	-5229	29	4	32	2	6462	441270	1.309	54.6	2	5.78
2207	1255.0	-4297	30	2	5	2	5552	406980	1.285	48.2	2	2.91
2209	616.0	-1988	4	-15	32	2	2604	195724	1.135	27.6	2	6.91
2210	745.0	-2563	5	-15	5	2	3308	284420	1.198	32.5	2	5.99
2211	652.7	-2252	5	-15	24	2	2905	272320	1.189	29.7	2	2.39
2212	966.8	-2084	-1	-3	6	2	3051	326460	1.228	30.7	2	2.04
2213	848.0	-2323	3	11	17	2	3171	343114	1.239	31.5	2	4.26
2214	586.4	-1570	3	-16	10	2	2156	282530	1.196	24.4	2	7.47
2215	938.0	-3248	2	-1	12	2	4186	391890	1.274	38.6	2	5.45
2020	607.0	-6403	14	-8	31	2	7010	349730	1.244	58.4	1	4.95
2072	902.3	-3165	2	-3	35	2	4067	363330	1.254	37.8	1	-1.38
2077	915.0	-5275	26	10	28	2	6190	219944	1.152	52.7	1	4.85
2078	1067.0	-4843	25	11	9	2	5910	443700	1.311	50.7	1	4.73
2083	838.0	-3872	23	15	14	2	4710	349035	1.244	42.3	1	4.38
2084	762.0	-4474	23	14	10	2	5236	355080	1.248	46.0	1	4.02
2089	808.6	-4269	25	13	31	2	5078	407930	1.285	44.9	1	4.80
2090	849.5	-5497	26	10	10	2	6346	422130	1.296	53.8	1	4.70
2091	915.7	-5866	26	10	12	2	6782	280140	1.195	56.8	1	0.41
2092	808.1	-2923	33	-3	3	2	3731	343690	1.240	35.5	1	3.90
2093	812.0	-2854	33	-3	3	2	3666	399790	1.280	35.0	1	4.12
2100	964.0	-3140	2	-4	19	2	4104	393590	1.275	38.1	2	6.38
2101	970.0	-3094	2	-4	36	2	4064	392300	1.274	37.8	2	5.99
2097	925.0	-2256	-1	4	27	2	3181	365700	1.256	31.6	1	3.76
2096	930.2	-2257	-1	4	34	2	3187	350500	1.245	31.6	1	5.31
2099	917.0	-2727	1	-7	18	2	3644	370460	1.259	34.8	1	2.83
2098			2	-3	17	2		380126	1.266		1	6.08
TRENTON-BLACK RIVER												
6601	1086.2	-3289	-4	2	9	6	4375	229560	1.159	40.0	2	0.24
6602	949.5	-3761	-1	5	25	6	4710	273040	1.190	42.3	2	6.04
6603	1044.6	-3155	-3	4	36	6	4200	201140	1.139	38.7	2	3.13
6604	1177.0	-2885	-5	2	31	0	4062	210375	1.145	37.8	2	8.99
6605	1125.2	-2907	-5	3	25	6	4032	189679	1.131	37.6	2	1.84
6606	1149.0	-2921	-6	2	5	6	4070	170930	1.117	37.8	2	2.32
6073	1179.0	-2893	-5	2	32	6	4072	150672	1.103	37.8	1	2.93
6074	1133.0	-2891	-5	3	23	6	4024	213336	1.147	37.5	1	2.01
6075	1071.0	-2875	-5	3	3	6	3946	209660	1.145	37.0	1	2.83
6076	1071.0	-2875	-5	3	3	6	3946	209424	1.145	37.0	1	2.60
6095	1113.4	-3304	-4	2	18	6	4417	231572	1.160	40.3	1	0.00
6094	1085.1	-3260	-4	2	7	6	4345	226794	1.157	39.8	1	0.10
St. PETER												
8040	1196.0	-9390	22	7	36	8	10586	403770	1.283	83.5	1	0.01

ID	Ca	K	Li	Mg	Na	pH	Sr	Rb	Cs	Si
BEREA										
7001	49500	580	8	8790	66700	4.6	2140	3.4		4.0
7005	38400	700	8	7600	58200	5.1	1780	3.9		4.4
7006	48300	650	8	8400	64500	5.0	2080	3.5	2.9	1.4
TRAVERSE										
1101	23400	1440	12	6640	78600		710			
