Origin and chemical evolution of formation waters from Silurian-Devonian strata in the Illinois basin, USA

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Abstract—A suite of formation-water samples from Silurian-Devonian reservoirs in the Illinois basin has been analyzed for major, minor, and trace element concentrations and for H, O, and Sr isotopic compositions in order to interpret origin of salinity and geochemical evolution of brine compositions in this evaporite- and shale-poor cratonic basin. Although chloride concentrations range from 2000 to 137,000 mg/L, Cl/Br ratios (291 ± 18) are consistent with those of seawater or seawater evaporated short of halite saturation (Cl/Br = 292). Thus, during Silurian-Devonian time, subaerially evaporated, penesaline brine entered the subsurface where it was chemically modified through brine-rock interactions. Cation/Br ratios and mineralogy of associated strata indicate that Na and K were depleted through interaction with clay minerals, Ca was enriched and Mg depleted by dolomitization, and Sr was enriched as a result of $CaCO_3$ recrystallization and dolomitization. Although significant dilution of the modified brine with meteoric water is supported by $\delta D - \delta^{18}O$ covariance, original marine waters have not been completely expelled from Silurian-Devonian strata. Hydrogen and oxygen isotopes exhibit covariant relations with cation and anion concentrations, implying that isotopic exchange between H_2O and minerals has not greatly influenced the $\delta D - \delta^{18}O$ trend. Brine $^{87}Sr/^{86}Sr$ ratios range from 0.7092 to 0.7108; when these ratios are plotted versus 1/Sr, a two-component mixing trend is suggested, although Sr concentrations have experienced local diagenetic modification. A ^{87}Sr-enriched fluid may have accompanied petroleum migration from New Albany shales into adjacent Silurian-Devonian carbonates where it mixed with remnant evaporated seawater. This event probably preceded the influx of meteoric water, as δD and $\delta^{18}O$ are not correlated with Sr isotopic compositions of formation waters.

INTRODUCTION

THE ORIGIN OF WATER AND solutes in sedimentary basin brines remains a controversial aspect of sedimentary and aqueous geochemistry. The Illinois basin in particular is enigmatic because of the presence of extremely saline brines in what is an unusually evaporite- and shale-poor basin. Furthermore, hydrologic modeling (BETHKE, 1986) suggests that warm, metal-rich brines from deep in the basin were transported to basin margins by gravity-driven fluid flow, emplacing MVT ore deposits. The present paper focuses on the isotopic and elemental chemistry of formation waters from Silurian-Devonian strata in the Illinois basin. Such integrated data sets, heretofore unavailable in the basin, suggest that remnant marine fluids may play a significant role for both solutes and H_2O molecules, implying that if gravity-driven recharge occurred in this basin it was insufficient to completely expel brines within these strata.

CLAYTON et al. (1966) carried out hydrogen and oxygen isotope analyses of waters from four sedimentary basins, including the Illinois basin, located at different latitudes in North America. Variation in deuterium content of the H_2O molecules was much greater between basins than within each basin, and δD values generally matched the value for local meteoric water. These authors concluded that original marine water molecules in each basin had been expelled and replaced by meteoric water, while the dissolved solids had been retained. As the sedimentary section of the Illinois basin contains no known bedded halite and only a small amount of anhydrite, GRAF et al. (1966) concluded that salinity was

achieved by shale-membrane filtration of original seawater. Thus, Illinois basin brines were interpreted as meteoric water that had been isotopically altered to various degrees, in terms of hydrogen by membrane filtration (GRAF et al., 1965) and in terms of oxygen by equilibration with carbonate minerals (CLAYTON et al., 1966).

More recently, serious concerns regarding the effectiveness of shale-membrane filtration as a brine-forming mechanism have been raised by many workers (summarized by HANOR, 1983). Vertical differences in hydraulic head in the deeper rocks of the Illinois basin today are totally inadequate to drive membrane filtration (BOND, 1972). GRAF (1982) concluded that rapid sedimentation of fine-grained materials produced overpressuring which decayed after uplift of the basin, the subsurface brines retaining chemical and isotopic evidence of an earlier period of membrane filtration. However, BETHKE (1986), using numerical modeling techniques to constrain basin hydrodynamics, determined that because of slow burial rates and low shale content the Illinois basin was not overpressured during its compaction, and he suggested that halite dissolution could be responsible for high salinities of formation waters.

Infiltration of subaerially evaporated seawater (CARPENTER, 1978) had not been considered as an explanation for the high salinities of Illinois basin brines, probably because the H-O isotope data of CLAYTON et al. (1966) demonstrate that the brines are isotopically dissimilar to seawater. However, it is now possible to interpret the $\delta D - \delta^{18}O$ trend of basin waters as a product of mixing between meteoric water and isotopically altered seawater, the seawater alteration being

due either to subsurface water-rock interaction (HANOR, 1983) or to subaerial evaporation (KNAUTH and BEENAS, 1986).

Prior interpretations of the origin and evolution of Illinois basin brines have been based on samples and analytical data gathered nearly 30 or more years ago by the Illinois State Geological Survey, summarized in MEENTS et al. (1952) and in GRAF et al. (1966). A compendium of major and minor element analyses from the Indiana portion of the basin, compiled from 1958 to 1972, was recently published by the Indiana Geological Survey (KELLER, 1983). As a result of a recent and continuing Sr isotope study of basin waters (STUEBER ct al., 1987), a large suite of new samples has been collected on which complete chemical and Sr isotopic analyses have been obtained. New and improved analytical techniques enable us to report minor and trace element data not available in previous studies, which may provide additional interpretive insight. Specifically, chloride-bromide relations can indicate sources of dissolved salts in formation waters, and cation-bromide relationships may reveal the nature of diagenetic modifications in the subsurface (RITTENHOUSE, 1967; CARPENTER, 1978; DAS et al., 1990). An earlier publication (WALTER et al., 1990) addressed Br-Cl-Na systematics of waters from Ordovician through Pennsylvanian reservoirs in the basin and indicated that the overall Cl budget of basin waters appears more significantly influenced by retention of subaerially evaporated seawater than by halite dissolution. The Br-Cl-Na systematics as well as the Sr isotope systematics of Mississippian and Pennsylvanian formation waters are distinct from those of waters from Ordovician through Devonian reservoirs. These two segments of the stratigraphic section are separated by the New Albany Shale Group, considered to be the major petroleum source rock in the basin (BARROWS and CLUFF, 1984).

Major, minor, and trace element analyses of 51 formation-water samples from Silurian and Devonian reservoir rocks

are presented here, along with H, O, and Sr isotope analyses of some selected samples. These new data are integrated with previously reported Sr isotopic analyses (STUEBER et al., 1987) to interpret the origin and chemical evolution of waters in this portion of the stratigraphic section.

GEOLOGICAL SETTING

The Illinois basin is an oval-shaped intracratonic basin located in Illinois, western Kentucky, and southwestern Indiana (Fig. 1). It initially formed during Paleozoic time by mechanical subsidence associated with rifting, followed by a period of thermal subsidence (HEIDLAUF et al., 1986). Late Cambrian through Pennsylvanian sediments reach a maximum present thickness of about 4.3 km in southern Illinois (WILLMAN et al., 1975) and probably exceed 6 km in thickness in portions of western Kentucky (BARROWS and CLUFF, 1984). The basin was open to the south throughout most of its development, but uplift of the Pascola arch resulted in closure sometime between the Pennsylvanian and Late Cretaceous (BUSCHBACH and ATHERTON, 1979; BETHKE, 1986).

The formation-water samples were collected within the state of Illinois (Fig. 1), where Cambrian and Ordovician sediments are dominated by carbonates and mature quartz arenites, and Silurian through middle Mississippian (Valmeyeran) sediments are almost entirely carbonates. The Maquoketa and New Albany groups are the only significant shale units in this portion of the stratigraphic section. Upper Mississippian (Chesterian) and Pennsylvanian strata consist of cyclic, interbedded sandstones, shales, and limestones, marking a change in environment and style of sediment deposition. Minor evaporites, consisting of gypsum and/or anhydrite, have been found in some Mississippian and Ordovician carbonate strata.

The Silurian and Devonian water samples were obtained from 30 oil fields (Fig. 1) producing from 9 reservoirs that are located stratigraphically below the New Albany Shale Group (Fig. 2). Only 2 of the 51 samples are from quartz sandstone reservoirs (Hardin and Dutch Creek); the remainder are from carbonate reservoirs. Carbonate strata within the Hunton Limestone Megagroup (SWANN and WILLMANN, 1961) have been dolomitized to varying degrees. Silurian carbonates are almost entirely dolomite in the northern portion of Illinois, whereas they are largely limestone to the south (WILLMAN et al., 1975). Devonian carbonates range from pure limestones to pure dolomites. None of the fields sampled had been subjected to waterflood operations for secondary petroleum recovery prior to sample collec-
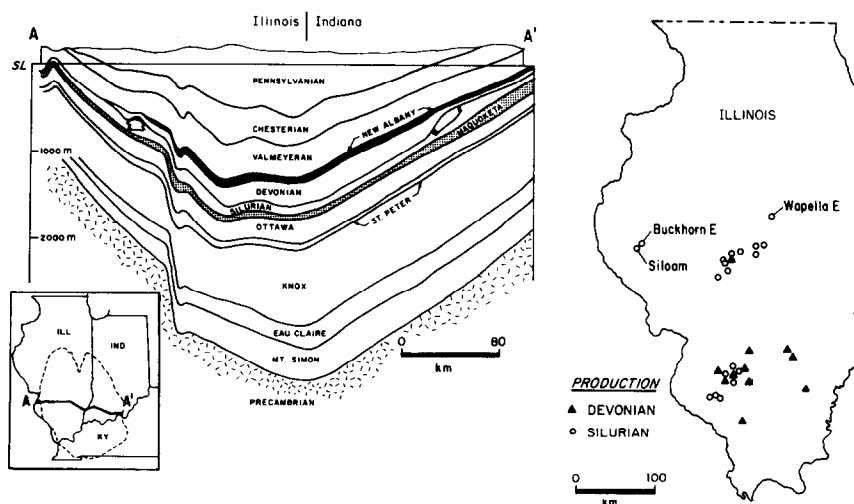

FIG. 1. The Illinois basin (inset) in the mid-continent region of the USA, an east-west subsurface cross-section, and locations of oil fields from which formation-water samples were collected. The Mt. Simon and Eau Claire formations are Cambrian, the Knox Megagroup is Upper Cambrian-Lower Ordovician, and the Ottawa Megagroup is Middle Ordovician; the Valmeyeran Series is Middle Mississippian, and the Chesterian Series is Upper Mississippian. Modified from SWANN (1967).

