

Geochemistry and isotope chemistry of Michigan Basin brines: Devonian formations

TIMOTHY P. WILSON* and DAVID T. LONG

Department of Geological Sciences, Michigan State University, East Lansing, MI 48824, U.S.A.

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Abstract—Detailed chemical and isotope analysis of 87 formation waters collected from six Devonian-aged units in the Michigan Basin are presented and discussed in terms of the origin of the dissolved components and the water. Total dissolved solids in these waters range from 200,000 to >400,000 mg/l. Upper Devonian formations produce dominantly Na–Ca–Cl brine, while deeper formations produce Ca–Na–Cl water. Ratios of Cl/Br and Na/Br along with divalent cation content (MCH_2), indicate that these brines are derived from evapo-concentrated seawater. Other ion concentrations appear to be extensively modified from seawater values by water–rock reactions. The most important reactions are dolomitization, which explains the Ca content of the brines, and reactions involving aluminosilicate minerals. Stable isotope ($\delta^{18}O$ and δD) compositions indicate that water molecules in the deeper formations are derived from primary concentrated seawater. Isotope enrichment by exchange with carbonates and perhaps gypsum cannot be discounted. Isotope values indicate water in the Upper Devonian formations is a mixture of seawater brine diluted with meteoric-derived water. Dilution has predominantly occurred in basin margins. Two scenarios are presented for the origin of the brines in the Devonian formations: (1) they originated when the Devonian sediments and evaporites were first deposited; or (2) they are residual brine liberated from the deeper Devonian and possibly Silurian salt deposits.

INTRODUCTION

REGARDLESS of the geological setting (e.g. deep basin, coastal geosyncline, near surface aquifer), basic problems remain to be addressed concerning the origin and evolution of subsurface brines. Most fundamental is determining the sources of solutes and solvent (H_2O) and developing evolutionary models for brines from these two components that are in agreement. While no single model can explain the origin and evolution of all brines, it is becoming clear that both the solutes and solvent of many brines are related to seasalts and seawater, and that many brines have evolved chemically and isotopically from their original marine source (RUBEY, 1951; CHAVE, 1960; WHITE, 1965; COLLINS, 1975; HANOR, 1982). Mechanisms suggested to cause the chemical and isotopic evolution of brine include evaporation, freshwater/seawater mixing, hyperfiltration, and water–rock interactions (CARPENTER, 1978; STOESSELL and MOORE, 1983; KNAUTH and BEEUNAS, 1986; DUTTON, 1987; BILLINGS *et al.*, 1969; DRESSEL and ROSE, 1982; SPENCER, 1987; CLAYTON *et al.*, 1966; HITCHON *et al.*, 1971; KHARAKA and BERRY, 1974; KHARAKA *et al.*, 1973; BASSETT and BENTLEY, 1983).

The Michigan Basin contains some of the most highly concentrated brine found in any sedimentary basin (CASE, 1945). These waters were first described by LANE (1899) and COOK (1914) as having high concentrations of Ca, Br and Cl, and relatively low concentrations of Mg, SO_4 and HCO_3 . Because the

Michigan Basin typifies intracratonic sedimentary basins, understanding the origin and evolution of its brines may help resolve unanswered questions concerning processes associated with all such basins, such as hydrocarbon origin and migration (DEGENS and CHILINGAR, 1964), basin hydrodynamics (BETHKE, 1985; DOMENICO and ROBBINS, 1985), low temperature ore formation (ROEDDER, 1967; BILLINGS *et al.*, 1969; BUSH, 1970; CARPENTER *et al.*, 1974; LONG and ANGINO, 1982), evaporite cycling (LAND, 1987), carbonate and clastic diagenesis (FRIEDMAN and SANDERS, 1967; BEIN and LAND, 1983; CERCONE and LOHMANN, 1987). In addition, knowledge of the geochemical nature of Michigan brines is important because deep formations in Michigan are used for disposal of hazardous waste.

PAST WORK

Various models have been proposed to explain the chemical and isotope signatures of the Michigan Basin brines. Dissolution of salt was suggested as the origin of the brines in both the early works of LANE (1899) and COOK (1914) and more recently by SORENSEN and SEGALL (1975). However, simple salt dissolution cannot account for the high Br values found in the brines (WILSON and LONG, 1986). EGLERSON and QUERIO (1969) suggested the brines may be trapped evaporated seawater chemically modified by dolomitization, which is in disagreement with BEECKER (1940). CLAYTON *et al.*, (1966) and GRAF *et al.* (1966) attributed the $\delta^{18}O$ and δD values of the brines to local meteoric water which had infiltrated the basin

*Now at Kent State University, Kent State, Ohio, U.S.A.

and reacted with minerals. They proposed that although the original formation waters may have been partly lost during basin compaction, the original solutes derived from seawater and salt dissolution were retained by shale filtration. Shale filtration was suggested to have, in part, concentrated and modified the relative abundances of solutes from seawater values. The role of shale filtration in brine origin has since been questioned (HANOR, 1982; KNAUTH and BEEUNAS, 1986).

Considering past works, the chemical and isotope signatures of the Michigan Basin brines have been accounted for by the following processes:

1. Calcium, Cl and Br: high concentrations are a function of the flushing of the basin by meteoric water and their selective retention in the system by shale membranes (Ca, Cl, Br), coupled with dolomitization (Ca).

2. Bicarbonate, SO_4 , Na and Mg: low concentrations are a result of precipitation of carbonates (HCO_3 , Mg), silicates (Mg), sulfates (SO_4), halite (Na); sulfate reduction (SO_4 -S); and selective passage by shale membranes (HCO_3 and Na).

3. $\delta^{18}\text{O}$ and δD : the isotope composition represents freshwater that had infiltrated and flushed the basin and later reacted with minerals.

Other processes affecting the Michigan brines have not been well characterized because either averages of whole basin chemistry were used rather than individual reservoir chemistries, or because few samples from each formation were studied. Many components in the brines, such as K, have not been studied. In order to define these processes better, the chemical and isotope data for brines from Devonian formations in Michigan are presented here and used to investigate the source of the solutes and water and the brine evolution.

STUDY AREA

The Michigan Basin is a mature, intracratonic sedimentary basin occupying $\sim 200,000 \text{ km}^2$ between the Canadian Shield and the Illinois Basin (Fig. 1). The geology of the basin has been reviewed by several authors, most notably by DORR and ESCHMAN (1984). At its deepest point the basin contains $>4000 \text{ m}$ of Paleozoic sedimentary rocks which range from Cambrian to Jurassic in age (Fig. 2). The basin is estimated to contain 47% carbonates, 23% sandstones, 18% shales and 12% evaporites by volume (COHEE and LANDES, 1958). WILSON (1989) estimated that $\sim 8.3 \times 10^4 \text{ km}^3$ of the basin strata are Devonian in age. The present geothermal gradient averages $22^\circ\text{C}/\text{km}$ (NUNN *et al.*, 1984), although measured gradients may vary considerably (WILSON, 1989). HOGARTH (1985) found that the paleo-geothermal gradient was probably similar to the present day gradient, but that Paleozoic strata may have been buried $\sim 1 \text{ km}$ deeper in the past. CERONE (1984) suggested both deeper burial and higher paleo-geothermal gradients for Michigan.

Water investigated in this study came from the Berea Sandstone in the Antrim Shale Formation, the Traverse Group, the Dundee Formation, the Richfield zone and the Detroit River sour zone of the Lucas Formation (Detroit

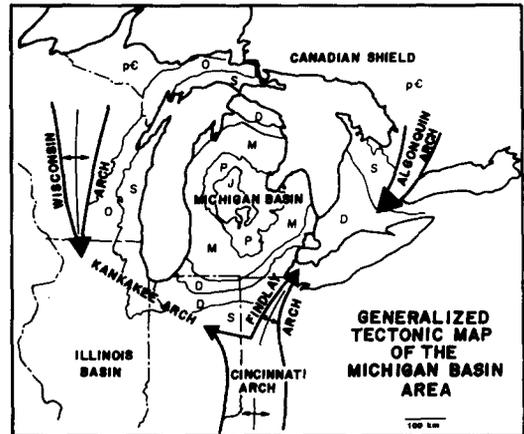


FIG. 1. Location and generalized tectonic map of the Michigan Basin.

River Group), and the Sylvania Sandstone of the Bois Blanc Formation (Fig. 2). Water from the Silurian Niagara and Salina Formations was also collected and is discussed in detail elsewhere (WILSON and LONG, 1992). Summaries of the general lithology, structure, thickness and depositional environments for these strata can be found in GARDNER (1974), MATTHEWS (1977), DORR and ESCHMAN (1984) and MONTGOMERY (1984).

Devonian-aged rocks in the Michigan Basin represent a shallow water transgressive–regressive sequence that followed the restricted marine conditions of the Silurian (GARDNER, 1974). The Bois-Blanc Carbonate Formation is lowest in the section and includes the Sylvania Sandstone, which is a wind and fluvial transported sand (GARDNER, 1974). The cyclic evaporite–carbonate sediments of the Middle Devonian Detroit River Group follow. The cyclic nature of the group is exemplified by the Richfield zone of the Lucas Formation which consist of 60 m of alternating anhydrite and dolomite layers. In the central basin area the Horner and the Iutzi Members of the Lucas Formation contain nearly 200 m of halite, anhydrite and dolomite (MATTHEWS, 1977). The Detroit River Group is also known for the highly brecciated dolomite outcrops near the basin margin that formed when underlying Salina salts were dissolved (LANDES *et al.*, 1945).

The Upper Devonian Dundee and Traverse Formations that follow are biostromal carbonate shelf deposits which grade into argillaceous carbonates in the central part of the basin. Both formations show evidence that large sabkhas and lagoons existed around the basin margins during the Late Devonian (Fig. 3, GARDNER, 1974). Devonian and Carboniferous shales and sandstones complete the section and include the Berea Sandstone which is a quartz sandstone deposited in a shallow near-shore environment (GARDNER, 1974).

The mineralogy of the Devonian rocks is dominated by calcite and dolomite, but also includes anhydrite, halite, quartz, chert and illitic-chloritic clays (GARDNER, 1974; MATTHEWS, 1977; NOWAK, 1978; DORR and ESCHMAN, 1984; MONTGOMERY, 1984). Dolomite and anhydrite abundances increase toward the basin margins, especially in the west (GARDNER, 1974), but are also present in the Lower Devonian evaporites of the central basin (MONTGOMERY, 1984).

Oil and brine have been produced from Devonian rocks in Michigan since the early 1900s, and occur along a broad band from the central basin west and southward (COHEE and LANDES, 1958; MONTGOMERY, 1984). Reservoirs include bioherms and anticlines, dolomitized porosity zones, and fracture zones (MONTGOMERY, 1984).