1102	20600	1220	9	7140	70200		734			
1103	17800	1330	12	5430	85200		650			
1104	21900	1620	18	5430	78400		470			
1105	20200	1480	27	7120	88700		940			
1107	31500	1760	33	7460	81500		1210			
1109	45400	2350	40	7830	73900		1540			
1110	67700	4750	81	9700	43700		2920			
1111	21200	1680	41	8320	82400		1330			
1112	44500	3130	46	8290	69400		1500			
1113	43500	3320	50	7430	64200		1690			
1114	28900	1630	35	6650	71300		960			
1115	38100	2050	40	8920	69700		1460			
1116	20000	1300	29	5840	78200		610			
1117	28000	2050	33	6930	63800		910			
1118	26700	1630	16	8450	68500		1160			
1119	23000	1520	18	6250	66800		577			
1008	40600	2330	38	6930	43720	5.3	1540	6.7		2.9
1009	39600	2310	38	6800	43000		1460	3.1		3.2
1011	49400	2930	48	8510	48500	4.8	1880	8.3		3.0
1014	41400	2410	48	6720	67000	4.9	1620	6.8		2.1
1017	21400	1160	30	4400	67100	5.9	800	3.3		2.9
1028	20400	480	18	4800	78000	5.4	900	2.2		1.4
1024	30200	930	32	5560	78100	4.5	1140	3.3		4.3
1048	34600	1920	40	5540	70200	5.8	1250	17.2		
1049	35600	1620	24	6300	73500		980			
1085	23100	1260	34	5870	75000	5.4	940	1.7	2.9	5.2
1088	11600	440	19	3840	62300	5.8	350	0.4		4.0
DUNDEE										
3301	20500	1980	20	7310	80600		675		0.2	
3302	35000	2950	33	7040	76300		1290		0.6	
3304	31000	2690	32	6350	61800		1020		0.6	
3305	33700	3350	41	5950	66300		1230		0.2	
3306	7390	1100	10	2640	92900		170		0.3	
3307	22100	1880	17	7010	56500		760		0.2	
3309	38500	4380	41	6530	57600		1180		0.3	
3311	73300	8360	68	11300	38800		2350		1.4	
3312	32100	2360	41	8330	67000		1200		0.2	
3313	26700	2180	27	5030	41000		910		0.5	
3314	20500	1220	29	4340	73600		470		0.2	
3315	17200	1930	22	5030	82000		460		0.4	
3002	25600	1880	36	4720	76600	4.8	780	5.2	2.5	1.8
3003	25600	980	14	5000	62500	5.3	946	3.6	2.4	2.1

ID	Ca	K	Li	Mg	Na	pH	Sr	Rb	Cs	Si
DUNDEE (Continued)										
3004	14400	380	6	4200	83500	4.5	420	1.8	1.3	2.4
3007	19800	1014	26	4020	87900	4.6	600	2.9	1.6	2.0
3012	33600	2150	40	6140	69300	5.2	1180	6.0	2.8	2.5
3015	51000	4040	54	7040	60500	5.2	1740	10.2	4.3	1.5
3016	51800	4160	52	6880	60400	5.0	1720	11.1	4.4	2.3
3022	21400	600	10	6810	81600	3.5	730	2.6	1.6	2.1
3029	28000	1880	52	5460	75300	5.3	2000	5.4	2.9	2.0
3033	36400	3010	44	5790	76100	5.5	1340	8.1	3.1	3.3
3042	26000	1870	33	5070	83500	5.2	780	5.2	2.3	1.2
3051	21800	1220	24	4000	86100		440	3.4	1.8	8.1
3052	11000	800	2	3000	68000	5.3	280	0.4	1.0	4.3
3070	29900	1680	18	5220	70400	4.8	1170	2.5	0.9	3.3
3071	25600	1120	18	5660	77200	4.3	1020	2.4	1.0	11.6
3027	25400	1910	32	4660	94200	5.2	740	5.3	2.1	1.9