CHOUTEAU
NEW ALBANY

Hardin
LINGLE
Hibbard
Hoing
GRAND TOWER
Geneva
Dutch Creek
CLEAR CREEK

BACKBONE
GRASSY KNOB

BAILEY

MOCCASIN SPRINGS
Silurian, Niagaran
(reef and nonreef)

ST. CLAIR
KANKAKEE
EDGEWOOD

MAQUOKETA

GALENA
Kimmswick, Trenton

PLATTEVILLE

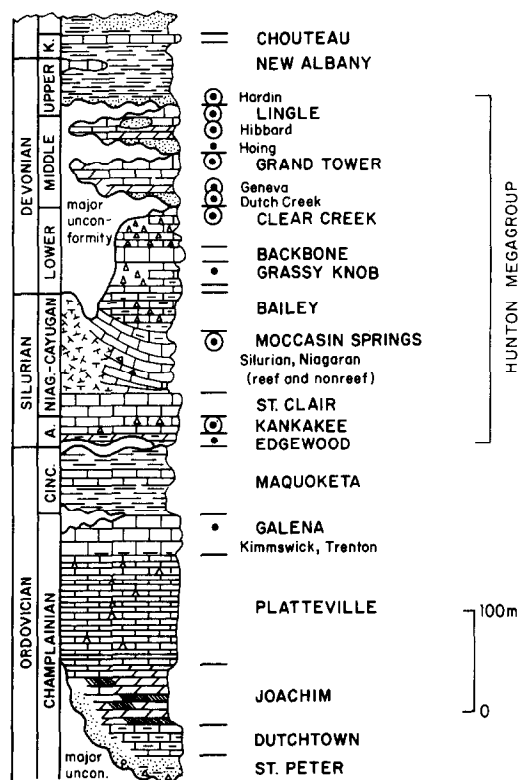JOACHIM

DUTCHTOWN
ST. PETER

HUNTON MEGAGROUP

100m

0

Fig. 2. Generalized geological column of Ordovician, Silurian, and Devonian strata in southern Illinois. Oil and gas pay zones are indicated by large dots; circled dot indicates analyzed formation water from the pay zone. Formation names are in capitals. From an Illinois State Geological Survey column, originally prepared by D. H. Swann.

tion. Meents et al. (1952) showed that the lowest salinities are found near the margins of the basin and that total dissolved solids in water from a particular formation increase downdip toward the center of the basin. Salinities of water samples (Table 1) range from 3.9 to 223.2 g/L, and are consistent with these structure-depth relationships. Illinois basin waters are generally slightly depleted in Na, strongly depleted in K, Mg, and SO_4, and noticeably enriched in Ca relative to seawater (Hanor 1979, 1983).

ANALYTICAL METHODS AND RESULTS

Most water samples analyzed in this study are from a larger suite collected during the period 1984–1988. Sampling procedures and preliminary treatment are described in Stueber et al. (1987). All samples were passed through a 0.45 μm filter, acidified to pH < 2 with Ultrex concentrated HNO_3, and stored in polyethylene bottles. Fifty-one samples were analyzed for concentrations of major, minor, and trace elements (Table 2) by inductively coupled plasma-atomic emission spectrometry (ICP-AES) using a Leeman Labs Plasma-Spec III instrument. Precision of the analyses ranges from ±1% for Sr to ±7% for K, based upon replicate analyses. Chloride, bromide, and SO_4 concentrations were measured on a Dionex 4000i series ion chromatograph with AS2 and AS5 columns and suppressed conductivity detection. Precision of anion analyses is ±1% for Cl and SO_4, and ±3% for Br. Analyses of some subsamples that had not been treated with HNO_3 yielded results identical to those for acidified samples.

Strontium isotope ratios (Stueber et al., 1987) are included in Table 2, along with analyses of 14 samples which had not been reported previously. The additional samples, after separation of Sr by cation exchange chromatography, were analyzed at Washington University according to procedures described in Popp et al. (1986). The mass spectrometer used is a VG Micromass 354 instrument

which has three independent Faraday cups for simultaneous ion collection. Eight of the samples were analyzed in triple-collector mode, for which the analytical error in $^{87}Sr/^{86}Sr$ ratios is ±0.00002 (2σ); others were run in single-collector mode with an analytical error of ±0.00003. Analytical uncertainty for Sr isotope ratios in Table 2, including those reported previously, is ±0.00006 or better, and ratios have been adjusted to the conventional value of 0.71014 for $^{87}Sr/$ ^{86}Sr in NBS-987.

The best evaluation of the reproducibility of the chemical and Sr isotope analyses, including sample collection and instrumental measurements, can be obtained by inspection of data for replicate formation-water samples collected from a designated test well in Tilden field (Table 3). Water from this well was sampled on a yearly basis between 1984 and 1988. Although concentrations of SO_4 and trace elements exhibit variability significantly greater than analytical precision, other parameters do not.

A small set of formation-water samples was collected in 1988 for hydrogen and oxygen isotope analyses. A single sample was obtained from each of 12 oil fields producing from Silurian and Devonian reservoirs. Samples from these fields, which are widely distributed in central and southern Illinois, had been included in the larger suite of analyzed samples. In a few cases it was impossible to sample a well from which an earlier sample had been collected; in such cases the sample numbers in Table 2 indicate that an alternate well was sampled. Untreated water samples, obtained at the wellhead, were collected in glass bottles which were filled to overflowing and capped with air-tight lids. The samples were analyzed at Arizona State University, where oxygen isotope ratio variations were determined using the standard CO_2 equilibration method (Epstein and Mayeda, 1953). Analyses were corrected for the effects of brine chemistry using the equation of Sofer and Gat (1972). The heated capillary method (Knauth and Beeunas, 1986) was used for hydrogen isotope analysis. Results (Table 2) are reported in concentration units as permil deviations from the SMOW standard (Craig, 1961). The probable errors are ±0.2‰ for $\delta^{18}O$ and ±2‰ for δD.

CHLORIDE-BROMIDE RELATIONS: SUBAERIAL EVAPORATION OF SEAWATER

During initial evaporation of seawater, both Cl and Br behave conservatively and increase in concentration while the Cl/Br ratio remains constant at the normal seawater value (Carpenter, 1978; McCaffrey et al., 1987). As halite and other chloride minerals are precipitated, Br preferentially remains in solution; the Cl/Br ratio of the residual brine decreases progressively, and each mineral develops a characteristic elevated Cl/Br ratio. Differences between Cl/Br ratios of evaporating seawater and those of evaporite minerals provide the theoretical basis for distinguishing between formation waters that are remnant evaporite brines and those which have formed in the subsurface by simple congruent dissolution of evaporite minerals (Rittenhouse, 1967; Carpenter, 1978).

Recrystallization of halite preferentially releases Br to solution (Land and Prezbindowski, 1981; Land et al., 1988), a process that has been supported by experimental work (Wilson and Long, 1984) and by theoretical considerations (Stoessel and Carpenter, 1986). Thus, incongruent dissolution of evaporite minerals may produce formation waters with Cl/Br ratios that could lead to ambiguous or erroneous interpretations. Whatever the nature of the Cl/Br ratios acquired by brines, whether through subaerial evaporation or subsurface interaction with evaporite deposits, they are subsequently preserved for interpretation because these anions generally do not participate in diagenetic reactions with other minerals.

Table 1. Formation-water samples and related information

Sample number	Reservoir rock	Field	Field production depth (m)	Salinity (g/L)
		DEVONIAN		
29	Hardin Ss	Elkton N	707	124.9
213	Hibbard Ls	Roby W	504	97.7
31	M. Devonian carb.	Nashville N	838	119.1
153	M. Devonian carb.	Vergennes	1006	95.1
176	M. Devonian carb.	Xenia	1371	157.0
177	Lingle Ls	Oskaloosa S	1328	163.6
187	M. Devonian carb.	Posey E	835	125.1
190	M. Devonian carb.	New Memphis N	625	69.7
34	Geneva Dol	Boulder E	868	67.1
2	Dutch Creek Ss	Aden	1622	223.2
7	Clear Creek Chert	Pyramid	943	85.0
		SILURIAN		
10	Niagaran reef	Bartelso	732	105.0
35	Niagaran reef	Baldwin	468	43.4
44	Moccasin Springs Ls	Okawville NC	671	84.6
45	Moccasin Springs Ls	Okawville NC		85.0
99	Moccasin Springs Ls	Okawville NC		85.5
49	Niagaran reef	Nashville	808	118.1
51	Niagaran reef	Nashville		98.1
54	Niagaran reef	Nashville		115.5
58	Niagaran reef	Tilden N	614	79.3
66	Niagaran reef	Tilden N		70.4
68	Niagaran reef	Tilden N		88.5
69	Niagaran reef	Tilden	659	102.7
70	Niagaran reef	Tilden		109.8
72	Niagaran reef	Tilden		124.6
75	Niagaran reef	Tilden		101.7
256	Niagaran reef	Bartelso E	777	121.8
257	Niagaran reef	Bartelso E		120.6
258	Niagaran reef	Bartelso E		120.8
259	Niagaran reef	Bartelso E		124.2
260	Niagaran reef	Bartelso E		122.5
262	Niagaran reef	Bartelso E		122.2
21	Niagaran reef	New City S	542	108.1
76	Niagaran reef	Springfield E	488	86.2
78	Niagaran reef	Blackland N	594	135.3
79	Niagaran reef	Blackland N		134.6
80	Niagaran reef	Wapella E	339	3.9
85	Niagaran reef	Wapella E		4.1
86	Kankakee Dol	Buckhorn E	200	9.6
89	Kankakee Dol	Buckhorn E		8.5
97	Kankakee Dol	Siloam	184	10.3
110	Kankakee Dol	Divernon	501	63.3
114	Kankakee Dol	Black Branch	488	86.8
117	Kankakee Dol	Mechanicsburg	529	82.2
120	Kankakee Dol	Illiopolis	538	116.0
122	Kankakee Dol	Harristown	625	135.1
125	Kankakee Dol	Forsyth	646	126.1

CARPENTER (1978) derived evolutionary trends for concentrations of major ions relative to Br in evaporating seawater, based on experiments of ZHEREBTSOVA and VOLKOVA (1966). These trends have recently been supported by field measurements (McCAFFREY et al., 1987). Comparison of formation-water compositions with evaporation trends for modern seawater is justified because the composition of seawater has remained more or less constant since Cambrian time (HOLLAND, 1978; HOLSER, 1979; DAS et al., 1990). Chloride-bromide relations in 51 formation-water samples from Silurian and Devonian strata in the Illinois basin are presented in Fig. 3. Silurian and Devonian data have been grouped because samples are all from reservoirs within the Hunton Limestone Megagroup. Based on Sr isotope relations, STUEBER et al. (1987) suggested that waters from Silurian and Devonian strata in the basin form a single hydrological system.