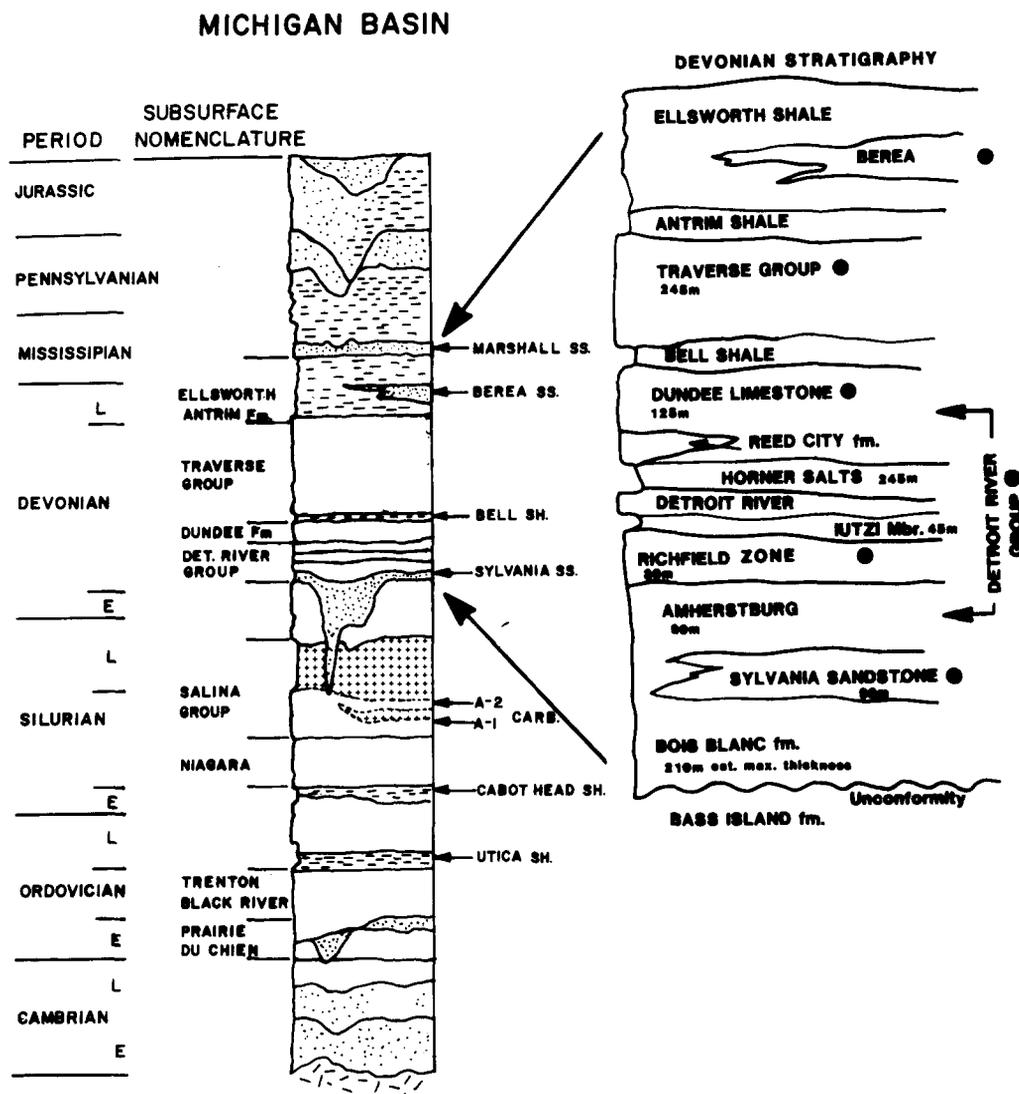


FIG. 2. Paleozoic stratigraphic column of the Michigan Basin. Dots indicate sampled reservoirs.

METHODS

Fifty-four brine samples were collected from Devonian strata and were supplemented with 33 other analyses obtained from oil companies and from the Michigan Department of Natural Resources (M.D.N.R. open file data). Twenty-seven analyses from the Silurian units were also obtained. All analyses were checked for their completeness and charge balance before use. Sample locations are shown in Fig. 4. Producing intervals were confirmed by operators and drilling records, and by geophysical logs when possible. Due to the common practice of flushing wells with freshwater, care was taken to avoid sampling wells that were recently flushed, wells from fields under waterflood or those located near brine disposal wells. The Sylvania Formation has long been used for brine disposal, therefore samples were not taken from this unit and only historic data for this formation were used.

Samples were collected directly from the well head, filtered through glass wool and Watman No. 1 paper filters, and stored in pre-rinsed plastic bottles. Because of the viscosity of the brine, it was not possible to filter the brines through 0.45 μ filters. Filtered samples for cation analysis

were diluted (in the field) by 50% with 5% HNO₃. Samples for anion analysis were diluted 50% with distilled water, with sub-samples preserved for SO₄ analysis. Untreated filtered samples were also collected for D/H, and ¹⁸O/¹⁶O analysis. Temperature, pH, Eh and 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. Interpretation of the pH values should be made with caution due to the many interferences that can occur when measuring pH in brine (HAWLEY and PYTKOWICZ, 1973; DICKSON, 1984). Formation temperatures were calculated using 10°C at 33 m plus a gradient of 23°C/km of depth, following methods in VUGRINOVICH (1986). Dissolved components were measured using colorimetric and atomic absorption techniques listed in BROWN *et al.* (1979), PRESELY (1971), COLLINS *et al.* (1969), COLLINS (1975) and the AMERICAN PETROLEUM INSTITUTE (1968). Details and modifications are described in WILSON (1989). Chemical analysis was done at the Geochemical Laboratory, Michigan State University. Stable isotope ratios (¹⁸O/¹⁶O, D/H) were measured using the methods of FRITZ *et al.*, (1986), at the Environmental Isotope Laboratory, University of Waterloo, Ontario, Canada, and at Teledyne Laboratories, New Jersey.

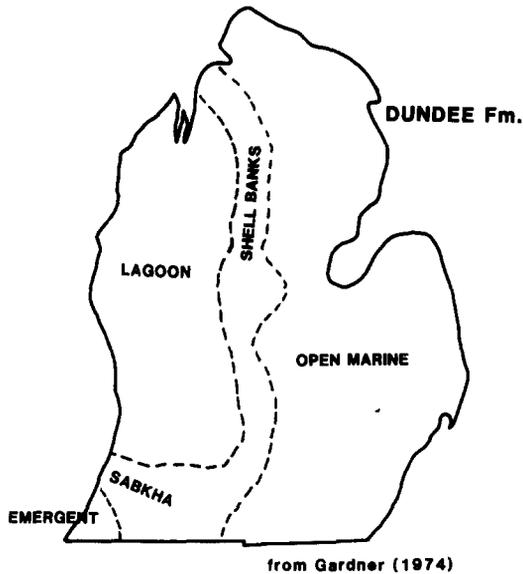


FIG. 3. Paleogeography of the Upper Devonian Dundee Formation as suggested by GARDNER (1974).

RESULTS

General

The results for the wells used in this study are presented in Table 1; information for the Silurian wells is presented elsewhere (WILSON and LONG, 1992). Only samples with charge balances $< \pm 5\%$ were used. The pH values ranged between 3 and 6 with no systematic trend among the units. Estimated temperatures range between 25° and 60°C. Chloride and Na are the dominant anion and cation, respectively. The brines also contained substantial quantities of trace elements (Rb, B, NH_4 , Li, Si), which although listed, are not discussed in this paper.

Figure 5 shows the relative molar percentage of major cations in brines, based on all available data. The brines fall in two major clusters, one containing Na-Cl brines from the Upper Devonian units (Berea, Traverse and Dundee), the second contains the more highly concentrated Ca-Cl brines from the Lower Devonian (Richfield, Detroit River and Sylvania) and Silurian units. The data fields define a linear trend suggesting mixing between Ca-rich and Na-rich water.

Formation waters in sedimentary basins generally increase in salinity with depth, as is the case for the Michigan Basin. Figure 6 shows how the total dissolved solids (TDS) vary as a function of depth. Although the data are scattered, the right boundary of the data follows a trend of increasing TDS with depth. The scatter is greater than that observed in other sedimentary basins such as the Illinois (GRAF *et al.*, 1966) and Western Canada (HITCHON *et al.*, 1971), but occurs only when the various formations are combined. When the units are studied individually or grouped based on similar geological con-

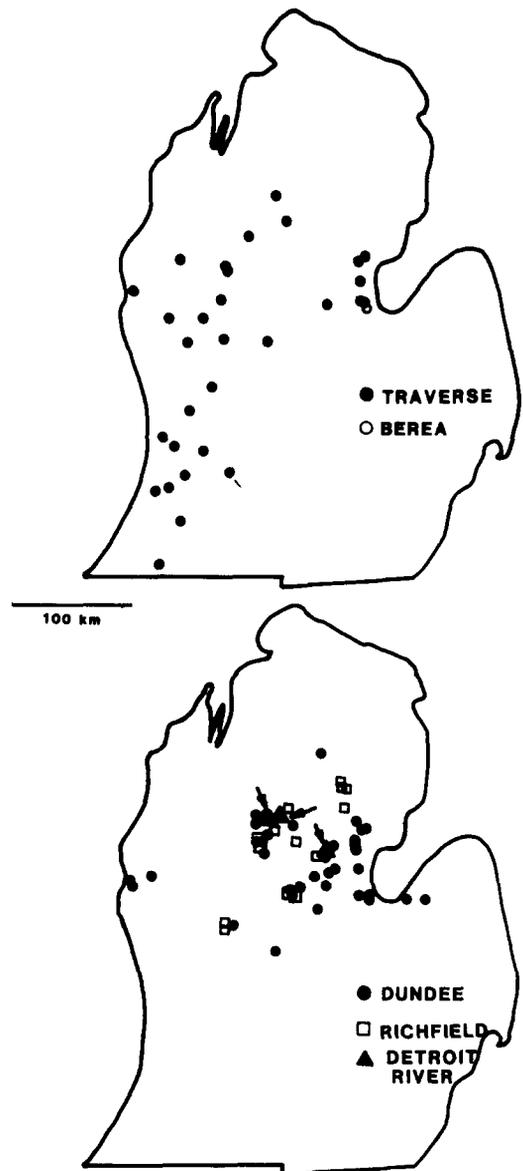


FIG. 4. Location of sampled wells. The Detroit River Group was sampled in three mid-basin locations indicated by arrows.

ditions, variations in chemistry may become evident. For example, the contiguous Traverse and Dundee Formations contain brine with similar major ion chemistry (Fig. 5). When the analyses from these formations are combined, a salinity gradient is observed that increases from the margins toward the central, deeper part of the basin. This is illustrated by the data in Fig. 6 and by the distribution of Br (Fig. 7A). Bromide in these waters varies directly with TDS ($\log_{10} \text{TDS} = 0.357 * \log_{10} \text{Br} + 4.33$; $r = 0.85$), and increases toward the center of the basin (Fig. 7A) indicating that TDS is a function of location and depth. Most of the major components (Ca, Mg, K, Sr, Na) and isotopes (δD - $\delta^{18}\text{O}$) also follow the Br trend. The SO_4 trend (Fig. 7B) is opposite to that of

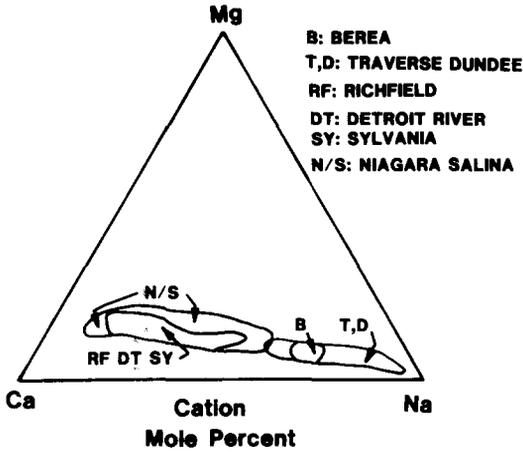


Fig. 5. Ternary diagram showing mole percentage of Ca, Mg and Na in the Michigan Basin brines.

Br, with higher concentrations being found nearer the basin margins. The observed distribution of Br and SO₄ may indicate either the original distribution of water in the basin with the more highly concentrated, dense brines in the deeper, central areas of the basin, or that fresh water has infiltrated along the basin margin.

RELATION OF BRINES TO EVAPORATED SEAWATER

COLLINS (1975) and CARPENTER (1978) demonstrated how brine chemistry can be compared to evapo-concentrated seawater in order to make interpretations as to the possible origin and evolution. CARPENTER (1978, 1979) and others compared divalent cation concentration (MCl₂) in brines with

seawater to determine if the solutes in a brine originated from evaporated seawater. The MCl₂ value is calculated as $Ca + Mg + Sr - (0.5 * HCO_3 - SO_4)$ (all in meq/l) and represents the sum of divalent cations that are balanced by Cl (CARPENTER, 1978). The MCl₂ value is not affected by precipitation or dissolution of halite, CaSO₄ and calcite, nor by dolomitization. Bromide is considered conservative in evaporating seawater (RITTENHOUSE, 1967; COLLINS, 1975; CARPENTER, 1978) and is used as an indicator of degree of concentration.