3034	44900	2820	44	7200	55800	4.1	1340	7.7	3.1	2.1
3025	15900	1120	24	3540	84400	4.7	460	3.3	1.6	1.7
3023	23000	920	24	4420	61300	5.9	750	2.9	1.7	1.2
3047	29600	3224	38	4900	68800	4.8	850	2.9	1.1	3.7
3039	32000	2540	44	5080	68400	5.3	1020	7.1	2.8	2.6
3026	21700	1120	22	4000	92400	4.8	480	3.0	1.6	1.4
3063	16000	520	2	5320	81100	5.1	580	1.7	1.4	2.5
3070	29900	1680	18	5220	70400	5.6	1170	2.5	0.9	3.3
3087	10300	1220	29	1820	103000	3.9	340	1.5		3.3
3043	33100	1650	41	6060	69900	5.1	1620	4.9		1.2
3082	20900	900	33	4110	73600	6.2	560	0.9	2.3	3.7
3086	19800	960	27	3860	62400	6.0	580	1.0	2.3	4.2
3081	12500	640	20	3750	64700		340	0.6	1.6	3.3
RICHFIELD										
4010	53000	4070	54	7180	58600	5.1	1720	10.4	3.9	
4013	51800	4020	54	6960	57800	5.0	1640	10.9	3.9	1.6
4018	50500	3570	50	7090	61500	5.0	1640	9.2	3.6	2.1
4035	61400	8320	42	8830	38400	4.2	2130	23.8	5.5	2.3
4036	27800	3800	24	3370	12400	5.9	1040	8.9	8.9	8.5
4037	65100	7700	32	7700	28600	4.6	2580	21.7	5.5	3.2
4068	82100	8660	44	9740	34500	4.7	3480	10.5	2.2	2.9
4069	86100	8700	46	10700	34100	4.3	3980	11.0	2.2	2.4
4046	77600	9300	76	10700	31300	3.7	2800	23.4	6.4	1.4
4050	69600	9020	40	9840	33000		2300	6.5	8.8	0.9
4403	73800	9110	65	9700	31000		2940			
4406	96200	12800	47	14600	32200		290			
4407	92000	13300	54	12600	25600		3390			
DETROIT RIVER										
5019	72400	9270	72	10400	22200	4.9	2340	33.8	6.4	1.6
5030	107000	19300	120	13300	24000	3.9	3070	41.2		2.3

ID	Ca	K	Li	Mg	Na	pH	Sr	Rb	Cs	Si
NIAGARA/SALINA										
2205	35400	9560	18	6970	8010		1960			
2206	124000	22600	61	12800	9820		6030			
2207	102000	21200	85	12600	16100		4010			
2208	40500	2110	17	14000	34300		650			
2209	35200	2300	18	6230	33500		800			
2210	55900	4070	39	7800	43100		1330			
2211	49900	3320	29	8350	39400		1120			
2212	65100	6470	50	10300	38300		1860			
2213	65100	9340	55	15100	40300		1630			
2214	48000	4460	36	11300	47800		910			
2215	85400	11800	83	14300	38300		2870			
2020	65200	11200	60	10400	48800	4.3	1790	23.4	5.3	6.3
2072	73400	8070	56	15500	28400	5.0	2230	14.3		0.9
2077	60000	9500	34	6080	23000		1800	27.7		3.5
2078	109200	24100	70	11000	27800	4.8	3590	77.7		1.3
2083	61100	11400	68	7700	27600		2040	35.2		2.5
2084	80300	19200	64	11300	23600		3460	49.5		1.4
2089	99100	19000	93	11600	26200		3440	60.5		3.1
2090	106000	21200	74	12600	21200	4.5	4330	71.1		2.3
2091	67700	14200	45	8670	21000	5.0	2750	48.5		4.0
2092	72900	5890	82	14600	38000	5.1	1800	10.7		2.3
2093	89800	6700	101	17500	34000	4.8	2140	12.3		1.3
2100	86500	8800	74	20000	33600	4.7	2580	16.1		