Chloride-bromide relations (Fig. 3a) generally show a close correspondence with the seawater evaporation trajectory and its extension below Br levels of seawater, the latter representing dilution with meteoric water. The five samples that are considerably more dilute than seawater are from three oil fields located near the northern perimeter of the basin (Fig. 1). Despite their low Cl and Br contents, these samples fall relatively close to the conservative dilution line for seawater with pure water (Fig. 3a). However, other ionic components in these samples are more profoundly affected by local water-rock interaction than by simple mixing with highly saline brines.

Silurian-Devonian formation waters more saline than seawater correlate very well with the seawater evaporation trajectory prior to halite precipitation (Fig. 3b). The mean Cl/Br ratio for these 46 samples is 291 ± 18, compared with the normal seawater value of 292 (RILEY and CHESTER, 1971).

Table 2. Chemical and isotopic analyses of formation-water samples (concentrations in mg/L)

Sample	Na	Ca	Mg	K	Sr	Cl	Br	SO$_4$	Si	B	Li	Ba	Fe	Mn	δ^{18}O‰	δD‰	^{87}Sr/^{86}Sr
							DEVONIAN										
29	39000	5510	2110	246	337	77320	249	54	1.23	7.24	-	4.93	19.1	1.61	-	-	0.70972
213	31500	4020	1570	375	225	59660	212	120	7.85	4.85	9.40	-	3.66	1.22	-	-	0.71028
31	36600	5860	2270	228	393	73460	235	nd	5.06	7.24	-	29.3	0.37	1.67	-	-	0.70971
153	30900	3390	1700	412	369	58010	215	10	7.51	13.0	-	66.5	1.74	0.18	-	-	0.70955
176	52100	6600	1510	542	260	94010	297	1647	8.04	11.9	-	0.67	0.42	0.90	+0.1	-18	0.70996
177	51200	9600	2430	1270	243	97220	397	1190	7.26	20.4	22.9	-	0.29	0.16	-	-	0.70961
187	38600	6310	2250	508	393	76690	250	nd	3.30	7.44	19.9	-	17.2	1.26	-	-	0.70991
187A	36400	6000	2110	576	379	75960	264	70	-	-	-	-	-	-	-0.9	-24	0.70990
190	22400	2790	1180	148	291	42610	151	127	7.20	4.53	13.3	-	0.18	0.16	-	-	0.70931
190A	16300	1800	792	108	186	30160	114	42	-	-	-	-	-	-	-3.7	-35	0.70936
34	21600	2400	960	436	177	41310	162	25	8.25	11.0	-	16.1	0.31	0.11	-	-	0.70978
2	68200	12150	2390	1870	431	136900	470	727	7.68	52.6	-	1.11	7.40	0.35	-	-	0.70962
7	26700	2900	1190	325	212	53380	185	72	7.56	13.6	-	7.74	2.84	0.16	-	-	0.71007
							SILURIAN										
10	30900	4630	2030	289	932	65840	216	162	6.80	6.73	-	4.22	0.94	0.15	-	-	0.70924
35	14100	980	760	141	103	27220	89	6	3.08	5.15	-	6.25	0.24	0.51	-	-	0.71070
44	26600	3470	1610	173	577	51960	188	8	6.56	5.15	-	20.1	0.30	0.17	-	-	0.70922
45	26800	3470	1610	159	504	52230	184	nd	6.57	5.34	-	19.4	0.31	0.15	-	-	0.70925
99	25800	3810	1710	260	541	53140	197	nd	6.51	6.15	-	18.9	0.31	0.18	-	-	0.70937
49	35900	6230	2010	513	160	71370	232	1706	5.10	9.35	-	0.39	0.44	0.13	-0.7	-21	0.70981
51	30500	4530	1650	369	177	59750	189	934	6.43	7.03	-	0.55	1.01	0.22	-	-	0.70970
54	35100	5830	2050	496	215	70580	235	925	7.32	10.3	-	0.99	1.68	0.20	-	-	0.70964
58	25300	3290	1530	188	193	48530	170	129	6.51	5.21	-	1.15	2.57	1.33	-	-	0.70988
58A	26700	4040	1560	260	202	50520	186	787	-	-	-	-	-	-	-1.8	-27	0.70995
66	22000	3210	1130	193	145	42910	147	649	5.58	5.41	-	0.78	44.7	2.03	-	-	0.71001
68	25800	5380	1600	230	172	53930	179	1197	8.78	5.80	-	0.53	15.7	0.99	-	-	0.70984
69	31300	5140	1980	278	284	62780	210	678	5.04	7.27	-	0.72	0.42	0.24	-1.6	-24	0.71007
70	33700	5420	1970	274	287	67350	219	603	5.88	6.70	-	0.91	0.46	0.20	-	-	0.70992
72	37600	6630	2190	355	321	76750	267	445	3.91	5.88	-	0.93	0.40	0.31	-	-	0.71011
75	31100	4830	1620	299	317	62890	219	413	6.19	5.84	-	1.37	1.66	0.19	-	-	0.70998
256	36030	6970	2490	621	204	75200	255	1367	7.11	11.3	20.7	-	-	-	-	-	0.70958
257	36100	6520	2420	608	276	74400	259	687	6.16	11.0	17.0	-	-	-	-	-	0.70954
258	36950	6380	2440	503	328	73900	258	693	6.45	9.68	19.7	-	-	-	-	-	0.70951
259	37400	6810	2440	663	228	76400	262	1133	6.43	10.7	15.1	-	-	-	-	-	0.70964
260	37150	6390	2430	632	345	75300	252	444	6.39	12.1	15.0	-	-	-	-	-	0.70950
262	34250	9090	2380	629	297	75300	230	93	11.7	8.96	15.8	-	-	-	-	-	0.70948
21	33100	4670	1550	379	183	66850	224	1139	6.72	4.13	-	0.49	0.83	0.34	-	-	0.71076
76	27200	3450	1310	322	213	53470	198	nd	5.27	3.81	-	12.4	0.28	0.22	-2.4	-25	0.71032
78	42900	5910	2110	440	265	82970	276	423	5.33	4.06	-	0.70	0.68	0.39	-	-	0.71012
79	41800	5910	2070	419	259	83350	274	469	4.82	4.60	-	0.63	11.7	1.21	+0.6	-12	0.71004
80	1550	38	22	23	1.9	2020	6.7	195	4.58	2.10	-	0.11	0.01	0.10	-	-	0.71010
85	1610	50	24	24	2.3	2130	7.1	217	5.63	2.13	-	0.10	0.06	0.18	-8.5	-57	0.71005
86	3840	55	49	26	7.0	5570	16.5	8	4.13	1.77	-	4.02	0.03	nd	-	-	0.70952
89	3310	100	72	40	6.5	4950	13.1	7	5.98	2.24	-	30.7	0.04	nd	-	-	0.70985
97	4130	50	54	32	8.3	6010	17.5	nd	4.29	1.77	-	34.6	0.03	nd	-	-	0.70978
110	20400	2170	990	249	145	39210	137	nd	5.67	3.77	-	25.2	0.25	0.17	-	-	0.71084
110A	23000	2350	1130	296	171	41440	156	nd	-	-	-	-	-	-	-3.0	-29	0.71067
114	27700	3550	1460	309	231	53340	199	7	5.22	3.86	-	3.18	0.30	0.15	-	-	0.71025
117	26800	2950	1360	322	164	50450	182	nd	5.30	3.91	-	5.80	0.29	0.38	-3.0	-29	0.71031
120	37400	4510	1990	424	223	71200	244	nd	3.60	4.16	-	4.83	0.35	0.30	-0.9	-21	0.71009
122	43500	6030	2010	526	258	82340	273	173	4.06	5.05	-	0.78	0.35	0.49	-	-	0.71026
125	41000	5380	1810	481	241	76580	233	342	4.30	5.08	-	0.98	0.35	0.67	-	-	0.71025

nd = not detected   Detection limits: SO$_4$ = 1 mg/L; Mn = 0.005 mg/L

Formation waters that plot on the Cl-Br seawater evaporation trajectory can be interpreted tentatively as ancient evaporite brines (HANOR, 1987; KNAUTH, 1988), although few subsurface waters actually fall on the trajectory (HANOR, 1987). Whereas Cl-Br compositions of formation waters from most basins have apparently been affected by water-rock interactions, Silurian-Devonian waters from the Illinois basin represent one significant data set coinciding with the evaporation trajectory prior to halite saturation. Thus, on the basis of their Cl-Br relations, these Silurian and Devonian formation waters may be interpreted as having originated from seawater that did not evaporate to the point of halite precipitation,

consistent with the absence of any type of evaporite deposit in this portion of the stratigraphic section in the Illinois basin (Fig. 2).

Formation-water samples that fall on the Cl-Br seawater evaporation trajectory prior to halite precipitation would not be displaced from the line through simple dilution with meteoric water or seawater after subaerial evaporation and concentration. Widespread distribution of data along the evaporation trajectory in Fig. 3b suggests that a conservative dilution process has subsequently affected these waters. The water sample with the highest Cl content (136,900 mg/L Cl) suggests a minimum seven-fold concentration of seawater,

Table 3. Replicate sampling and analysis of formation
waters from a single well in Tilden field
(element concentrations in mg/L)

Collection Date	9/14/84	8/20/85	10/25/86	6/25/87	9/09/88
Na	31300	31300	31300	31500	31000
Ca	5160	5130	5150	5170	5090
Mg	1940	1950	1940	1950	1940
K	271	274	269	271	305
Sr	284	286	284	283	283
Cl	62910	62930	62400	62960	62960
Br	202	212	219	215	201
SO_4	708	654	706	696	625
Si	4.39	1.93	6.11	6.32	6.45
B	7.09	7.16	7.14	7.29	7.65
Ba	0.67	0.68	0.68	0.84	0.75
Fe	0.47	0.66	0.38	0.38	0.21
Mn	0.46	0.36	0.15	0.15	0.10
TDS (g/L)	102.8	102.7	102.3	103.1	102.4
$^{87}Sr/^{86}Sr$	0.71015	0.71009	0.71001	0.71008	0.71001

representing approximately 75% of the evaporative concentration needed to reach halite saturation at 183,950 mg/L Cl.