Values of MCl₂ for the Devonian samples generally exceed values in evaporating seawater (Fig. 8). One reason for this may be analytical error, which is reflected in the charge imbalance. Although charge balances for the samples used are within ±5%, such imbalances can represent a major error if attributed to a single species. In a brine with TDS of 315,000 mg/l, for example, a charge imbalance ((anion meq/l - cation meq/l)/(anion meq/l + cation meq/l) × 100) of + 5% represents nearly 600 meq/l of "missing" anions. This could represent a maximum error in Br of 47,900 mg/l. While it is unlikely that a charge balance error is due only to a single component, this illustrates that in highly concentrated brine, a large amount of a single species can be lost in a small charge balance error. To adjust for possible charge imbalance error, the charge imbalance was redistributed throughout all components following the method of CARPENTER (1978). The adjustment is made to the raw data based on the relative percentage each component contributes to the overall charge. The log of the adjusted MCl₂ value, MCl₂^{adj}, for the samples is plotted vs log Br (mg/l) in Fig. 8, along with the seawater trajectory of McCAFFREY *et al.* (1987). In spite of this adjustment, the MCl₂^{adj} values still plot generally above the seawater line. Thus, either Br has been depleted or divalent cations have been enriched in these brines.

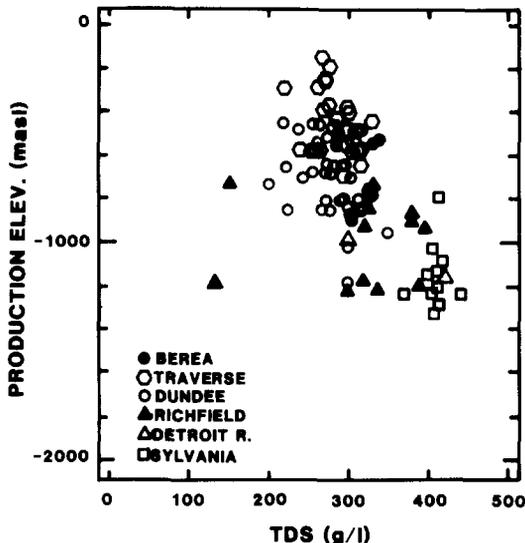


Fig. 6. Production elevation (m) vs TDS (g/l) in the Michigan Basin brines.

The Br values generated in this study compare well with Br values in the M.D.N.R. and oil company analyses; therefore, it is felt that the Br analyses used in this study are not in error. In addition, few mechanisms are known which deplete Br from natural waters. Bromide is removed from evaporating seawater 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, it seems unlikely that significant amounts of Br could be depleted by ion exchange. Because of these points, and the fact that a close agreement exists between the brines and seawater on the Cl-Br diagram, it is assumed that the Michigan brines are enriched in divalent cations (MCl₂) and not depleted in Br with respect to evaporating seawater. This is a common feature in brines from many sedimentary basins (WILSON and LONG, 1986). If seawater was the original source of solutes then the mechanism that increased the MCl₂ requires explanation.

Table 1. Results for Devonian formation waters in Michigan

ID	Surface elevation (m)	Production elevation (m)	TWN			Depth (m)	TDS (mg/l)	Specific gravity	Temperature (°C)	Data source	Ca	K	Li	Mg	Na
			RNG	SEC											
<i>Berea</i>															
7001	196.0	-542	14	-3	7	738	328 650	1.229	26.3	1	49 500	580	8	8790	66 700
7005	198.1	-552	15	-2	36	750	284 278	1.198	26.6	1	38 400	700	8	7600	58 200
7006	201.7	-530	14	-2	1	777	335 300	1.230	26.4	1	48 300	650	8	8400	64 500
<i>Traverse</i>															
1008	296.3	-575	16	10	27	872	254 280	1.176	29.3	1	40 600	2330	38	6930	43 720
1009	296.4	-576	16	10	27	873	249 883	1.173	29.4	1	39 600	2310	38	6800	43 000
1011	302.8	-574	16	10	28	877	301 253	1.210	29.5	1	49 400	2930	48	8510	48 500
1014	278.3	-571	12	10	1	849	316 363	1.220	28.8	1	41 400	2410	48	6720	67 000
1017	372.3	-573	18	9	6	945	235 642	1.163	31.0	1	21 400	1160	30	4400	67 100
1024	195.1	-483	17	-4	18	678	298 312	1.208	24.9	1	20 400	480	18	4800	78 000
1028	218.9	-395	19	-3	36	614	299 466	1.208	23.4	1	30 200	930	32	5560	78 100
1048	348.1	-555	22	4	18	903	297 052	1.207	30.1	1	34 600	1920	40	5540	70 200
1049	372.5	-691	19	10	36	1064	294 026	1.205	33.8	1	35 600	1620	24	6300	73 500
1085	270.7	-429	19	13	19	700	282 070	1.196	25.4	1	23 100	1260	34	5870	75 000
1088	192	-290	16	17	6	483	215 250	1.149	20.4	1	11 600	440	19	3840	62 300
1101	211.6	-196	1	13	10	408	273 504	1.190	18.7	2	23 400	1440	12	6640	78 600
1102	251.2	-293	3	11	8	544	258 184	1.179	21.8	2	20 600	1220	9	7140	70 200
1103	197.5	-251	4	14	34	448	268 000	1.186	19.6	2	17 800	1330	12	5430	85 200
1104	204.2	-259	4	15	2	463	268 468	1.186	20.0	2	21 900	1620	18	5430	78 400
1105	216.4	-376	19	-4	21	593	295 324	1.206	22.9	2	20 200	1480	27	7120	88 700
1107	195.1	-483	17	-4	18	678	306 690	1.214	24.9	2	31 500	1760	33	7460	81 500
1109	267.4	-445	9	11	5	712	326 440	1.228	25.7	2	45 400	2350	40	7830	73 900
1110	197.3	-755	15	1	13	952	325 110	1.227	31.2	2	67 700	4750	81	9700	43 700
1111	358.2	-435	24	5	16	793	286 836	1.199	27.5	2	21 200	1680	41	8320	82 400
1112	301.8	-644	12	6	10	946	315 300	1.220	31.1	2	44 500	3130	46	8290	69 400
1113	278.3	-571	12	10	1	849	308 690	1.215	28.8	2	43 500	3320	50	7430	64 200
1114	254.8	-455	12	13	11	710	278 481	1.194	25.6	2	28 900	1630	35	6650	71 300
1115	317.9	-529	14	11	8	847	303 560	1.211	28.8	2	38 100	2050	40	8920	69 700
1116	254.5	-386	14	14	5	640	264 686	1.184	24.0	2	20 000	1300	29	5840	78 200
1117	374.9	-573	18	9	6	948	260 692	1.181	31.1	2	28 000	2050	33	6930	63 800
1118	219.2	-367	7	13	36	586	272 433	1.189	22.8	2	26 700	1630	16	8450	68 500
1119	219.0	-147	-1	14	17	376	263 852	1.183	18.0	2	23 000	1520	18	6250	66 800
<i>Dundee</i>															
3002	214.4	-1020	17	-1	30	1234	296 662	1.206	37.7	1	25 600	1880	36	4720	76 600
3003	183.4	-671	15	-4	30	854	251 291	1.174	28.9	1	25 600	980	14	5000	62 500
3004	182.2	-677	15	-4	26	859	267 592	1.186	29.1	1	14 400	380	6	4200	83 500
3007	245.2	-489	20	-4	3	734	283 407	1.197	26.2	1	19 800	1014	26	4020	87 900
3012	—	—	—	—	—	—	298 387	1.208	—	1	33 600	2150	40	6140	69 300
3015	297.6	-782	13	9	36	1080	328 379	1.229	34.1	1	51 000	4040	54	7040	60 500
3016	296.6	-789	13	9	36	1085	328 880	1.229	34.3	1	51 800	4160	52	6880	60 400
3022	182.9	-647	14	-8	29	830	286 155	1.199	28.4	1	21 400	600	10	6810	81 600
3023	196.7	-704	17	-4	18	901	240 643	1.167	30.0	1	23 000	920	24	4420	61 300
3025	240.0	-638	19	-3	22	878	277 895	1.193	29.5	1	15 900	1120	24	3540	84 400
3026	238.2	-641	19	-3	15	880	292 162	1.203	29.5	1	21 700	1120	22	4000	92 400
3027	224.5	-850	18	1	23	1075	313 898	1.219	34.0	1	25 400	1910	32	4660	94 200
3029	227.4	-864	18	1	14	1092	298 884	1.208	34.4	1	28 000	1880	52	5460	75 300
3033	240.1	-844	15	4	2	1084	315 206	1.220	34.2	1	36 400	3010	44	5790	76 100
3034	229.9	-884	15	4	13	1113	301 726	1.210	34.9	1	44 900	2820	44	7200	55 800
3039	364.2	-809	22	7	25	1173	269 534	1.187	36.3	1	32 000	2540	44	5080	68 400
3042	360.6	-832	21	7	22	1192	299 414	1.208	36.7	1	26 000	1870	33	5070	83 500
3043	—	—	21	7	30	—	298 021	1.207	—	1	33 100	1650	41	6060	69 900
3047	346.2	-854	21	3	30	1200	276 568	1.192	36.9	1	29 600	3224	38	4900	68 800
3051	246.5	-487	20	-4	10	734	283 464	1.197	26.2	1	21 800	1220	24	4000	86 100
3052	179.9	-654	14	-4	12	834	218 059	1.151	28.5	1	19 000	800	2	3000	68 000
3063	179.1	-639	14	-8	29	818	269 155	1.187	28.1	1	16 000	520	2	5320	81 100
3070	342.2	-1179	20	6	31	1521	298 290	1.208	44.3	1	29 900	1680	18	5220	70 400
3071	338.0	-801	20	6	29	1139	309 790	1.216	35.5	1	25 600	1120	18	5660	77 200
3081	196.2	-446	16	17	8	642	213 550	1.147	24.1	1	—	—	—	—	—
3082	180.2	-449	16	18	1	629	261 758	1.182	23.8	1	29 900	900	33	4110	73 600
3086	213.4	-472	17	16	25	686	232 360	1.161	25.1	1	19 800	960	27	3860	62 400
3087	211.0	-472	17	16	26	683	315 100	1.220	25.0	1	10 300	1220	29	1820	103 000
3301	181.2	-694	19	-3	26	875	273 921	1.190	29.8	2	20 500	1980	20	7310	80 600
3302	181.2	-694	14	-4	2	875	301 830	1.210	29.4	2	35 000	2950	33	7040	73 300
3304	336.5	-851	19	6	33	1188	264 050	1.183	36.6	2	31 000	2690	32	6350	61 800
3305	346.3	-805	20	6	12	1151	291 750	1.203	35.8	2	33 700	3350	41	5950	66 300
3306	345.0	-542	27	1	28	887	258 517	1.179	29.7	2	7390	1100	10	2640	92 900
3307	220.4	-853	17	-2	18	1073	220 063	1.152	34.0	2	22 100	1880	17	7010	56 500
3309	230.0	-878	16	3	28	1108	300 650	1.209	34.8	2	38 500	4380	41	6530	57 600
3311	202.8	-949	16	1	26	1152	348 500	1.243	35.8	2	73 300	8360	68	11 300	38 800
3312	361.3	-802	22	6	26	1163	287 310	1.200	36.1	2	32 100	2360	41	8330	67 000
3313	242.6	-726	10	5	3	969	196 796	1.136	31.6	2	26 700	2180	27	5030	41 000
3314	182.9	-447	16	18	1	630	252 806	1.175	23.8	2	20 500	1220	29	4340	73 600
3315	256.1	-501	21	-3	16	757	271 217	1.188	26.7	2	17 200	1930	22	5030	82 000