2101	86700	7920	68	19300	33900	4.7	2500	13.0		1.1
2097	76600	7320	69	10700	43400	5.1	1980	13.1		1.5
2096	74200	6960	67	10300	43400	3.5	1940	13.2		1.9
2099	77000	8610	89	10700	42200	5.0	1840	14.2		3.1
2098	79600	8780	74	16700	40200		2290	17.9		3.1
TRENTON-BLACK RIVER										
6601	25600	5440	42	6150	48400		840			
6602	35500	3960	47	9110	59000		1040			
6603	23200	4360	36	6020	43800		740			
6604	23100	3820	37	5300	55500		680			
6605	19200	4010	33	5360	43600		640			
6606	17400	3490	29	4780	39900		600			
6073	15800	2180	26	3200	37200		540	4.5		0.7
6074	23400	3200	40	4700	50200	5.4	760	7.4		5.7
6075	23000	3220	40	4800	49800	5.4	760	7.4		3.8
6076	22800	3220	40	4600	50000	5.4	760	7.4		3.5
6095	25800	4300	43	4750	51600	5.8	870	11.3		5.7
6094	24600	4120	43	4740	51300	6.1	870	11.4		4.4
St. PETER										
8040	90100	19500	44	9710	28200	3.8	3160	58.1	11.9	19.9

ID	Br	Cl	ALK as HCO$_3$	I	SO$_4$	B	N^{18}O ^{o}/oo	ND ^{o}/oo	^{87}Sr	NH$_4$N	N^{a}D ^{o}/oo	MCl$_2$ meq/l
BEREA												
7001	940	200000	25	28	100		1.10	-10.70	0.70915	50	1.04	3240.4
7005	1600	176000	25	25	85		0.29	-24.10	0.70909	64	-14.80	2580.6
7006	1840	209000	10	17	11					126		3148.7
TRAVERSE												
1101	710	162000	13	4	22							1729.9
1102	2290	156000	2	24	110							1630.0
1103	590	177000	16	4	31							1349.4
1104	650	160000	32	6	215							1546.2
1105	880	176000	1	9	17							1615.0
1107	1260	182000	2	5	85							2211.6
1109	1420	194000	7	10	100							2942.9
1110	2340	194000	2	28	30							4242.5
1111	910	171000	73	5	2							1773.5
1112	1480	187000	20	12	160							2933.8
1113	1550	187000	27	18	60							2819.6
1114	1040	168000	68	7	73							2010.3
1115	1330	182000	1	11	80							2666.9
1116	730	158000	24	6	9							1492.5
1117	1000	158000	44	10	70							1987.1
1118	990	165000	7	5	5							2054.1
1119	710	165000	33	4	155							1672.2
1008	1560	158000	38	18	208	22				193		2627.3
1009	1510	155000	36	20	297	24				180		2563.1
1011	1930	188000	31	25	86	68	-0.57	-23.80		121	-12.43	3206.7
1014	1510	196000	11	18	59	27	-0.70	-31.50		146	-21.52	2654.7
1017	880	140000	59	12	109	18	-3.60	-40.00		83	-34.16	1446.4
1028	890	175000	3	12	67		-0.49	-32.50	0.70940	76	-26.45	1432.1
1024	1260	182000	5	12	106		0.56	-29.10	0.70909	106	-21.21	1988.4
1048	1247	184600	18	10	162	117						2207.7
1049	1050	182000	18	12	150							2314.3
1085	900	175000	61	71	28		-1.83	-43.60	0.70845	174	-36.89	1657.1
1088	720	136000	156	10	607		-7.06	-61.20		76	-57.26	891.5
DUNDEE												
3016	1920	202000	59	20	103	84	1.31	-35.50	0.70813	216	-23.69	3188.6