The Cl-Br relations in Fig. 3 are inconsistent with simple congruent dissolution of halite, which would yield values with extremely high Cl/Br ratios. STOESSELL and CARPENTER (1986), observing that the Br content of freshly precipitated halite does not appear to be in thermodynamic equilibrium with the associated liquid, employed the concept of stoichiometric saturation to explain liquid control on the precipitation of halite. Incongruent halite dissolution as an approach to equilibrium is a feasible means of increasing the relative Br content of formation waters and thereby reducing their Cl/Br ratios compared to halite. However, it would seem fortuitous that such waters should acquire the Cl/Br ratio of seawater over a significant range of Cl concentrations (Fig. 3b). The Cl/Br ratio acquired by a formation water during incongruent dissolution of halite is very sensitive to Br content of original halite, rock/water ratio, and value chosen for the distribution coefficient for Br in halite. A strongly halite-dominated system is required for incongruent halite dissolution to yield a formation water with the Cl/Br ratio of seawater (STOESSELL and CARPENTER, 1986). Therefore, the salinity of Silurian-Devonian formation waters in the basin is most simply interpreted as the result of subaerial evaporation of seawater.

The thick evaporite sequences that characterize Silurian-Devonian strata in the eastern Great Lakes region do not extend into the Illinois basin. Our interpretation that Silurian-Devonian formation waters in the basin originated through seawater evaporation short of halite precipitation is consistent with the paucity of evaporite deposits throughout the stratigraphic section and with the absence of bedded halite. Ordovician carbonates contain anhydrite (SAXBY and LAMAR, 1957; STEVENSON et al., 1975), and bedded gypsum and anhydrite occur in a portion of the Mississippian St. Louis Limestone (Fig. 1; Valmeyeran Series) in Illinois (SAXBY and LAMAR, 1957), Indiana (MCGREGOR, 1954), and Kentucky (MCGRAIN and HELTON, 1964). However, according to BETHKE (1986) the only evidence of halide occurrence in the Illinois basin is found in occasional cubic casts.

Recent studies of Silurian-Devonian paleoenvironments in the Illinois basin (COBURN, 1986; WHITAKER, 1988) provide the potential for subaerial evaporation of seawater. According to these reconstructions, Illinois was situated on a gently dipping carbonate shelf or ramp along the western flank of a large basin. Reefs formed on this stable ramp across most of the proto-Illinois basin during the Silurian; regressing seas during the late Silurian and early Devonian subaerially exposed reef crests and terminated their growth. Lagoonal environments could have developed within this setting, restricting water circulation and leading to penesaline conditions. A Silurian-Devonian paleolatitude of about 25°S (VAN DER VOO, 1988) provided an appropriate subtropical climate for subaerial evaporation. Dense saline water forming in this type of environment could penetrate underlying sediments; progressive burial and compaction would then disperse the brine into other sedimentary units. Those who favor brine origin through halite dissolution point out that the volumes of surficially generated brines that could be buried with evaporite strata of negligible porosity are insufficient to account for the large volumes of existing saline formation waters (LAND and PREZBINDOWSKI, 1985; CASAS and LOWENSTEIN, 1989). This argument is not applicable in the Illinois basin, where seawater evaporation did not reach the point of forming significant evaporite strata and the penesaline water was underlain by porous sediments. Syndepositional loss of residual evaporite brines has been suggested for portions of the Gulf Coast and Alberta Basins (STOESSELL and MOORE, 1985; KHARAKA et al., 1987; and SPENCER, 1987).

CATION-BROMIDE RELATIONS: CHEMICAL CHANGES IN THE SUBSURFACE

Changes in the chemical composition of evaporated Silurian-Devonian seawater that have occurred as a result of diagenetic reactions in the subsurface are revealed by departures of formation-water compositions from cation-Br evaporation trends. Such relations for Na and K are shown in Fig. 4. Sodium concentrations tend to lie slightly below the seawater evaporation trajectory (Fig. 4a), forming a trend generally parallel to that line. Sodium concentrations have
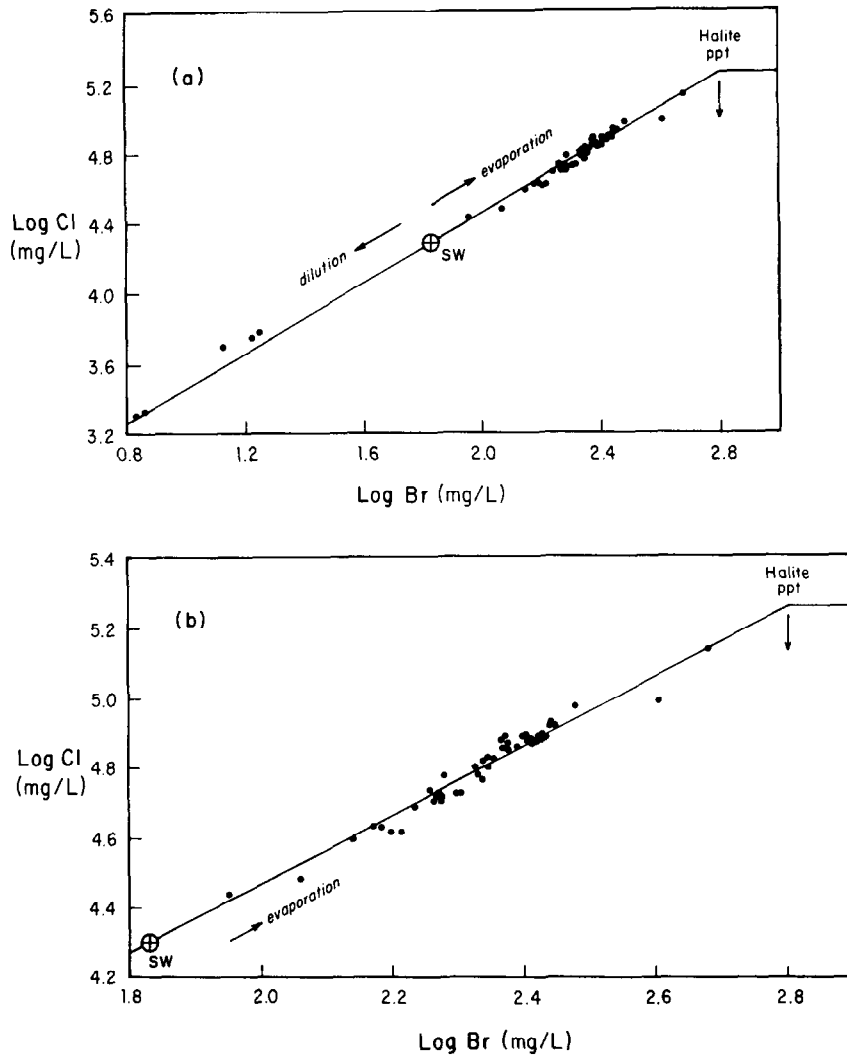
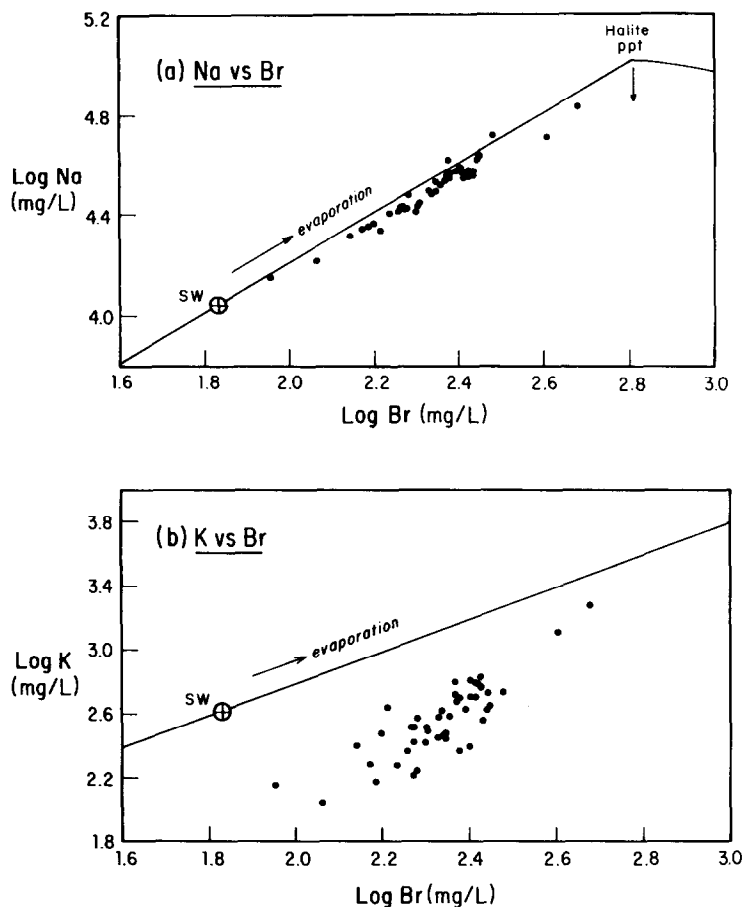FIG. 3. (a) Cl-Br relations in 51 formation-water samples from Silurian and Devonian reservoirs in the Illinois basin (see Figs. 1 and 2). Seawater evaporation-dilution trajectory from CARPENTER (1978); SW indicates seawater composition. (b) Enlarged portion of (a), showing formation-water samples that are more saline than seawater.

been depleted on average by about 9%, as indicated by a mean Na/Br ratio of 148 compared with a value of 163 for seawater (Table 4). Potassium concentrations lie well below the seawater evaporation trajectory (Fig. 4b), indicating significant depletion of K in the subsurface. Although there is a considerable degree of scatter in the data points, reflecting variability in the extent of diagenetic interaction, the mean K/Br ratio of 1.77 when compared with a seawater value of 6.12 yields an average K depletion of about 71% (Table 4).

Loss of Na from saline formation waters is frequently attributed to albitization of plagioclase feldspar (CARPENTER, 1978; LAND and PREZBINDOWSKI, 1981, 1985; LAND, 1987). CARPENTER (1978) suggested that K loss from brines is due to reaction with low-K clay minerals such as kaolinite to produce K-rich clays such as illite, as well as authigenic K-feldspar. Potassium depletion in brines has also been attributed to formation of K-feldspar from albite (EGEBERG and AAGAARD, 1989). Feldspars, however, are not abundant in detrital sediments of the Illinois basin (POTTER and GLASS,

1958; POTTER, 1962; SWANN, 1967), which are principally shales and quartz sandstones. Silurian-Devonian strata, dominantly carbonates, contain only a few minor sandstone units (Fig. 2), and these are mature quartz arenites. Also, NESBITT (1980, 1985) found that Illinois basin formation waters from upper Mississippian and Pennsylvanian sandstone reservoirs are equilibrated with clay minerals but not with feldspars, which he ascribed to the much greater relative abundance of the clays. NESBITT (1985) proposed that Na contents of Mississippian and Pennsylvanian formation waters are controlled by mineral reactions involving clay minerals and calcite.