Table 1. *Continued*

pH	Sr	Rb	Cs	Si	Br	Cl	ALK	I	SO ₄	B	δ ¹⁸ O (‰)	δD (‰)	⁸⁷ Sr/ ⁸⁶ Sr	NH ₄ N	MCl ₂
<i>Berea</i>															
4.6	2140	3.4	—	4.0	940	200 000	25	28	100	—	1.10	-10.70	0.70915	50	3240.4
5.1	1780	3.9	—	4.4	1600	176 000	25	25	85	—	0.29	-24.10	0.70909	64	2580.6
5.0	2080	3.5	2.9	1.4	1840	209 000	10	17	11	—	—	—	—	126	3148.7
<i>Traverse</i>															
5.3	1540	6.7	—	2.9	1560	158 000	38	18	208	22	—	—	—	193	2637.3
—	1460	3.1	—	3.2	1510	155 000	36	20	297	24	—	—	—	180	2563.1
4.8	1880	8.3	—	3.0	1930	188 000	31	25	86	68	-0.57	-23.80	—	121	3206.7
4.9	1620	6.8	—	2.1	1510	196 000	11	18	59	27	-0.70	-31.50	—	146	2654.7
5.9	800	3.3	—	2.9	880	140 000	59	12	109	18	-3.60	-40.00	—	83	1446.4
5.4	900	2.2	—	1.4	1280	194 000	5	12	106	—	0.56	-29.10	0.70909	106	1988.4
4.5	1140	3.3	—	4.3	890	175 000	3	12	67	—	-0.49	-32.50	0.70940	76	1432.1
5.8	1250	17.2	—	—	1247	184 600	18	10	162	117	—	—	—	—	2207.7
—	980	—	—	—	1050	182 000	18	12	150	—	—	—	—	—	2314.3
5.4	940	1.7	2.9	5.2	900	175 000	61	71	28	—	-1.83	-43.60	0.70845	174	1657.1
5.8	350	0.4	—	4.0	720	136 000	156	10	607	—	-7.06	-61.20	—	76	891.5
—	710	—	—	—	710	162 000	13	4	22	—	—	—	—	—	1729.9
—	734	—	—	—	2290	156 000	2	24	110	—	—	—	—	—	1630.0
—	650	—	—	—	590	177 000	16	4	31	—	—	—	—	—	1349.4
—	470	—	—	—	650	160 000	32	6	215	—	—	—	—	—	1546.2
—	940	—	—	—	880	176 000	1	9	17	—	—	—	—	—	1615.0
—	1210	—	—	—	1260	182 000	2	5	85	—	—	—	—	—	2211.6
—	1540	—	—	—	1420	194 000	7	10	100	—	—	—	—	—	2942.9
—	2920	—	—	—	2340	194 000	2	28	30	—	—	—	—	—	4242.5
—	1330	—	—	—	910	171 000	73	5	2	—	—	—	—	—	1773.5
—	1500	—	—	—	1480	187 000	20	12	160	—	—	—	—	—	2933.8
—	1690	—	—	—	1550	187 000	27	18	60	—	—	—	—	—	2819.6
—	960	—	—	—	1040	168 000	68	7	73	—	—	—	—	—	2010.3
—	1460	—	—	—	1330	182 000	1	11	80	—	—	—	—	—	2666.9
—	610	—	—	—	730	158 000	24	6	9	—	—	—	—	—	1492.5
—	910	—	—	—	1000	158 000	44	10	70	—	—	—	—	—	1987.1
—	1160	—	—	—	990	165 000	7	5	5	—	—	—	—	—	2054.1
—	557	—	—	—	710	165 000	33	4	155	—	—	—	—	—	1672.2
<i>Dundee</i>															
4.8	780	5.2	2.5	1.8	1180	186 000	26	15	141	39	0.20	-30.80	—	119	1680.9
5.3	946	3.6	2.4	2.1	1070	155 000	23	18	295	11	-2.38	-28.10	—	29	1704.5
4.5	420	1.8	1.3	2.4	690	164 000	20	13	382	1	-3.02	-28.60	—	64	1066.0
4.6	600	2.9	1.6	2.0	750	169 000	64	28	319	20	-4.51	-52.00	—	—	1326.4
5.2	1180	6.0	2.8	2.5	1420	185 000	28	13	112	52	-0.40	-34.20	—	228	2206.7
5.2	1740	10.2	4.3	1.5	1860	202 000	51	19	109	80	—	—	—	200	3162.1
5.0	1720	11.1	4.4	2.3	1920	202 000	59	20	103	84	1.31	-35.50	0.70813	216	3188.6
3.5	730	2.6	1.6	2.1	1020	174 000	37	8	166	2	—	—	—	45	1641.8
5.9	750	2.9	1.7	1.2	950	149 000	21	9	189	6	-2.27	-39.90	0.70898	81	1524.8
4.7	460	3.3	1.6	1.7	780	172 000	75	10	295	26	-4.99	-55.40	—	71	1089.7
4.8	480	3.0	1.6	1.4	790	192 000	86	12	429	28	—	—	—	73	1414.7
5.2	740	5.3	2.1	1.9	1190	186 000	28	10	220	37	—	—	—	125	1663.5
5.3	2000	5.4	2.9	2.0	1240	185 000	43	19	139	19	0.43	-26.10	—	162	1889.6
5.5	1340	8.1	3.1	3.3	1570	191 000	27	17	160	31	-0.53	-30.80	—	185	2320.3
4.1	1340	7.7	3.1	2.1	1570	188 000	27	20	96	85	—	—	—	164	2861.8
5.3	1020	7.1	2.8	2.6	1190	188 000	42	17	118	47	-0.38	-30.00	—	135	2036.0
5.2	780	5.2	2.3	1.2	1140	181 000	11	13	137	8	-2.03	-39.20	0.70831	107	1729.7
5.1	1620	4.9	—	1.2	1090	185 000	35	14	94	8	-1.05	-30.95	—	174	2185.7
4.8	850	2.9	1.1	3.7	1090	168 000	40	9	67	53	—	—	—	161	1898.6
—	440	3.4	1.8	8.1	1500	169 000	10	20	200	38	—	—	0.70838	—	1422.9
5.3	280	0.4	1.0	4.3	480	143 000	17	21	314	—	-6.11	-47.60	—	—	795.8
5.1	580	1.7	1.4	2.5	650	158 000	27	8	20	1	-3.39	-41.60	—	—	1249.2
4.8	1170	2.5	0.9	3.3	1220	189 000	2	15	31	31	—	—	—	—	1947.6
4.3	1020	2.4	1.0	11.6	1290	198 000	29	15	30	66	—	—	—	—	1766.1
—	—	—	—	—	620	131 000	106	12	745	—	-6.85	-52.70	—	78	925.5
6.2	560	0.9	2.3	3.7	690	161 000	84	7	364	—	-4.02	-46.30	—	73	1387.0
6.0	580	1.0	2.3	4.2	760	144 000	98	8	510	—	-5.71	-55.80	—	115	1309.1
3.9	340	1.5	—	3.3	490	181 000	11	5	491	11	—	—	—	109	661.4
—	675	—	0.2	—	860	162 000	63	6	317	—	—	—	—	—	1633.8
—	1290	—	0.6	—	1250	178 000	59	5	150	—	—	—	—	—	2352.6
—	1020	—	0.6	—	1190	160 000	43	10	410	—	—	—	—	—	2084.5
—	1230	—	0.2	—	1220	180 000	63	12	122	—	—	—	—	—	2197.3
—	170	—	0.3	—	315	154 000	2	5	810	—	—	—	—	—	573.0
—	760	—	0.2	—	820	131 000	52	4	676	—	—	—	—	—	1683.3
—	1180	—	0.3	—	1460	191 000	39	12	140	—	—	—	—	—	2482.8
—	2350	—	1.4	—	2390	212 000	139	26	40	—	—	—	—	—	4641.5
—	1200	—	0.2	—	1320	175 000	49	11	33	—	—	—	—	—	2314.4
—	910	—	0.5	—	980	120 000	71	8	1130	—	—	—	—	—	1744.1
—	470	—	0.2	—	680	152 000	54	3	364	—	—	—	—	—	1383.7
—	460	—	0.4	—	590	164 000	9	7	660	—	—	—	—	—	1269.0

Table 1. *Continued*

ID	Surface	Production				Depth	TDS	Specific	Temperature	Data	Ca	K	Li	Mg	Na
	elevation	elevation	TWN	RNG	SEC										
<i>Richfield</i>															
4010	274.2	-733	12	10	1	1007	326 500	1.228	32.5	1	53 000	4070	54	7180	58 600
4013	277.7	-738	12	10	1	1016	327 135	1.228	32.7	1	51 800	4020	54	6960	57 800
4018	278.0	-729	12	10	12	1007	146 374	1.100	32.5	1	50 500	3570	50	7090	61 500
4035	425.3	-837	24	-2	33	1263	320 218	1.223	38.3	1	61 400	8320	42	8830	38 400
4036	235.3	-1180	15	4	11	1415	125 260	1.085	41.8	1	27 800	3800	24	3370	12 400
4037	239.7	-1217	16	4	35	1457	294 832	1.205	42.8	1	65 100	7700	32	7700	28 600
4046	348.1	-1212	22	4	8	1560	334 670	1.233	45.2	1	77 600	9300	76	10 700	31 300
4050	384.0	-916	24	-1	26	1300	317 460	1.221	39.2	1	69 600	9020	40	9840	33 000
4068	346.2	-854	20	6	30	1200	379 680	1.265	36.9	1	82 100	8660	44	9740	34 500
4069	346.9	-1194	19	6	19	1541	386 780	1.270	44.7	1	86 100	8700	46	10 700	34 100
4403	338.9	-1171	20	5	8	1509	315 240	1.220	44.0	2	73 800	9110	65	9700	31 000
4406	307.8	-926	22	-2	18	1233	294 297	1.277	37.7	2	96 200	12 800	47	14 600	32 200
4407	381.6	-893	24	-1	14	1274	375 940	1.263	38.6	2	92 000	13 300	54	12 600	25 600
<i>Detroit River</i>															
5019	197.2	-989	14	-8	36	1186	298 670	1.208	36.6	1	72 400	9270	72	10 400	22 200
5030	224.2	-1151	18	1	36	1375	421 420	1.295	40.9	1	107 000	19 300	120	13 300	24 000
5501	295.4	-314	5	-11	36	610	337 100	1.239	24	2	59 300	8080	50	11 000	59 600

Further insight into the possibility that the solutes in the brines originated from evaporated seawater is gained from log-log plots of individual component concentrations vs Br (Fig. 9). The seawater trajectory during evaporation from McCaffrey *et al.* (1987) is also plotted. Chloride and Br values in most of the samples plot along the seawater trajectory and show that the brines are concentrated beyond the onset of halite precipitation. A few of the Richfield and Detroit River samples plot below the trajectory which indicates dilution by either seawater or freshwater (Carpenter, 1978; Kharaka *et al.*, 1987). Because these data are historic analyses which did not report the condition of the wells, it is possible that they have been affected by production-related dilution, or by water derived from gypsum dehydration.

Although the Cl, Na and Br data indicate seawater as the source for the solutes in the brines, it is clear that components such as Ca, Mg and K have been modified from seawater values. Compared with equivalently concentrated seawater, the brines have significantly higher amounts of Ca and Sr and lower amounts of Mg. Calcium and Sr are removed from seawater as carbonates and sulfates early in the evaporation process while Mg remains in solution until late stages of evaporation (Carpenter, 1978). However, the samples in Fig. 9 plot with a high degree of linearity; best-fit-lines to the log Ca-Br data have slopes between 0.8 and 1.0 ($r = 0.8-0.9$), slopes for log Mg-Br range between 0.4 and 0.6 ($r = 0.6-0.7$), and slopes for log Sr-Br range between 1.0 and 1.2 ($r = 0.8-0.9$). Thus the brines appear to have

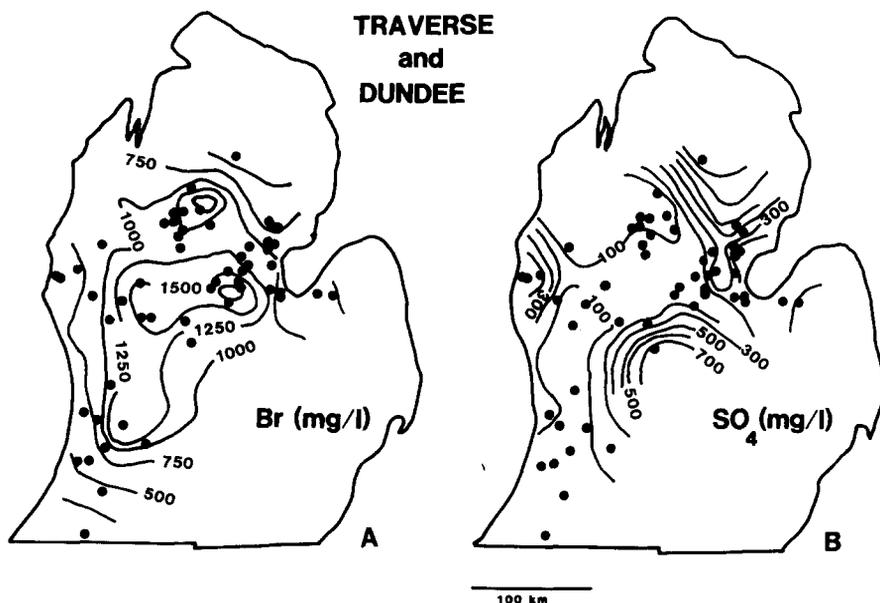


FIG. 7. Concentration distribution (A) Br and (B) SO₄ in the combined Dundee and Traverse brine data set. Values in mg/l.