3301	860	162000	63	6	317							1633.8
3302	1250	178000	59	5	150							2352.6
3304	1190	160000	43	10	410							2084.5
3305	1220	180000	63	12	122							2197.3
3306	315	154000	2	5	810							573.0
3307	820	131000	52	4	676							1683.3
3309	1460	191000	39	12	140							2482.8
3311	2390	212000	139	26	40							4641.5
3312	1320	175000	49	11	33							2314.4
3313	980	120000	71	8	1130							1744.1
3314	680	152000	54	3	364							1383.7
3315	590	164000	9	7	660							1269.0
3002	1180	186000	26	15	141	39	0.20	-30.80		119	-23.84	1680.9
3003	1070	155000	23	18	295	11	-2.38	-28.10		29	-21.50	1704.5

ID	Br	Cl	ALK as HCO_3	I	SO_4	B	$N^{18}O$ $^{o}/oo$	ND $^{o}/oo$	^{87}Sr	NH_4N	$N^{a}D$ $^{o}/oo$	MCl_2 meq/l
DUNDEE (continued)												
3004	690	164000	20	13	382	1	-3.02	-28.60		64	-23.65	1066.0
3007	750	169000	64	28	319	20	-4.51	-52.00			-46.04	1326.4
3012	1420	185000	28	13	112	52	-0.40	-34.20		228	-25.69	2206.7
3015	1860	202000	51	19	109	80				200		3162.1
3022	1020	174000	37	8	166	2				45		1641.8
3029	1240	185000	43	19	139	19	0.43	-26.10		162	-18.58	1889.6
3033	1570	191000	27	17	160	31	-0.53	-30.80		185	-21.66	2320.3
3042	1140	181000	11	13	137	8	-2.03	-39.20	0.70831	107	-31.95	1729.7
3043	1090	185000	35	14	94	8	-1.05	-30.95		174	-22.56	2185.7
3051	1500	169000	10	20	200	38			0.70838			1422.9
3052	480	162000	17	21	314		-6.11	-47.60			-43.81	795.8
3070	1220	189000	2	15	31	31						1947.6
3071	1290	198000	29	15	30	66						1766.1
3027	1190	186000	28	10	220	37				125		1663.5
3034	1570	188000	27	20	96	85				164		2861.8
3025	780	172000	75	10	295	26	-4.99	-55.40		71	-50.26	1089.7
3023	950	149000	21	9	189	6	-2.27	-39.90	0.70898	81	-33.91	1524.8
3047	1090	168000	40	9	67	53				161		1898.6
3039	1190	188000	42	17	118	47	-0.38	-30.00		135	-22.06	2036.0
3026	790	192000	86	12	429	28				73		1414.7
3063	650	158000	27	8	20	1	-3.39	-41.60			-36.16	1249.2
3070	1220	189000	2	10	31	31						1947.6
3087	490	181000	11	5	491	11				109		661.4
3082	690	161000	84	7	364		-4.02	-46.30		73	-40.45	1387.0
3086	760	144000	98	8	510		-5.71	-55.80		115	-50.45	1309.1
3081	620	131000	106	12	745		-6.58	-52.70		78	-48.57	925.5
RICHFIELD												
4010	1930	200000	56	29	112	75				214		3272.9
4017\	1920	203000	48	17	74	81	1.49	-27.00	0.70819	203	-15.24	3193.9
4018	1870	202200	45	11	109	65				198		3138.9
4035	1240	200000	114	40	33	371	4.31	-51.70	0.70809	401	-37.99	3839.4
4036	1050	75800	229	8	348	137				115		1682.9
4037	2610	182000	213	25	161	180				242		3939.4
4068	1200	240000	240	28	0	39						4979.7