Concentrations of the divalent cations Ca, Mg, and Sr (Fig. 5) are apparently controlled primarily by diagenetic reactions between the formation waters and carbonates. Relations between Ca and Br (Fig. 5a) reveal large Ca enrichments relative to evaporated seawater. The mean Ca/Br ratio of 21.7 (Table 4) indicates an average 3.5-fold Ca enrichment over evaporated seawater as a result of water-rock interactions. Mag-
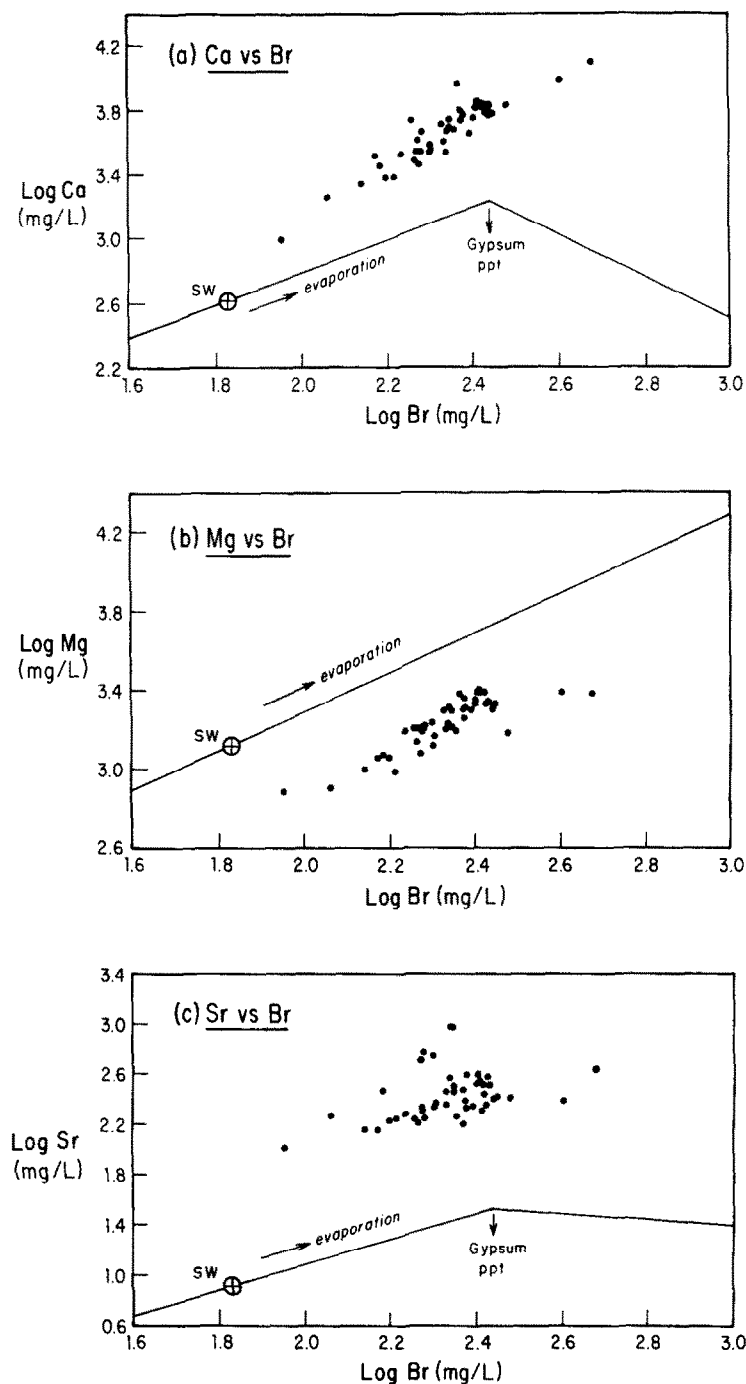
FIG. 4. (a) Na-Br and (b) K-Br relations in 46 formation-water samples from Silurian and Devonian reservoirs in the Illinois basin. Seawater evaporation trajectories from CARPENTER (1978); SW indicates seawater composition.

nesium-bromide relations in Fig. 5b show a complementary Mg depletion; Mg concentrations have been reduced on average by about 59% compared with evaporated seawater (Table 4). Proponents of halite dissolution as a source of saline formation waters (LAND and PREZBINDOWSKI, 1981, 1985) invoke albitization of detrital plagioclase as a mechanism to

elevate Ca concentrations, whereas other workers (CARPENTER, 1978; STOESSELL and MOORE, 1983, 1985) believe that dolomitization of limestone is more important. The paucity of detrital plagioclase in rocks of the Illinois basin and its virtual absence in the Hunton Megagroup, as well as the complementary behavior of Ca and Mg in formation waters

Table 4. Summary of chemical changes in Silurian-Devonian formation waters through diagenetic processes (all ratios by weight)

Ion	Ion/Br (Seawater)*	Ion/Br (Fm. Waters)	Enrichment (Depletion) Factor**	Dominant Diagenetic Process
Cl⁻	292	291 ± 18		
Na⁺	163	148 ± 9	0.91	reaction with clay minerals
K⁺	6.12	1.77 ± 0.63	0.29	reaction with clay minerals
Ca²⁺	6.21	21.7 ± 4.9	3.49	dolomitization
Mg²⁺	19.5	8.07 + 1.21	0.41	dolomitization
Sr²⁺	0.12	1.32 ± 0.68	11.0	CaCO₃ recrystal. dolomitization

* Riley and Chester, 1971

** (Fm. Waters)/(Seawater)

FIG. 5. (a) Ca-Br, (b) Mg-Br, and (c) Sr-Br relations in 46 formation-water samples from Silurian and Devonian reservoirs in the Illinois basin. Seawater evaporation trajectories from CARPENTER (1978); SW indicates seawater composition.

produced largely from partially dolomitized carbonate strata support the latter point of view.

Strontium-bromide relations (Fig. 5c) show a significant enrichment in Sr concentrations over evaporated seawater. The mean Sr/Br ratio of 1.32 (Table 4) reveals an average 11-fold enrichment in Sr subsequent to subaerial evaporation, indicating that nearly all the Sr in these formation waters has been acquired through diagenetic reactions. Although Sr may be contributed through dissolution and albitization of detrital

feldspars (LAND, 1987), it seems more likely that most Sr has been derived by recrystallization and dolomitization of carbonate minerals. On a molar basis, Mg depletion exceeds (Ca + Sr) enrichment by about 17%, suggesting that other diagenetic reactions have affected these divalent cations. Magnesium in Illinois basin waters may be consumed in regrading partially weathered chlorite and by formation of chlorite from degraded illite (GRAF et al., 1966). Such reactions would not return Ca to solution and might account, at least in part, for
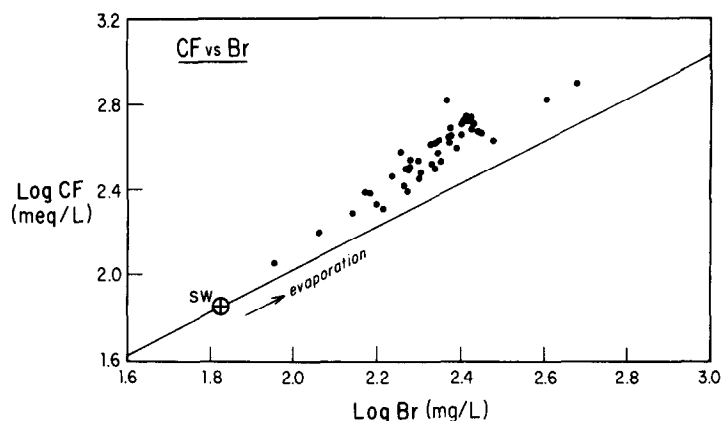
FIG. 6. Relations between Carpenter Function (CF; defined in text) and Br concentrations in 46 formation-water samples from Silurian and Devonian reservoirs in the Illinois basin. Seawater evaporation trajectory from CARPENTER (1978); SW indicates seawater composition.

the excess Mg depletion inferred here. On the other hand, some Ca and Sr have undoubtedly been lost through precipitation of gypsum or anhydrite, and also through precipitation of calcite following bacterial sulfate reduction. These reactions would not extract Mg and could explain the observed relations.

CARPENTER (1978) devised an approach to account for diagenetic reactions involving divalent cations and carbonate and sulfate minerals to deduce whether a brine originated from evaporation of seawater followed by such reactions or if the brine had a more complex origin. Additional complexities might include diagenetic reactions involving monovalent cations, silicate minerals, or halite. The quantity of divalent cations charge-balanced only by Cl was defined as the Carpenter Function (CF) by KNAUTH (1988):

$$CF = Ca + Mg + Sr - SO_4 - HCO_3 \text{ (in meq/L).} \quad (1)$$

When this function is plotted versus Br, evaporating seawater defines a trajectory unaffected by dolomitization, recrystallization or precipitation of $CaCO_3$, or $CaSO_4$ precipitation.

Carpenter Function–bromide relations in Silurian-Devonian formation waters and in evaporating seawater are illustrated in Fig. 6. Bicarbonate concentrations, which were not determined in the water samples, were not considered in calculating CF values. However, as pointed out by CARPENTER (1978), HCO_3 concentrations in most brines are very low and are generally negligible relative to Cl concentrations. The data of GRAF et al. (1966) show that this is the case in Illinois basin waters. Formation-water data in Fig. 6 lie on a trend above the seawater evaporation trajectory, indicating enrichment in divalent cations or depletion in Br relative to evaporated seawater. Because Cl-Br relations coincide with the seawater evaporation trajectory (Fig. 3b), these formation waters must have gained divalent cations by diagenetic reactions other than those accounted for by the Carpenter Function. Depletion of Na and K in these waters has been attributed to formation of sodic clays, illite, and authigenic K-feldspar from kaolinite. During these reactions hydrogen ions are
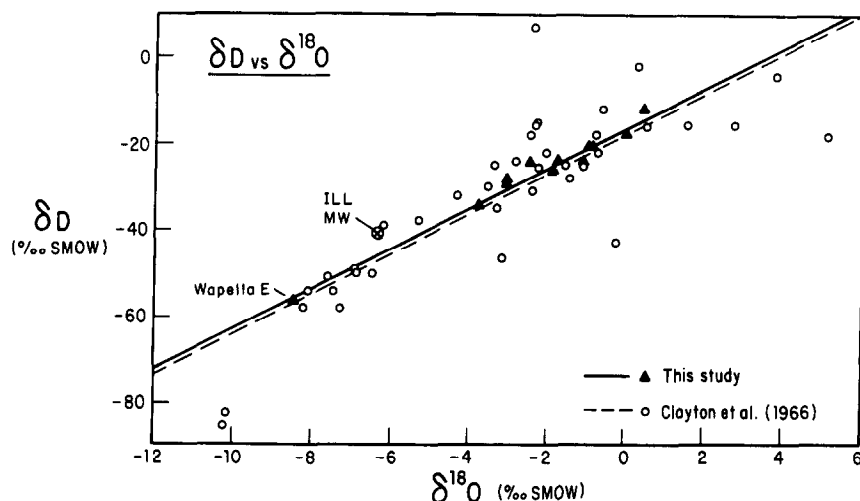
FIG. 7. Hydrogen-oxygen isotope compositions of formation waters from the Illinois basin, including 12 Silurian-Devonian waters from this study and 38 samples from various reservoirs reported by CLAYTON et al. (1966). A regression line is shown for each set of data. ILL MW indicates the isotopic composition of present-day local meteoric water.

released which are available to react with carbonate minerals, increasing the Carpenter Function value.