Table 1. Continued

pH	Sr	Rb	Cs	Si	Br	Cl	ALK	I	SO ₄	B	δ ¹⁸ O (‰)	δD (‰)	⁸⁷ Sr/ ⁸⁶ Sr	NH ₄ N	MCl ₂
<i>Richfield</i>															
5.1	1720	10.4	3.9	2.5	1930	200 000	56	29	112	75	—	—	—	214	3272.9
5.0	1640	10.9	3.9	1.6	1920	203 000	48	17	74	81	1.49	-27.00	0.70819	203	3193.9
5.0	1640	9.2	3.6	2.1	1870	202 200	45	11	109	65	—	—	—	198	3138.9
4.2	2130	23.8	5.5	2.3	1240	200 000	114	40	33	371	4.31	-51.70	0.70809	401	3839.4
5.9	1040	8.9	8.9	8.5	1050	75 800	229	8	348	137	—	—	—	115	1682.9
4.6	2580	21.7	5.5	3.2	2610	182 000	213	25	161	180	—	—	—	242	3939.4
3.7	2800	3.4	6.4	1.4	3200	220 000	244	13	0	377	—	—	—	333	4818.7
—	2300	6.5	8.8	0.9	2700	191 000	240	10	0	137	—	—	—	—	4337.3
4.7	3480	10.5	2.2	2.9	1200	240 000	240	28	0	39	—	—	—	—	4979.7
4.3	3980	11.0	2.2	2.4	1200	242 000	240	30	0	82	2.93	-41.60	—	—	5269.7
—	2940	—	—	—	2690	186 000	278	19	0	—	—	—	—	—	4550.2
—	290	—	—	—	4210	235 000	385	66	4	—	—	—	—	—	6011.5
—	3390	—	—	—	4050	225 000	207	68	34	—	—	—	—	—	5706.0
<i>Detroit River</i>															
4.9	2340	33.8	6.4	1.6	3060	179 000	326	57	2	383	2.58	-51.70	—	441	4524.6
3.9	3070	41.2	—	2.3	3750	251 000	100	25	54	134	4.36	-16.70	0.70782	689	6503.5
—	1390	—	0.3	—	2440	195 000	98	29	110	—	—	—	—	—	5378.8

Key

ID: identification number of sample.
 Surface elevation: ground surface elevation of well (m. asl).
 Prod. elevation: elevation of producing zone (m. asl).
 TWN: township of well location, + North, - South.
 RNG: range of well location, + West, - East.
 SEC: section of well location.
 Depth: depth of well intake (m).
 TDS: total dissolved solids (mg/l), calculated from analysis.
 Data Source: (1) analysis generated in this research, (2) data obtained from MDNR or oil-company files.
 Temperature: estimated bottomhole temperature (°C).
 % Charge Imbalance, defined as $(\sum \text{cation epl} - \sum \text{anion epl}) / (\sum \text{cation epl} + \sum \text{anion epl}) \times 100$.
 Chemical data: all values reported as mg/l, except pH and MCl₂. ND = not detected. —: not measured
 Isotope data: δ¹⁸O and δD in ‰, SMOW. ALK: alkalinity as HCO₃.
 MCl₂ = Ca + Mg + Sr - (0.5 × HCO₃ - SO₄), all in meq/l.

gained Ca and Sr and lost Mg in a systematic manner. The linear relations of Ca, Sr and Mg with Br (Fig. 9) are suggestive of dolomitization (COLLINS, 1975; CARPENTER, 1978).

WATER-ROCK REACTIONS

The graphical analysis indicates that water-rock reactions have caused K, Ca, Sr, Mg and MCl₂ to differ from values expected for evaporated seawater.

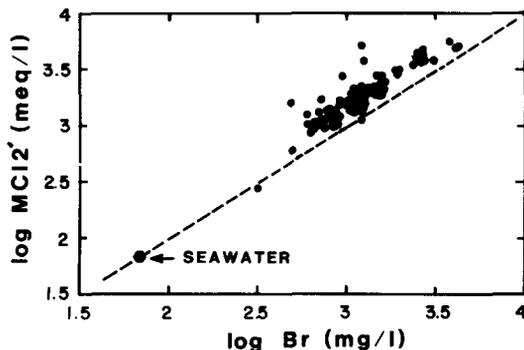


Fig. 8. Log MCl₂ (meq/l) vs log Br (mg/l). MCl₂ represents the sum of divalent cations balanced by Cl. Values are corrected for charge imbalance as described in text.

Considering mineralogy and basin history, reactions might include dolomitization, aluminosilicate reactions and evaporite mineral diagenesis.

Dolomitization

If these brines are simply evapo-concentrated seawater then they should contain little, if any, Ca (McCAFFREY *et al.*, 1987), which is clearly not the case. Dolomitization of calcite or aragonite by the following reaction is one process by which Ca may be added to the waters: $Mg^{2+} + 2CaCO_3 = CaMg(CO_3)_2 + Ca^{2+}$. Based on this stoichiometry, it should be possible to predict the amount of Ca in the brines released during dolomitization based on the relative depletion of Mg from equivalently concentrated seawater (COLLINS, 1975). This was evaluated by first calculating the difference between measured Mg in each sample and Mg in equivalently concentrated seawater, using Br as the indicator of degree of concentration. This difference was converted to a predicted Ca concentration based on a 1 for 1 mole replacement. The predicted Ca is converted to concentration and compared with the measured Ca in Fig. 10.

The predicted and measured Ca values agree quite well, supporting the hypothesis that dolomitization

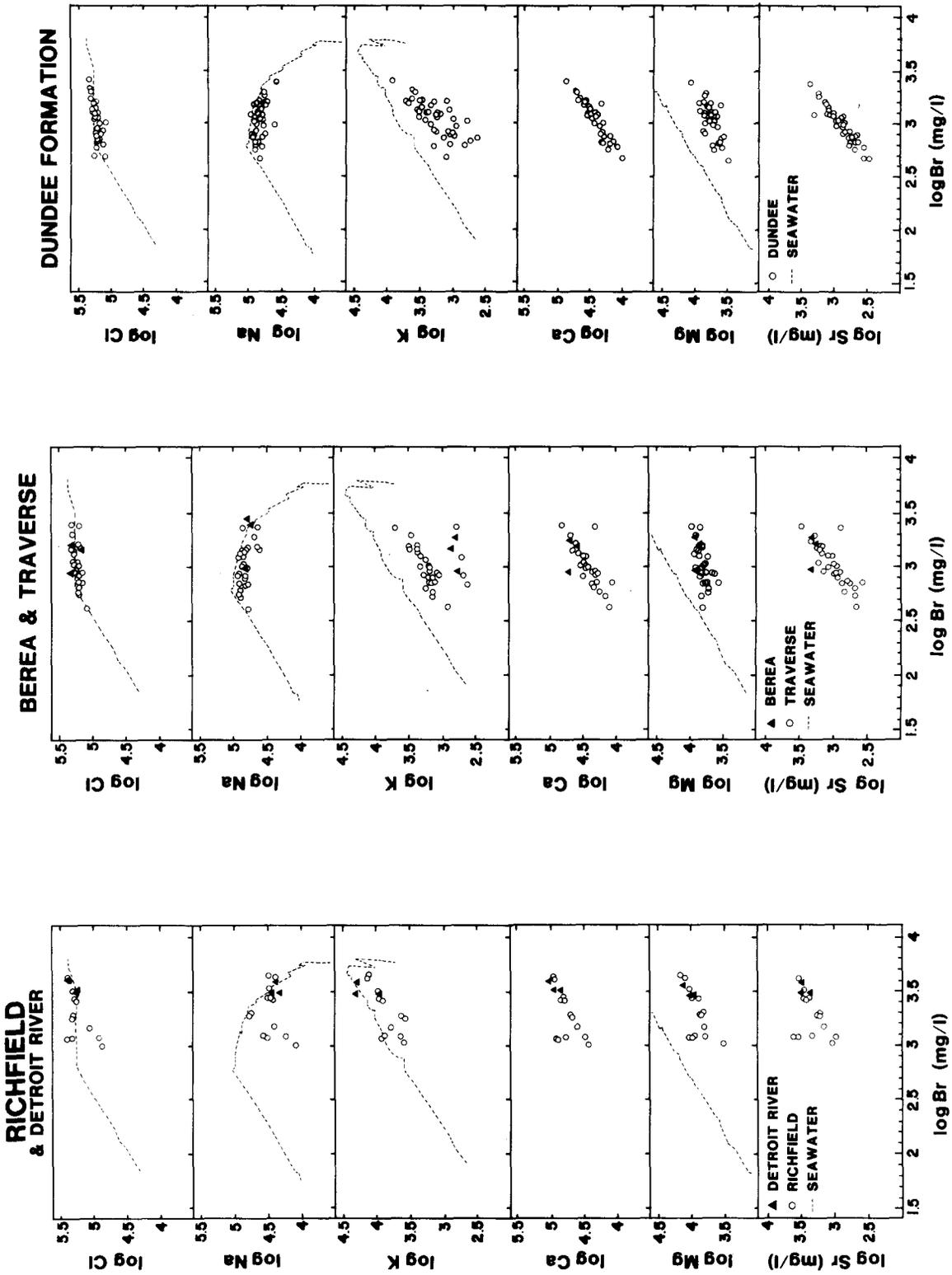


Fig. 9. Log concentration (mg/l) vs log Br (mg/l) in brines from Devonian strata in Michigan. Also shown are the seawater trajectories from McCaffery *et al.* (1987).

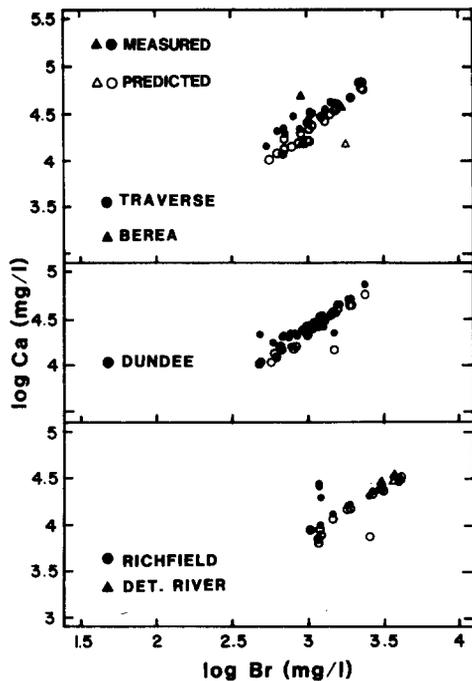


Fig. 10. Results of the dolomitization model, comparing the predicted Ca concentrations with the measured Ca in the brines. The predicted values are based on a 1:1 replacement for the Mg depleted from equally concentrated seawater.

has been a major control on the brine chemistry. However, closer inspection shows that these calculations under-predict Ca in some samples, especially the Traverse Formation samples. Analytical error may explain some of this difference, but more likely, other reactions have affected the Ca and Mg concentrations, such as dissolution of CaSO_4 and precipitation of Fe-rich dolomite. A better agreement is obtained when Ca supplied by CaSO_4 dissolution is accounted for by subtracting equivalents of measured SO_4 from the measured Ca. The precipitation of Fe-rich dolomite: $2\text{CaCO}_3 + \text{Mg}_{(1-x)}^{2+} + \text{Fe}_x^{2+} = (\text{CaMg}_{(1-x)}\text{Fe}_x)(\text{CO}_3)_2 + \text{Ca}^{2+}$, reduces the amount of Mg depletion attributed to dolomitization, resulting in a smaller predicted Ca value by the model. The Fe content of Devonian dolomites in Michigan is not known, but dolomite with ~10–15% Fe occurs in the basin (TAYLOR, 1982).