4069	1200	242000	240	30	0	82	2.93	-41.60			-22.96	5269.7
4046	3200	220000	244	13	0	377				333		4818.7
4050	2700	191000	240	10	0	137						4337.3
4403	2690	186000	278	19	0							4550.2
4406	4210	235000	385	66	4							6011.5
4407	4050	225000	207	68	34							5706.0
DETROIT RIVER												
5019	3060	179000	326	57	2	383	2.58	-51.70		441	-36.13	4524.6
5030	3750	251000	100	25	54	134	4.36	-16.70	0.70782	689	6.97	6503.5

ID	Br	Cl	ALK as HCO_3	I	SO_4	B	$N^{18}O$ °/oo	ND °/oo	^{87}Sr	NH_4N	N^aD °/oo	MCl_2 meq/l
NIAGARA/SALINA												
2206	3020	263000	614	28	10							7383.4
2207	3070	248000	258	27	6							6220.2
2208	1150	140000	101	22	152							3185.5
2209	690	117000	52	7	71							2286.4
2210	2220	170000	31	19	70							3460.4
2211	2230	168000	3	23	30							3202.1
2212	2430	202000	108	22	29							4138.8
2213	2640	211000	49	13	87							4526.9
2214	2060	168000	32	14	154							3342.9
2215	3220	236000	53	22	18							5503.8
2020	3340	209000	50	19	110	220	0.75	-37.40	0.70799	437	-22.15	4148.3
2072	2730	233000	150	9	56	81				235		4989.1
2077	1270	153000	150	32	119	106				283		3534.2
2078	3010	265000	150	50	22	239	2.87	-48.70	0.70879	56	-24.61	6437.0
2083	1800	169000	150	41	106	354				672		3728.1
2084	2360	213000	150	64	131	346				784		5014.3
2089	3060	244000	150	50	75	498				1087		5977.9
2090	2940	253000	374	31	85	226				1053		6426.4
2091	1820	190000	207	29	28	152				667		4155.6
2092	2500	218000	17	17	34	25	-3.39	-49.80	0.70830	356	-32.86	4879.7
2093	3300	248000	36	19	25	123				415		5969.7
2100	3110	239000	39	22	42	98	0.30	-40.80		549	-19.84	6020.5
2101	2980	239000	240	21	52	72				476		5972.5
2097	2700	223000	123	27	75	81	-1.99	-24.30		451	-7.32	4747.5
2096	2700	211000	84	38	82	72				431		4593.4
2099	3110	227000	88	54	75	61				641		4764.0
2098	2560	230000	352	28	34	86				588		5400.7
TRENTON-BLACK RIVER												
6601	1130	142000	27	9	369							1795.2
6602	1430	163000	39	11	113							2542.8
6603	1020	122000	40	8	393							1662.1
6604	980	121000	43	8	530							1593.7
6605	870	116000	55	7	249							1409.0
6606	760	104000	90	6	717							1261.1
6073	750	91000	25	10	250	6				45		1059.1
6074	1080	130000	25	13	238	13	-1.85	-26.40		73	-20.39	1567.0
6075	1080	127000	25	13	125	13				70		1557.6
6076	1040	127000	25	10	125	15				78		1531.2
6095	1250	143000	67	15	100	15	-1.76	-26.70		120	-20.15	1696.6
6094	1160	140000	39	26	100	21	-1.99	-24.30	0.71031	126	-17.97	1635.7
St. PETER												
8040	3100	250000	10	20	0	107	-2.96	-46.50	0.70920	247	-26.66	5367.3

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