In summary, diagenetic modification of the chemistry of evaporated Silurian-Devonian seawater has been traced through relations between cations and Br anions in formation waters. Chloride and bromide concentrations were established by subaerial seawater evaporation short of halite precipitation. Relative to evaporated seawater, Na and K concentrations have been depleted through interactions with clay minerals, Ca has been enriched and Mg depleted by dolomitization of carbonates, and Sr has been enriched through $CaCO_3$ recrystallization and dolomitization. Thus a K, Mg-rich brine formed by evaporation of seawater evolved through rock-water interactions into the Na-Ca-Cl brine.

δD-$\delta^{18}O$ RELATIONS: MIXING WITH METEORIC WATER

Widespread distribution of brine compositions along the Cl-Br seawater evaporation trajectory (Fig. 3b) suggests that mixing of evaporated seawater with meteoric water and/or seawater has occurred. A conservative mixing event is also inferred by cation-Br trends in Figs. 4 and 5, which generally are linear and subparallel to the respective evaporation trajectories despite diagenetic modifications of cations. In addition, ionic concentrations generally increase with brine production depth, suggesting influx of dilute surface waters. Mixing of saline formation waters with dilute waters such as the samples encountered in the northern portion of the Illinois basin (data points less saline than seawater in Fig. 3a) would also yield apparently conservative element-element mixing relations. Although these dilute water samples have element/Br ratios which differ substantially from more saline brines, the saline endmember would be the dominant lever in the mixing process.

Our δD and $\delta^{18}O$ data (Table 2) and those of CLAYTON et al. (1966) are plotted in Fig. 7. Agreement between the two data sets is excellent. Greater scatter of the earlier data may

reflect wider stratigraphic distribution of their samples and differences in sampling and analytical techniques. Regression lines do not pass through present-day local meteoric water, as they are strongly influenced by samples that are isotopically lighter than present meteoric water. One sample in this group is from our collection, a very dilute water from an oil field (Wapella E) located near the northern perimeter of the basin (Fig. 1). The isotopic composition of this water may have been influenced by Pleistocene glacial water, an explanation offered by CLAYTON et al. (1966) for the isotopically anomalous nature of two of their samples that are shown near the lower left corner of Fig. 7.

Isotopic data for the 12 Silurian-Devonian waters reported here are shown in Fig. 8 relative to the meteoric water line (CRAIG, 1961) and standard mean ocean water (SMOW). A regression line has been drawn through 11 of the data points and present-day local meteoric water, excluding the sample from Wapella E field from consideration. The latter sample lies on the meteoric water line at a position consistent with precipitation under colder-than-present climatic conditions. This interpretation depends on an accurate evaluation of the isotopic composition of local meteoric water; a regression line can be drawn equally well through the 12 sample points alone (Fig. 7). The composition of Illinois meteoric water ($\delta D = -40‰$, $\delta^{18}O = -6.3‰$) used by CLAYTON et al. (1966) agrees with analyses of precipitation collected over a one-year period at Bondville in east-central Illinois (T. F. ANDERSON, pers. comm., 1989). CLAYTON et al. (1966) interpreted their $\delta D - \delta^{18}O$ trend in Illinois basin waters (Fig. 7) as the result of infiltration and subsequent isotopic alteration of meteoric water that originated as precipitation under climatic conditions not greatly different from those prevailing today. The regression lines in Fig. 7 suggest that the infiltrating meteoric water may have formed in part under somewhat colder-than-present climatic conditions.

In many sedimentary basins, chemical studies of brines have inferred the presence of remnant evaporated seawater; positive covariant $\delta D - \delta^{18}O$ relations in the same samples
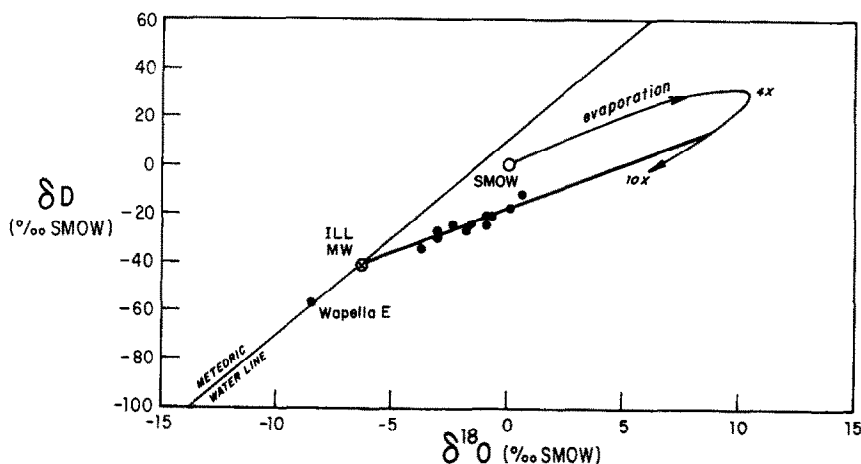

FIG. 8. Hydrogen-oxygen isotope compositions of 12 formation waters from Silurian and Devonian reservoirs in the Illinois basin, shown relative to the meteoric water line (CRAIG, 1961) and SMOW. ILL MW indicates the isotopic composition of present-day local meteoric water. A regression line, drawn through 11 of the data points and local meteoric water, has been extended to its intersection with the seawater evaporation trajectory of HOLSER (1979).

could be interpreted as mixing trends between evaporated seawater and meteoric water. There has been a reluctance to accept such an interpretation, however, because the waters are commonly depleted in deuterium relative to SMOW, inconsistent with isotopic fractionation during seawater evaporation (LAND and PREZBINDOWSKI, 1981). During evaporation to the point of gypsum precipitation ($\sim4\times$) residual seawater becomes enriched in the heavier isotopes (KNAUTH and BEEUNAS, 1986; following the work of GONFIANTINI, 1965; HOLSER, 1979; and PIERRE et al., 1984), as shown in Fig. 8. However, with further evaporation toward halite saturation ($\sim11\times$), residual liquid becomes progressively depleted in D and ^{18}O, forming a curved or hooked trajectory. Therefore, evaporating seawater can yield a residual brine with a negative δD composition relative to SMOW.

Chloride-bromide relations (Fig. 3b) indicate that original marine waters have not been completely expelled from Silurian-Devonian strata. The $\delta D - \delta^{18}O$ trend in Fig. 8 is consistent with mixing of remnant brine with meteoric water, but the isotopic composition of the saline endmember is not well defined. The seawater evaporation trajectory in Fig. 8 was proposed by HOLSER (1979), but the shape and extent of the trajectory is variable and dependent on humidity and other local climatic conditions at the time of evaporation (SOFER and GAT, 1975; HOLSER, 1979; KNAUTH and BEEUNAS, 1986). Nevertheless, the $\delta D - \delta^{18}O$ trend line intersects

the evaporation trajectory at a point beyond gypsum precipitation but prior to halite saturation, consistent with degree of seawater evaporation deduced from Cl-Br relations. If the saline endmember was located on a seawater evaporation trajectory such as that shown in Fig. 8, these formation waters have been diluted by 50% or more with meteoric water.

According to the hypothesis of CLAYTON et al. (1966), the O isotope alteration of infiltrating meteoric water in the Illinois basin is due to isotope exchange between water and calcite, which results in a progressive enrichment of the water in ^{18}O with temperature and depth. The much smaller hydrogen isotope shift was not accounted for, due to lack of information on H isotope fractionation between water and hydrous minerals. It now seems unlikely that Illinois basin waters have been significantly affected by exchange of H isotopes with hydrous minerals in basin sediments. Although experimental data of O'NEIL and KHARAKA (1976) and other workers strongly suggest H isotope exchange between clay minerals and water at temperatures below 100°C, the integrated mineral/water ratio for hydrogen is generally very low in carbonate and coarse-grained clastic rocks so that little effect is actually observed (LONGSTAFFE, 1989). HITCHON and FRIEDMAN (1969) studied formation waters in the Alberta basin that revealed a $\delta D - \delta^{18}O$ trend similar to that observed in Illinois basin waters. However, they attributed the trend to mixing of diagenetically altered remnant seawater with
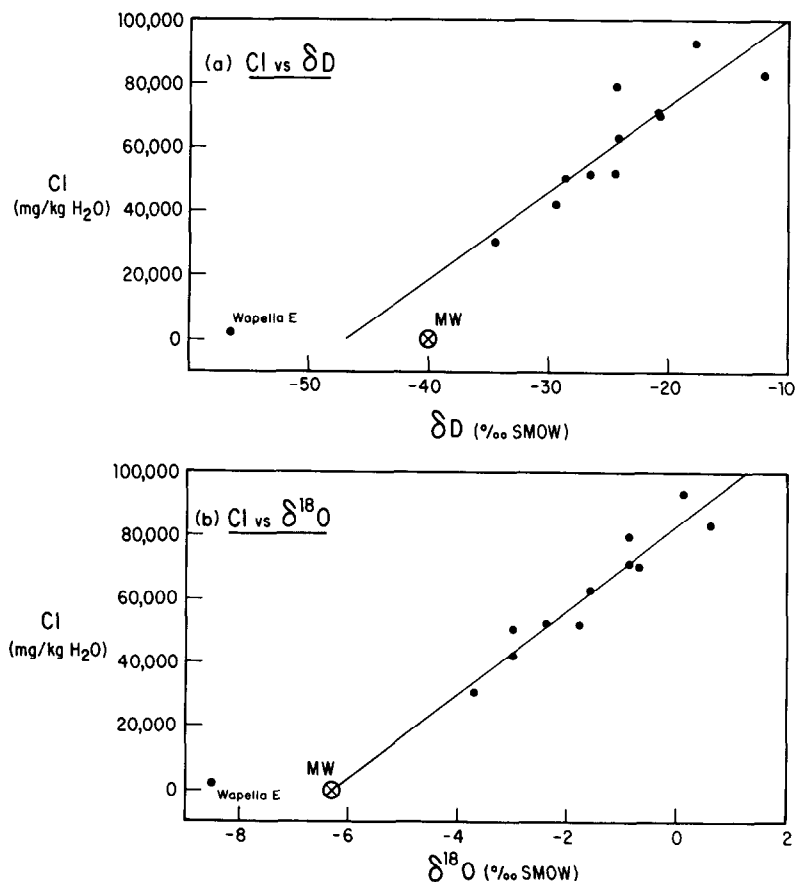

FIG. 9. Chloride concentrations in Silurian-Devonian waters as a function of hydrogen (a) and oxygen (b) isotope compositions. Chloride concentrations from Table 2 have been expressed in mg/kg H_2O. Regression lines have been drawn exclusive of Wapella E sample and meteoric water (MW).

infiltrating meteoric water. The remnant marine water was enriched in ^{18}O through extensive exchange of oxygen isotopes with the rock matrix, but variations in H isotopes were interpreted as reflecting the degree of mixing with meteoric water.