Strontium in the brines may also be attributed to dolomitization of aragonite. The Michigan brines contain very high concentrations of Sr compared to values in evaporated seawater, which would be devoid of Sr at these levels of concentration (ZHERBTSOVA and VOLKOVA, 1966). SASS and STARINSKY (1979) demonstrated that Sr/Ca ratios can be used to identify the carbonate reactions that supply Sr to formation water. Molar Sr/Ca in the brines ranges between 0.01 and 0.023, with ratios independent of the formation studied. The bulk of the samples fall within the Sr/Ca range predicted by SASS and STARINSKY (1979) to occur from dolomitization of arago-

nite. This implies that the brines reacted with Sr-rich minerals, perhaps aragonite that had not yet undergone diagenesis. A few samples have lower Sr/Ca ratios which are consistent with dissolution-precipitation of Sr-rich calcite.

The result of the dolomitization model has implications for other components such as SO_4 . The brines have very low SO_4 concentrations, which has been related to the precipitation of CaSO_4 during dolomitization (MATTHEWS, 1977). While some SO_4 may have been removed during dolomitization, the fact that most of the Ca can be explained by the amount of Mg depleted from seawater suggests that SO_4 was probably removed before dolomitization occurred. Bacterial reduction is a more viable explanation for the low SO_4 concentrations.

High Ca/Na ratios are another characteristic that may be attributed to dolomitization. GRAF *et al.* (1966) noted an increase in Ca/Na with increasing TDS and depth in Michigan Basin brines. They suggested that this results from membrane filtration, where Ca is selectively retained behind shale layers while Na is able to pass through and out of the basin. This relation is also explained by evapo-concentrated seawater enriched in Ca by dolomitization. In the "normal" evaporation scheme of seawater, Mg steadily increases during evaporation (increasing with TDS and Br) while Ca is almost completely removed early by gypsum or anhydrite precipitation. Sodium in seawater also increases during evaporation, but decreases during halite precipitation. As discussed earlier, Ca in the Michigan brines can be explained by direct exchange for Mg during dolomitization. The samples having the largest Br and TDS content also have the greatest loss of Mg and enrichment of Ca over seawater (Fig. 9). The amount of Ca in these brines represents charge that was originally present as Mg before dolomitization affected the brines; therefore the Ca and TDS increase in the brines just as Mg had originally increased with TDS, at concentrations that exceed Na. When the effects of dolomitization were coupled with the removal of Na by halite precipitation, the observed trend of increasing Ca/Na vs TDS was developed in these waters.

Aluminosilicate reactions

Potassium plots are parallel to, but below, the seawater path. Depletion of K has been found to occur early in the evaporative evolution of seawater in modern environments, due to adsorption or ion exchange reactions (LONG and GUDRAMOVICS, 1983; EUGSTER and JONES, 1979; EUGSTER and HARDIE, 1978). Other possible reactions include the formation of K-feldspar, illite and chlorite, and cation exchange (KHARAKA *et al.*, 1973; MERINO, 1975; LAND and PREZBINDOWSKI, 1981).

The formation of illite and/or authigenic feldspar coupled with reactions involving calcite may explain

the K depletion and $MgCl_2$ enrichment. Examples include the conversion of kaolinite to illite (CARPENTER, 1978): $2K^+ + CaCO_3 + 3Al_2Si_2O_5(OH)_4 = 2KAl_2(AlSi_3)O_{10}(OH)_2 + Ca^{2+} + 4H_2O + CO_2$; and smectite to illite (HOWER *et al.*, 1976): $3[Ca_{0.33}(Mg_{0.33}Al_{1.66})Si_4O_{10}(OH)_2 \cdot nH_2O] + 2K^+ + Al^{3+} + CaCO_3 = 2[KAl_2(AlSi_3)O_{10}(OH)_2] + 6SiO_2 + 2Ca^{2+} + Mg^{2+} + CO_2 + (n+1)H_2O$; and the formation of authigenic feldspar. Although rare in the Devonian carbonates of Michigan (Sibley, pers. commun., 1988), feldspars have been found in the clastic and carbonate units in the basin that may be authigenic (NOWAK, 1978; SAWELLE, 1958; Longstaff, pers. commun., 1991). The depletion of K from brine in clastic units such as the Berea, Traverse and Sylvania supports that these reactions have affected the brines. Feldspar diagenesis must be considered, but at this point, its volumetric effect on the brines cannot be quantified.

Aluminosilicate reactions may also help explain the excess divalent cation ($MgCl_2$) in the brines. A mass balance model similar to that used to test dolomitization was used to determine if illitization could explain the depletion of K and the slight excess of Ca not explained by dolomitization. In the kaolinite-illite reaction written above, 2 moles of K are used to produce 1 mole of Ca. When the amount of K depleted from equivalently concentrated seawater is plotted vs the Ca underestimated by the dolomitization model, the bulk of samples agree with the predicted 2:1 relation. This also helps support that illitization is a likely cause for the K deletion and Ca excess.

Other salts

Considering the large volumes of salts in the basin, the diagenesis of evaporite minerals may have affected the brine chemistry. Most important may be the transformation of gypsum to anhydrite and the replacement of gypsum by glauberite or polyhalite. Water released during the thermal metamorphism of gypsum to anhydrite can dissolve $CaSO_4$ minerals along with halite if present (BORCHERT and MUIR, 1964). The units that contain large amounts of anhydrite may have been affected by this source of water. For example, the "massive anhydrite" at the base of the Horner Salts is >30 m thick and contains ~3200 km³ of anhydrite (WILSON, 1989). If originally gypsum, then $\sim 1.5 \times 10^{15}$ l of $CaSO_4$ -saturated water would have been liberated, representing ~18% of the estimated total water in the Devonian rocks of the basin (WILSON, 1989). This might explain the several Richfield-Detroit River samples that plot below the seawater Cl-Br trajectory (Fig. 9). The replacement of gypsum by glauberite or polyhalite also liberates Ca-rich water: $2CaSO_4(H_2O)_2 + 2Na^+ = Na_2Ca(SO_4)_2$ (glauberite) + $Ca^{2+} + 2(H_2O)$; and $4CaSO_4(H_2O)_2 + Mg^{2+} + 2K^+ =$

$K_2MgCa_2(SO_4)_4$ (polyhalite) + $2Ca^{2+} + 8(H_2O)$. Both glauberite and polyhalite are present in the Salina salts of Michigan (DELLWIG, 1955). However, a detailed examination of mineralogy of the Devonian salts is needed before these reactions can be confirmed.

In order to evaluate the possibility of equilibria with evaporite minerals, the brine chemistry was modeled using the PHRQPITZ computer program (PLUMMER *et al.*, 1989). This model uses the specific interaction approach for calculating activity coefficients (PITZER, 1973) and is well suited for evaluating evaporite minerals (HARVIE and WEARE, 1980). Only samples collected in this study with complete analyses were modeled, using estimated temperatures. The model adjusts thermodynamic variables for temperature but not for pressure and only the Na and Cl activity coefficients are adjusted for temperature. The model does not evaluate aluminosilicate equilibria.

Calculated disequilibrium indices (log IAP/Ksp) (Fig. 11) indicate that the brines are apparently saturated with anhydrite, gypsum and halite and are undersaturated or approach saturation with glauberite, polyhalite, carnallite and sylvite. Until a detailed examination of the mineralogy of the Devonian salt deposits in the basin can be made, it remains possible that reactions involving these minerals have affected the brine chemistry.

STABLE ISOTOPE RESULTS

The δD and $\delta^{18}O$ values for the brines collected in this study are shown in Figs 12 and 13. To help determine the source of water in the brines, the values are compared to δD and $\delta^{18}O$ values for near-surface ground water in the Michigan Basin from the Saginaw Lowland Area, SLA (LONG *et al.*, 1988); the Greater Lansing Area, GLA (Long and Larson, in prep.); and the Leelenau Peninsula Area, LPA (REGALBUTO, 1989), shown on Fig. 12. The modern meteoric water line (MWL) is from CRAIG (1961) and is defined by the equation $\delta D = 8 \times \delta^{18}O + 10$.

The GLA and LPA groundwaters plot as tight, but distinct clusters along the MWL (Fig. 12). The GLA and LPA data are typical for near-surface aquifers in the basin which are recharged by modern meteoric water at mid-basin latitudes (LONG *et al.*, 1988). The SLA groundwaters also plot along the MWL, but show a large range, from present-day values to extremely light values ($\delta D = -140\text{‰}$; $\delta^{18}O = -19\text{‰}$). These data are presented because in areas of Michigan, modern recharge waters are found to be mixing with isotopically lighter water which entered the basin when the climate was cooler, >10,000-a ago (LONG *et al.*, 1988; CLAYTON *et al.*, 1966).

The brine samples plot to the right of the meteoric water line and below SMOW, which is typical for

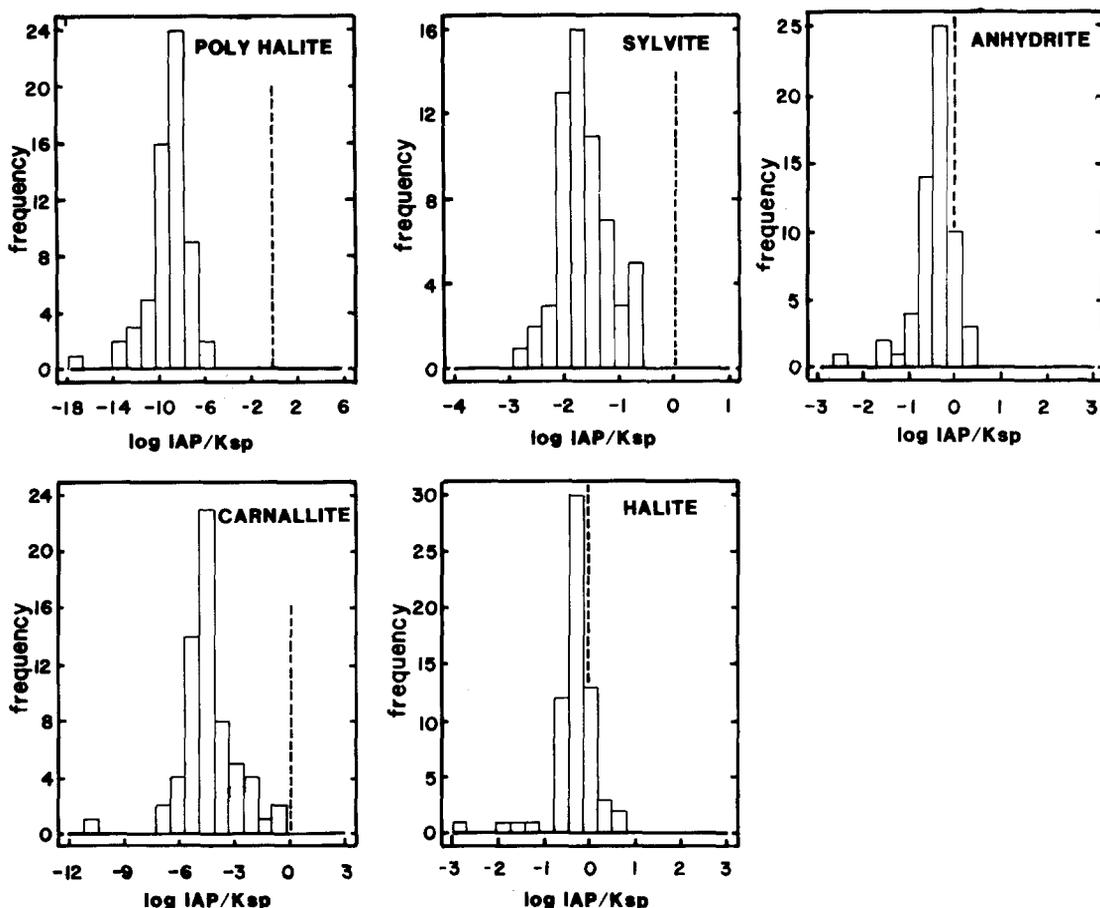


FIG. 11. Histograms of saturation indices ($\log IAP/K_{sp}$) calculated using the PHRQPITZ program of PLUMMER *et al.* (1989).

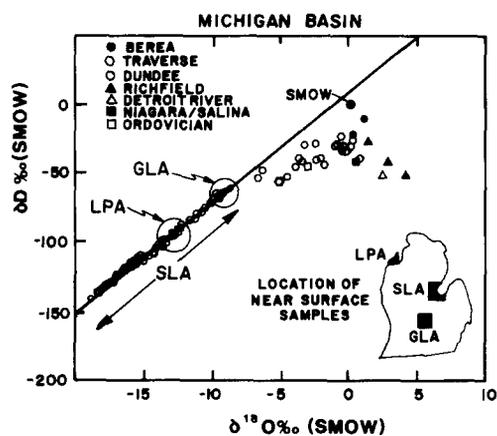


FIG. 12. Plot of δD vs $\delta^{18}O$ (‰, SMOW) in Michigan Basin waters. Also shown are the isotope composition of near-surface ground waters from the Greater Lansing Area (GLA) the Leelanau Area (LA) and the Saginaw Lowland Area (SLA), which all plot on the meteoric water line. The global meteoric water line from CRAIG (1961).

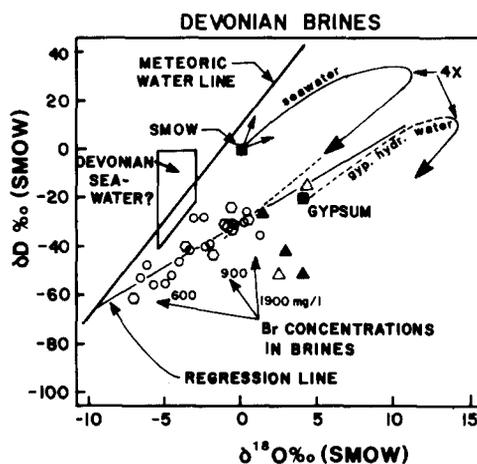


FIG. 13. Plot of δD vs $\delta^{18}O$ (‰, SMOW) for the Devonian brines collected in this study. Also shown is the field of compositions that Devonian seawater may have had (POPP *et al.*, 1986; CARPENTER *et al.*, 1991), a suggested evapo-concentration path for seawater (KNAUTH and BEEUNAS, 1986), the composition of gypsum hydration water as a function of evaporation stage, and the best-fit regression line to the Devonian formation waters. The three lower arrows point toward samples having the indicated Br concentrations, and illustrates the concentration gradient that exists along the sample trend.

basin brines (KHARAKA *et al.*, 1987; KNAUTH and BEEUNAS, 1986). The more saline samples from the Richfield zone and Detroit River Group have more positive $\delta^{18}\text{O}$ values and show the most scatter, while the less concentrated Traverse and Dundee brines plot along a linear trend that appears to intersect the meteoric water line near the GLA data. The brine data are similar to that of CLAYTON *et al.* (1966), however, no samples were found that plot on the MWL or have extremely light values.

Various interpretations can be made from the patterns on Fig. 12 as to the source of water for the brines (KNAUTH and BEEUNAS, 1986), including the following:

1. Evaporated meteoric water: the trend of the isotope values in the brines is consistent with an origin from evaporated meteoric water; that is, δ values become more positive while maintaining a covariance between δD and $\delta^{18}\text{O}$ (GONFIANTINI and FONTES, 1963). In addition, as the samples become more concentrated (as indicated by Br values) the δ values become more positive, which is consistent with evaporation. However, the Br-Cl chemistry of the brines is not consistent with this interpretation. For example, typical values for Na and Cl in present-day Michigan surface waters are ~ 9 and 30 mg/l, respectively (WOOD, 1969). Assuming these values are typical of meteoric water entering the Michigan Basin in the geological past, the PHROPITZ model (PLUMMER *et al.*, 1989) can be used to calculate the trajectory that this water would follow during evaporation. The results show that \log_{10} Cl (mg/l) in this water concentrated to halite saturation would be > 5.5 . Therefore, brines generated from the evaporation of typical surface water would plot above the seawater curve. In addition, if the meteoric water had a Br concentration of 0.02 mg/l, which is representative of typical surface waters (GARRELS and MACKENZIE, 1971), then the calculated evaporation trajectory would plot to the left of the seawater curve. The data do not plot in either of these areas in Fig. 9, thus it is unlikely that meteoric water was the major water source for the Michigan Basin brines.

2. Evaporated seawater brine: the isotope composition of seawater also becomes more positive during evaporation. The δD - $\delta^{18}\text{O}$ composition of evaporating seawater varies as a function of initial composition, humidity, rate of evaporation, isotope values in the vapor phase, and degree of seawater circulation and mixing within the basin (LLOYD, 1966; SOFER and GAT, 1972, 1975; NADLER and MAGARITZ, 1979). Considering these complex environmental factors, it is not surprising that the isotope composition of seawater may vary greatly during evaporation (KNAUTH and BEEUNAS, 1986). It has also been suggested that the isotope composition of seawater differed in the past from the present-day SMOW value. CARPENTER *et al.* (1991) and others (POPP *et al.*, 1986) suggested that Middle Devonian seawater may have been depleted by 2–5.5‰ in $\delta^{18}\text{O}$ relative to

modern seawater. If δD -covaried directly with $\delta^{18}\text{O}$ in ancient seawater, then Devonian seawater may have had an isotope composition plotting anywhere in the field shown on Fig. 13.

The trajectory for evaporating modern-day seawater from HOLSER (1979) and others (e.g. GONFIANTINI, 1965; NADLER and MAGARITZ, 1979; PIERRE *et al.*, 1984; KNAUTH and BEEUNAS, 1986) starts at SMOW (Fig. 13) and increases until an evaporation ratio of about $4\times$ is reached, after which it “hooks” and becomes isotopically lighter with continued evaporation. The hook is thought to be caused by the exchange of water between the atmosphere, water of hydration, and unbound water (HOLSER, 1979). The exact shape and path is a complex function of the environmental factors listed above and the degree of concentration (KNAUTH and BEEUNAS, 1986). NADLER and MAGARITZ (1979) have demonstrated the complex and variable nature of this trajectory in seawater evaporated in salt-pans. They found that after seawater concentrates to the start of halite precipitation, its isotope composition was near SMOW.

Included in Fig. 13 is the extension of the trajectory of HOLSER (1979) to an extreme evaporation ratio of $45\times$. This extension was proposed by KNAUTH and BEEUNAS (1986) and differs from the path reported by NADLER and MAGARITZ (1979). Interestingly, the extended trajectory intersects the more concentrated Richfield and Detroit River samples and continues down the trend of the Traverse and Dundee data. Without knowledge of the content of dissolved solids and the chemical trends in these brines, the isotope composition of these samples could be interpreted to show that the brines are seawater concentrated to extremely high degrees by evaporation. In fact, the degree of concentration of these samples as demonstrated by the Br values indicated in Fig. 13, decreases down the trajectory opposite the relation expected for continued evaporation. The fit of the data to this trajectory must be explained by other processes.

It is also interesting to consider how a change in the starting composition of seawater might affect this interpretation. If the seawater source for the brines had an initial isotope composition within the field for Devonian seawater suggested by CARPENTER *et al.*, (1991), then the starting point for the evaporation curve would be shifted toward lighter isotope values. This would shift the seawater trajectory sufficiently to where the samples would plot along the curve at an evapo-concentration ratio of $10\times$ to $20\times$, a range more consistent with the salinity and Br in the brines. Thus some of the isotopically heavier samples might have a composition similar to seawater evaporated to this degree. However, the decrease in isotope composition and Br content of the samples along the regression line is not consistent with simple evaporation.

3. Meteoric water enriched by isotope exchange with carbonates: CLAYTON *et al.* (1966) suggested that

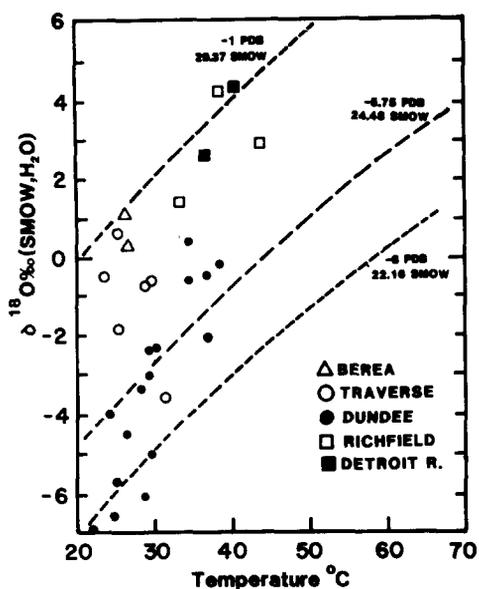


Fig. 14. Plot of $\delta^{18}\text{O}$ of water (‰, SMOW) versus formation temperature ($^{\circ}\text{C}$) for the Devonian samples. The dashed lines show the composition of water in isotope equilibrium with calcite having a $\delta^{18}\text{O}$ composition of -1 , -5.75 and -8% PDB, respectively.

the Michigan brines originated from meteoric water based on two reasons. First, they noted that the best-fit lines to isotope data from many basins, including Michigan, intersect the meteoric-water line at values similar to modern precipitation in each basin. Second, they noted that when water-rock ratios are low, diagenetic dissolution-precipitation and isotope exchange reactions involving marine carbonates will increase the $\delta^{18}\text{O}$ of the reacting water. Based on this, GRAF *et al.* (1966) presented the hypothesis that the original water in the basin had been flushed out by meteoric water that had become enriched in ^{18}O by exchange with carbonate minerals.

While problems exist with an origin via shale filtration (HANOR, 1982) it nevertheless remains possible that the $\delta^{18}\text{O}$ signature of the brines has been enriched by exchange with carbonate minerals (HITCHON and FRIEDMAN, 1969; LAND, 1980). In order to test for isotope equilibrium, the $\delta^{18}\text{O}$ value of water in equilibrium with calcite was calculated as a function of temperature, and compared with measured brine values (Fig. 14). The $\delta^{18}\text{O}$ of equilibrated water was calculated using: $\alpha \times (\delta^{18}\text{O}_{\text{rock}} + 1000) = (\delta^{18}\text{O}_{\text{water}} + 1000)$, where the fractionation factor (α) is given by: $10^3 \ln \alpha = 2.78 \times 10^6 T^{-2} - 2.89$ (O'NEIL and EPSTEIN, 1966). A $\delta^{18}\text{O}_{\text{rock}}$ value of -5.75% PDB (24.93 SMOW) was used, which is an average value reported for Detroit River Group calcites by GARDNER (1974). Because very few other measurements of Devonian carbonates in Michigan have been reported, the calculations were repeated using values of -1 and -8% PDB, typical values of Paleozoic calcite (BATHURST, 1975). The brines have a wide range of $\delta^{18}\text{O}$ values over a narrow range of

formation temperatures, and plot across the trend of the equilibrium line for Detroit River calcite (Fig. 14). There does not appear to be a single calcite value that will allow all of the brine values to be predicted. While the data do not clearly follow the equilibrium lines, they do plot between reasonable limits for Paleozoic carbonates, suggesting that equilibrium with calcite is possible. The scatter in the data on this plot might indicate that the brines equilibrated with a variety of calcite or dolomite compositions, or that the subsurface temperatures used were incorrect. This latter explanation might imply the brines equilibrated with carbonates at higher temperatures, perhaps at those thought to have occurred in the past at depth (HOGARTH, 1985) or at the surface (CARPENTER *et al.*, 1991). The fact that the data plot between equilibrium lines calculated for realistic calcite values suggests that isotope equilibrium is possible and the $^{18}\text{O}/^{16}\text{O}$ of the brines may have been altered from their original values.