The relative importance of mixing versus diagenetic effects in determining the $\delta D - \delta^{18}O$ trend in Fig. 8 can be assessed through a comparison of the chemical and isotopic compositions of the formation waters. Whereas the mass of hydrogen in waters is large compared with that in hydrous minerals and other H-bearing compounds, exchangeable oxygen in minerals is large relative to oxygen in water. Thus, diagenetic effects on δD of formation waters may be negligible, especially at low temperatures, and covariant trends between δD and chemical constituents should reflect mixing of two dissimilar bodies of water. If a mixing event is thereby indicated, the relative contribution of diagenesis to $\delta^{18}O$ variations can be evaluated from relations between $\delta^{18}O$ and dissolved species.

The relation between δD and Cl concentration in Silurian-Devonian formation waters is illustrated in Fig. 9a. Chloride (as well as other chemical species analyzed) shows a covariant relation with δD; the regression line excludes the sample from Wapella E field. Projection of the trend line to zero chemical concentration indicates an endmember δD composition approximately midway between present-day meteoric water and Wapella E formation water (Fig. 9a). This observation is consistent with the ambivalent relations between the $\delta D - \delta^{18}O$ regression lines in Fig. 7 and the isotopic composition of meteoric water. These formation-water samples probably contain a meteoric component that formed in part under colder-than-present climatic conditions. The Wapella E sample may represent water that is almost entirely of such an origin. CLAYTON et al. (1966) reported a number of samples that are isotopically lighter than present-day meteoric water (Fig. 7), similar in composition to the Wapella E water. SIEGEL and MANDLE (1984) concluded that recharge of Pleistocene glacial meltwater was responsible for isotopic compositions of waters from Cambrian-Ordovician strata in the north-central United States, including 12 samples from northern Illinois which showed δD and $\delta^{18}O$ values virtually identical to those of Wapella E water. Covariant chemical–δD relations such as that in Fig. 9a support our interpretation that the $\delta D - \delta^{18}O$ trend in Fig. 8 represents a mixing event between remnant marine water and meteoric water.

When Cl concentration is plotted as a function of $\delta^{18}O$ (Fig. 9b), a covariant relation almost identical to that in Fig. 9a is obtained. In this case, however, projection of the trend to zero concentration coincides with the $\delta^{18}O$ composition of present-day meteoric water. Covariant chemical–$\delta^{18}O$ trends such as that in Fig. 9b indicate that $\delta^{18}O$ variations have been produced primarily by a mixing event between a remnant marine water and meteoric water. KNAUTH and BEEUNAS (1986) pointed out that δD covariance with $\delta^{18}O$ in formation waters suggests that whatever is causing the δD variations may also be affecting the $^{18}O/^{16}O$ ratios. If the meteoric water component had an isotopic composition as indicated by the δD trend in Fig. 9a ($\delta D \sim -48‰$), then the trend in Fig. 9b suggests a small oxygen isotope enrichment ($\sim +0.9‰$) due to exchange between waters and carbonates.

The precise isotopic composition of meteoric waters that

have infiltrated the Illinois basin can only be resolved by a more thorough isotopic study using current analytical methods, but our limited data infer that oxygen isotope exchange with calcite could have played only a very small role in establishing the δD and $\delta^{18}O$ trends in basin waters. We conclude that covariance of δD and $\delta^{18}O$ in Illinois basin waters is due to infiltration of meteoric waters which have mixed with remnant evaporated seawater, and that the increases in δD and $\delta^{18}O$ with water salinity observed by CLAYTON et al. (1966) are a manifestation of this mixing process. Our observations in the Illinois basin are in accord with the suggestion of KNAUTH and BEEUNAS (1986) that remnant evaporite brines may be more commonly preserved in sedimentary basins than isotopic arguments have previously indicated.

The age of the meteoric water component in the Silurian-Devonian formation waters is difficult to evaluate. Our isotopic data and that of CLAYTON et al. (1966) suggest that the water entered the subsurface when the climate was not greatly different from that of the present. However, samples from shallow wells near recharge areas have isotopic compositions which infer that the meteoric component formed under colder-than-present conditions, probably during the Pleistocene epoch. Therefore, the meteoric water in the deeper brines must be pre-Pleistocene in age (CLAYTON et al., 1966). Changes in local climatic conditions before the Pleistocene cannot be assessed adequately. The isotopic composition of seawater and the position of the meteoric water line have remained essentially constant for at least the last 150 Ma (TAYLOR, 1979) and probably since at least Permian time (KNAUTH and BEEUNAS, 1986).

STRONTIUM ISOTOPE RELATIONS: MIXING WITH A RADIOGENIC FLUID

Most samples reported here had been analyzed for Sr isotope ratios (STUEBER et al., 1987). The range of $^{87}Sr/^{86}Sr$ ratios in Silurian-Devonian waters (0.7092–0.7108) is variably more radiogenic than the range of seawater values for this interval of geologic time (BURKE et al., 1982), indicating that a portion of the dissolved Sr had been acquired from a detrital source material. When the sample data were plotted within coordinates of $^{87}Sr/^{86}Sr$ and 1/Sr, a linear pattern with a positive slope was revealed. It was proposed that the Silurian-Devonian waters show a two-component mixing relation, suggesting that they comprise a single hydrogeological system that evolved when ^{87}Sr-enriched water and petroleum from New Albany shales entered Silurian-Devonian carbonate rocks and mixed with marine interstitial water.

When $^{87}Sr/^{86}Sr$ ratios are plotted versus concentrations of major and minor elements (Table 2) other than Sr, no evidence for a mixing trend is found in any case. The relation between $^{87}Sr/^{86}Sr$ and Sr suggests a hyperbolic mixing trend, but one with considerable internal scatter. Normalization of elements to Cl concentrations to compensate for meteoric water dilution does not improve the relations among elemental data and Sr isotopic composition. If the two-component mixing event suggested by the Sr isotope data involved formation waters of significantly different chemical compositions, subsequent chemical modifications due to water-rock interactions have masked mixing trends between $^{87}Sr/^{86}Sr$

and major and minor elements other than Sr. Even Sr concentrations seem to have been diagenetically modified to a significant extent.

Mixing relations among formation waters can also be investigated through element versus element plots. If linear concentration scales are used, conservative mixing trends will be represented by straight lines (HANOR, 1987). When the concentrations of any pair of the elements Na, Ca, Mg, K, Sr, Cl, and Br in the Silurian-Devonian waters are plotted within such coordinates, sub-linear trends directed toward the origin are obtained, as illustrated by Ca versus Na in Fig. 10. The general trend of the data points reflects the dominant mixing event between remnant evaporated seawater and meteoric water, whereas the scatter of points about the trend has apparently been produced by chemical modifications through water-rock interactions.

Water samples that represent mixtures of two components in different proportions will form a straight-line relation in the coordinates $^{87}Sr/^{86}Sr$ versus $1/Sr$ (FAURE, 1986). Data for 46 Silurian-Devonian water samples are shown within these coordinates in Fig. 11a. The scatter within the general trend of data points could be caused by dilution and precipitation effects on Sr concentrations, which would displace points parallel to the abscissa. Normalization of Sr to Cl, to compensate for dilution, does not appreciably diminish the scatter of points. Scatter of data points in Fig. 11a may also be due to modification of $^{87}Sr/^{86}Sr$ ratios by local water-rock interactions.

We have examined intra-field variability in elemental and Sr isotopic composition by analyzing six samples from closely spaced wells in Bartelso E field, producing from a Silurian reef. The results (Table 2; samples 256–262) show a high degree of chemical uniformity for major and minor elements with the exception of Ca, Sr, and SO₄. Strontium concentrations range from 204 to 345 mg/L in the six samples, but $^{87}Sr/^{86}Sr$ ratios are essentially constant. Locations of data points for these samples are indicated in Fig. 11a; their significant lateral separation must be due to a process other than meteoric water dilution because the samples have essentially uniform concentrations of conservative elements such as Cl. Precipitation of solids that incorporate Sr also

could displace data parallel to the abscissa because Sr isotopic fractionation would not have taken place during the process. Strontium is incorporated as a minor constituent in gypsum, anhydrite, and calcite. Calcium concentrations in the six samples are quite variable, ranging from 6380 to 9090 mg/L, and SO₄ concentrations range from 93 to 1367 mg/L (Table 2). It seems quite possible that precipitation of gypsum or anhydrite in the reservoir rock is causing the intra-field variability of Ca and Sr.

Because sulfate concentrations in Silurian-Devonian formation waters are highly variable (Table 2) and because this variability is not related to meteoric water dilution, local precipitation of gypsum, anhydrite, or calcite in the carbonate reservoir rocks may have had a significant effect on the Sr contents of many of the samples. Multiple water samples from each of nine individual oil fields show that intra-field Sr variability is common, whereas $^{87}Sr/^{86}Sr$ ratios are internally quite consistent (Table 2). In examining the data for a two-component mixing relationship it therefore seems appropriate to use only the sample with maximum Sr concentration from each field to minimize possible effects of post-mixing precipitation. These data have been plotted in Fig. 11b along with the data for each of 18 fields represented by a single water sample. The scatter of data points is reduced relative to that in Fig. 11a, as indicated by a correlation coefficient of 0.74 compared with a value of 0.62 when all samples are considered. It seems likely that further improvement in definition of a trend line would have been obtained if this approach had been applied to the 18 fields represented by only one sample. Clearly, in future work of this nature, multiple samples should be analyzed from each oil field in order to evaluate the effects of local diagenetic processes on Sr concentrations in formation waters.