4. Water from gypsum dehydration: if the abundant anhydrite in the Michigan Basin formed from gypsum, then the water released during dehydration may have altered the isotope signature of the formation brine. Gypsum hydration water is enriched in $\delta^{18}\text{O}$ over the seawater from which it precipitates (GONFIANTINI and FONTES, 1963; HOLSER, 1979). During the transformation of gypsum to anhydrite, the water released would have an isotope composition falling along the trajectory in Fig. 13. Water on this path is $\sim 10\%$ enriched in $\delta^{18}\text{O}$ over the most enriched sample collected. Thus an input of water derived from gypsum would shift the brine values in Fig. 13 toward the right. Also, if the seawater source had a lighter isotope composition (CARPENTER *et al.*, 1991; POPP *et al.*, 1986), then the hydration water curve would shift toward lighter values, causing it to intersect the most enriched brine samples. At this point, it is not possible to determine if gypsum dehydration has affected the isotope composition of the brines.

5. Mixing of concentrated seawater brine with meteoric water: KNAUTH and BEEUNAS (1986) interpreted the linear trend in δ values in brines to indicate mixing of isotopically-heavy evapo-concentrated seawater with isotopically light meteoric water. For the Michigan brines, the dilute meteoric-water end-member appears to be isotopically similar to the modern-day ground water of the GLA area, based on where the best-fit line intersects the MWL. The linear trend of the data does not suggest that the diluting water had as wide a range of compositions as those exhibited by the SLA waters. The composition of the saline end-member is difficult to evaluate, because it may plot anywhere along or near the hooked evaporation trajectory after the start of halite precipitation ($10\times$). As discussed earlier, this trajectory is poorly known and there is no *a priori* reason to expect that a single δ signature would represent the saline end-member for a basin. The isotope compositions of the

samples plotting near the right end of the linear trend may be those of concentrated seawater, perhaps modified by mineral exchange and gypsum dewatering.

DISCUSSION

The interpretation of the isotope data presented here is the Devonian formation brines originated from seawater that has mixed with meteoric water, which is an evolution that has been advanced for other saline formation waters (for example, KNAUTH and BEUNAS, 1986). This is consistent with: the salinity of the brines, as represented by Br, decreases as the isotope values become lighter and plot closer to the meteoric water line (Fig. 13); the trend followed by the isotope data intersects the meteoric-water line near modern precipitation values (Fig. 13); and brine from shallow depths at the edge of the basin is more dilute than brine found deeper in the basin center (Fig. 7A). This interpretation forces a re-evaluation of the interpretation made from the geochemical data, which was that the brines are seawater *concentrated* to various degrees by evaporation and were modified only by water-rock reactions (WILSON and LONG, 1986). Many of the Traverse and Dundee samples are apparently mixtures of concentrated seawater brine and meteoric water, which raises several questions: what is the chemical/isotopic nature of the end-member waters? Can the interpretations from the isotope and chemical data be made consistent with one another? And what is the time frame in which dilution has occurred? Although discussed here, the latter question is addressed in more detail elsewhere (LONG and WILSON, in prep.).

Evidence for a seawater source comes, in a large part, from the apparent agreement between Cl-Br in the brines and seawater (Fig. 9). Because of the possible variance in composition of seawater during evaporation, and because evaporative conditions occurred often in the basin history, the exact end-member is difficult to characterize. Most likely it cannot be characterized by one isotope or chemical composition as it may have been seawater originally trapped in the Upper Devonian sediments or in the salts of the Detroit River, Richfield, or Silurian units.

Evidence for a freshwater input comes from the extrapolation of the isotope data and from the linear trends in the major-ion chemistry when plotted vs Br. The intersection of the isotope data with the MWL at values typical of present-day ground water in the basin suggests that modern-day meteoric-derived water is responsible, as was suggested by CLAYTON *et al.* (1966). If this is the case, then the dilute end-member may have had a chemical composition similar to the present-day shallow ground waters in the basin.

Insight into the amount of brine that has been diluted can be obtained from plots of log Cl-Br

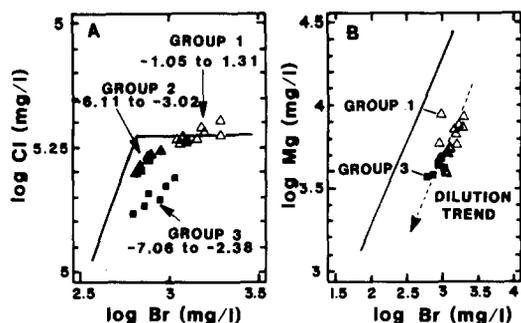


Fig. 15. (A) Log Cl and (B) log Mg vs log Br (mg/l) for the Dundee and Traverse formation brines. Note the expanded scale. The three groups are based on range of $\delta^{18}\text{O}$ values.

(CARPENTER, 1978). Seawater concentrated past the start of halite saturation and subsequently diluted will plot below and to the right of the seawater trajectory either along a curve approaching the dilute end-member (CARPENTER, 1978) or in a cluster (SANDERS, 1986). At first, dilution is not suggested because the samples appear to plot along the seawater Cl-Br trajectory (Fig. 9). Closer inspection of the Cl-Br and Na-Br plots (Fig. 9) shows that many of the samples having lower Br content do plot in a linear pattern slightly below the seawater trend line. Figure 15A is an expanded scale Cl-Br plot for the Traverse and Dundee samples analyzed for $\delta^{18}\text{O}$ and δD . The data appear to fall into three clusters. The two clusters which plot below the trajectory are isotopically lighter, as indicated by both $\delta^{18}\text{O}$ and δD , than the third group which plots on the trajectory. The isotopically heavier brines that plot on the seawater curve probably resemble the evaporated seawater end-member, while the two isotopically light clusters that plot below the trajectory may represent diluted brine. A similar interpretation can be made from the Na-Br plot (Fig. 9). The isotopically lighter samples of groups 2 and 3 were collected from shallow wells (avg. depth of 837 m and 705 m, respectively) near Lake Michigan and from the eastern SLA area (Figs 4 and 12), while the isotopically heavier group 1 samples were collected from deeper wells (avg. depth of 965 m) near the basin center. The cause for the clusters below the trajectory is not clear at this time, but it does not appear to be related to the sampling location.

The angle of trajectories followed by data on log-log concentration plots can be altered by mineralogical reactions, which may have caused an apparent lack of dilution on the Cl-Br diagram. This is especially the case for brine in salt basins such as Michigan where dilution can be masked by halite dissolution. For example, consider a seawater brine which plots on the seawater evaporation trajectory well into the halite saturation facies. If this brine were to become diluted by meteoric water but re-equilibrates with halite (either at the surface or underground) which adds Na and Cl to solution, then as long as the dilution did not lower Br in the mixture below the

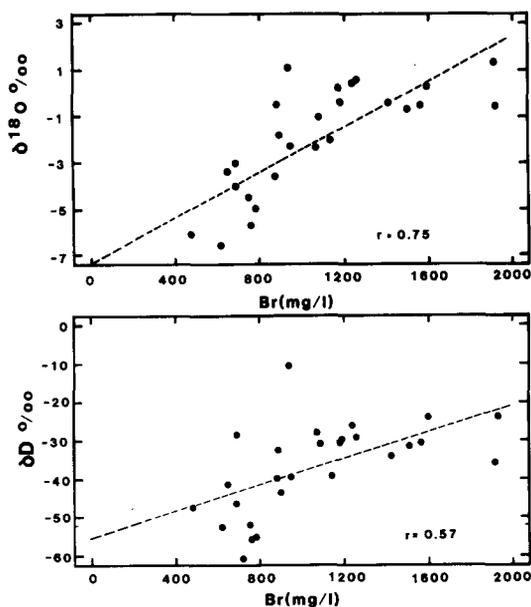


Fig. 16. Plot of $\delta^{18}\text{O}$ (‰, SMOW) vs Br (mg/l) and (B) δD vs Br (mg/l) in the Traverse and Dundee samples. Dashed lines are the best-fit linear regression to the data.

range of evapo-concentrated seawater, the diluted seawater could match primary concentrated seawater in Na, Cl and Br. This may be the case for the Michigan brines, because inspection of the Cl-Br plot does not immediately indicate that the brines have been diluted, although the Br and SO_4 distribution (Fig. 7) and the linear trends in the isotope and chemical data (Figs 8 and 9) are consistent with dilution. Where a linear dilution trend is not clearly indicated, such as in the Mg data, the isotopic values again help show the effects of dilution. Figure 15B shows that samples having lower Mg values also have lighter isotope values, which is consistent with dilution.

The relation between Br and $\delta^{18}\text{O}$ - δD provide further evidence that the chemical and isotope data can be linked. To determine what the isotope composition would be in the diluting water, the δD and $\delta^{18}\text{O}$ values were regressed individually against Br to a value of $\text{Br} = 0 \text{ mg/l}$, a value indicative of meteoric water (Fig. 16). The intercepts of the best-fit lines predict a composition of $\delta\text{D} = -56\text{‰}$ and $\delta^{18}\text{O} = -7.2\text{‰}$ for the diluting water. These values plot on the meteoric water line and are typical of near-surface ground water found in the GLA and SLA areas of Michigan (Fig. 12). In this light, the chemical and isotope data appear to be consistent and indicate dilution.

BRINE ORIGIN AND EVOLUTION

Two scenarios for the origin and evolution of the brines emerge from the interpretations of the chemical and isotope data. The first is that the brines

formed syngenetically during the deposition of the Devonian sediments. Residual brine may have been entrapped in the Lower Devonian salts and adjacent strata where evaporitic conditions clearly occurred. Brine in the Upper Devonian units may have been generated in the coastal sabkhas and lagoons which existed around the basin margin (Fig. 3; GARDNER, 1974). The dense seawater brine would have infiltrated and migrated down into the underlying sediments, reacting with carbonates and clays. The brine was apparently diluted by meteoric-derived water which entered around the basin margins, possibly reacting with halite. The underlying Devonian-Silurian salt layers, the basin shape, and the lack of a strong hydraulic gradient in the basin (WILSON and LONG, 1986) would have kept the brine from either refluxing deeper into the basin or being flushed from the basin over time.

The second scenario is that the brine in the Devonian strata originated as residual seawater brine squeezed from the deeper Silurian salts during their compaction. The chemistry of the brine may have been set by reactions with sediments before it was entrapped in the salts. Upon compaction of the salt, brine would have been forced into overlying strata where it either mixed with meteoric water already present in these rocks, or was diluted by infiltrating meteoric water. Several observations lend support to this origin. It is questionable whether the environmental conditions during the Late Devonian were extreme enough to produce the large volume of highly concentrated brine presently found in these strata. Conditions favoring the evapo-concentration of seawater into the halite facies are far more consistent with the Lower Devonian and especially the Silurian geology in the basin. The volume of water in the Upper Devonian rocks, for example, based upon the volumes listed in WILSON (1989) and assuming 10% porosity, represent <10% of the present volume of Silurian salt in the basin. Thus, fluids displaced from a small volume of Silurian salt during basin compaction could explain the Devonian formation brines.

SUMMARY

The following conclusions are made concerning these Michigan Basin brines:

1. The Cl, Na and Br values suggest that brine in these units originated from evapo-concentrated seawater. This is further supported by the relation between the other components and Br.

2. The Ca, Mg, Sr, K and MCl_2 values suggest that the concentrated seawater source which formed these brines was modified by water-rock reactions, most importantly by dolomitization and aluminosilicate reactions.

3. The isotope compositions support the view that brine in the Upper Devonian rocks has been diluted

by meteoric water infiltrating near the basin margins. Brine samples from the Lower Devonian units have both isotope and chemical compositions which suggest that non-diluted, concentrated seawater remains in the basin. The isotope composition of the brines may have been affected by equilibration with carbonates or mixing with water derived from gypsum.

4. Two scenarios that may explain the origin for Devonian formation brine are

(a) The brines may have formed syngenetically with Devonian sediments in which they reside. The Upper Devonian brines may have originated in coastal sabkhas and lagoons, and reacted with carbonates and clays during its downward migration. Brine in the Lower Devonian units may have originated during the deposition of the Devonian salts.

(b) Alternatively, the brines may have originated from water squeezed from the Lower Devonian and possibly the Silurian evaporites. The chemical signature of the brine would represent reactions that occurred before entrapment as well as reactions that occurred during brine migration.

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