Although Sr concentrations of Silurian-Devonian waters have been diagenetically modified to some extent, there is evidence of a positive correlation between $^{87}Sr/^{86}Sr$ and $1/Sr$ (Fig. 11b), which suggests that a two-component mixing event may have taken place. A mixing line has been drawn through the points representing waters which apparently experienced minimal diagenetic modification (i.e., highest Sr contents). The positive slope of the line indicates that the proposed
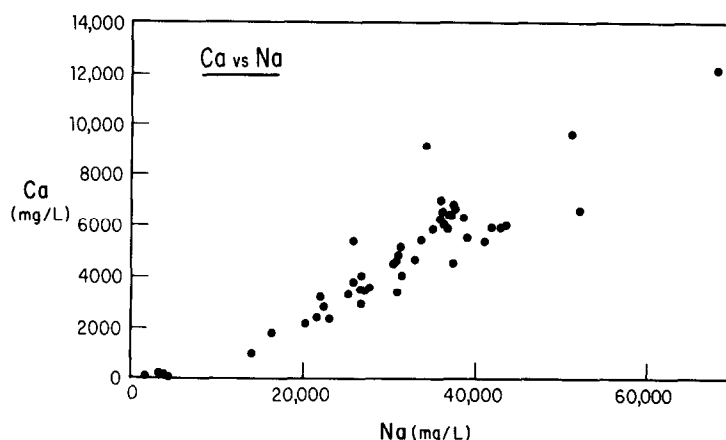

FIG. 10. Calcium vs. sodium relations in formation-water samples from Silurian and Devonian reservoirs in the Illinois basin including five dilute samples from the northern perimeter of the basin.
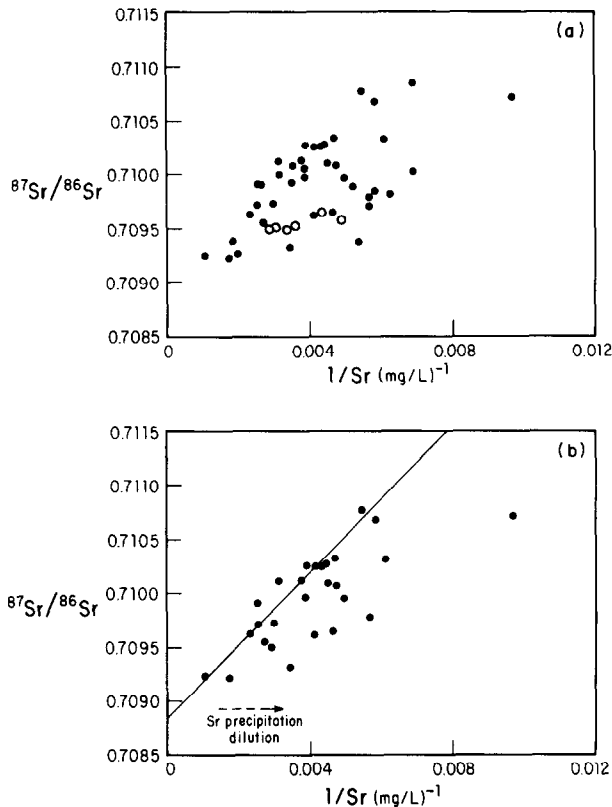
FIG. 11. (a) $^{87}Sr/^{86}Sr$ vs. 1/Sr relations in 46 formation-water samples from Silurian and Devonian reservoirs in the Illinois basin. Open circles represent samples from Bartelso E Field. (b) $^{87}Sr/^{86}Sr$ vs. 1/Sr relations for 27 oil fields producing from Silurian and Devonian reservoirs, using only the sample with maximum Sr concentration from each field. A mixing line has been drawn through data points that represent waters which apparently experienced minimal diagenetic modification.

mixing involved a formation water with a relatively high $^{87}Sr/^{86}Sr$ ratio and low Sr concentration, and another formation water characterized by a relatively low $^{87}Sr/^{86}Sr$ ratio and high Sr concentration. The $^{87}Sr/^{86}Sr$ intercept of the mixing line at 0.7088 is compatible with Silurian seawater values (BURKE et al., 1982), suggesting that one of the components was remnant evaporated seawater in the carbonate strata.

Association of the present formation waters with petroleum accumulations undoubtedly derived from stratigraphically adjacent New Albany shales (BARROWS and CLUFF, 1984) suggests that the ^{87}Sr-enriched component water acquired radiogenic Sr from the petroleum source rock. Because Silurian and Devonian oil production occurs mostly toward the margins of the basin (Fig. 1), well away from the area of probable oil generation in southeastern Illinois (BARROWS and CLUFF, 1984), the ^{87}Sr-enriched fluid and petroleum must have migrated relatively great distances through the carbonate strata while mixing with marine interstitial water in different proportions. Such long-range migration of New Albany fluids is consistent with the organic geochemical studies of BETHKE et al. (1991) which correlated thermally mature New Albany shale in southeastern Illinois with petroleum from Silurian reservoirs in central Illinois. Notably, because $^{87}Sr/^{86}Sr$ ratios of Silurian-Devonian formation waters are not correlated with

δD or $\delta^{18}O$ values, mixing between remnant evaporated seawater and a ^{87}Sr-enriched fluid and dilution with meteoric water cannot represent a single mixing event.

The positive correlation between $^{87}Sr/^{86}Sr$ and 1/Sr in Fig. 11 must have significance in terms of the evolutionary history of Silurian-Devonian formation waters despite scatter of data points within the general trend. Water samples from Mississippian and Pennsylvanian sandstone reservoirs in the Illinois basin show no correlation between these parameters, apparently because extensive cross-formational migration of New Albany fluids resulted in major diagenetic modification of the Sr isotope system (STUEBER et al., 1987). We have analyzed 27 formation-water samples from another important carbonate reservoir, the Mississippian Ste. Genevieve Limestone (unpubl. data), which also reveal completely unsystematic relations between $^{87}Sr/^{86}Sr$ and 1/Sr. It is clear that water-rock interactions have affected concentrations of all the major and minor cations in the Silurian-Devonian formation waters, but the effects on Sr were sufficiently small to preserve evidence of a mixing relation. Although most of the scatter of data in Fig. 11 is probably due to local diagenetic modification in Sr concentrations, it is also likely that ^{87}Sr-enriched water from New Albany shales was not entirely homogeneous in its $^{87}Sr/^{86}Sr$ and Sr content prior to mixing. The Sr isotope data, in conjunction with Cl-Br and $\delta D - \delta^{18}O$ relations, indicate that Silurian-Devonian formation waters represent three-component mixtures involving remnant evaporated Silurian-Devonian seawater, a ^{87}Sr-enriched fluid that probably migrated from New Albany shales, and a major component of meteoric water. Mixing between remnant evaporated seawater and the ^{87}Sr-enriched fluid probably preceded dilution with meteoric water.

SUMMARY

Chemical and isotopic analyses of formation waters from Silurian-Devonian strata in the Illinois basin provide evidence
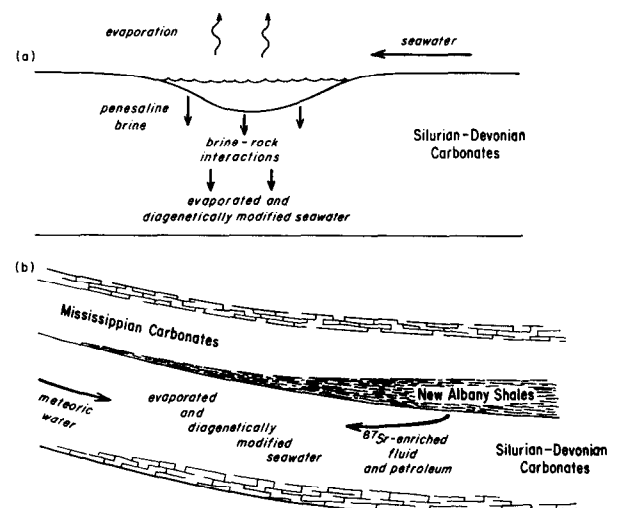

FIG. 12. (a) Schematic diagram showing subaerial evaporation of Silurian-Devonian seawater in the Illinois basin, followed by chemical modification of the penesaline brine in the subsurface. (b) Schematic diagram showing subsequent mixing of the remnant brine with a ^{87}Sr-enriched fluid from New Albany shales and with meteoric water from recharge areas.

of the geologic processes and events responsible for present brine compositions (Fig. 12). Chloride-bromide relations indicate that Silurian-Devonian seawater evaporated to a point short of halite saturation in a subtropical, restricted shallow-marine environment. After this penesaline water entered the subsurface, diagenetic processes transformed the K, Mg-rich brine into a Na-Ca-Cl formation water. Comparisons of cation/Br ratios with corresponding ratios in evaporating seawater provide quantitative evaluation of Na and K depletion through interaction with clay minerals, Ca enrichment and Mg depletion by dolomitization of carbonates, and Sr enrichment as a result of $CaCO_3$ recrystallization and dolomitization. Strontium isotope analyses of the formation waters suggest mixing between diagenetically modified brine and a ^{87}Sr-enriched fluid that probably migrated, along with petroleum, into Silurian-Devonian carbonates from stratigraphically adjacent New Albany shales. Covariance of δD and $\delta^{18}O$ in the formation waters reveals mixing with a significant component of meteoric water that diluted the remnant evaporated seawater by as much as 50% or more. Thus, present Silurian-Devonian formation waters are interpreted as mixtures of fluids from three different sources.

These results suggest that high salinities in Illinois basin waters from Silurian-Devonian strata have not been produced by halite dissolution or by shale-membrane filtration of marine pore fluids and/or meteoric water. Furthermore, the presence of remnant evaporated seawater indicates that the original marine waters have not been completely expelled and replaced by meteoric water. Thus, if gravity-driven recharge has occurred in these reservoirs, it was insufficient to displace completely the dense brines. The $\delta D - \delta^{18}O$ trend in Silurian-Devonian waters is the result of mixing between brines and meteoric water. Isotope exchange with minerals apparently played a very limited role in establishing the $\delta D - \delta^{18}O$ relations.

Editorial handling: H. P. Schwarcz

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