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Recent cross-formational fluid flow and mixing in the shallow Michigan Basin

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ABSTRACT

Ground water with total dissolved solids (TDS) ranging from 10 to >50 g/L exists at depths between 90 and 140 m in Devonian oil-bearing formations in the shallow Michigan Basin of southwestern Ontario. These formations comprise mainly limestone and dolomite, and the sources of the saline ground water have not been identified previously. Isotopic and major-ion data from ground water from Devonian oil-bearing formations in southwestern Ontario indicate that the highest-salinity fluids were emplaced locally from depths of several hundred meters. During the later stages of, or following, the Wisconsinan glaciation, saline water and petroleum were also emplaced into overlying Pleistocene clay-rich glacial deposits. Isostatic rebound leading to fracturing and enhanced formation permeability due to matrix expansion was probably the primary mechanism that enabled these saline fluids to migrate into discrete areas of the Devonian and Pleistocene formations. Variations in ground-water salinity from <10 to >50 g/L TDS over distances of a few hundred meters indicate that this cross-formational fluid flow from depth probably occurred along discrete fractures. Stable-isotope data coincident with the local meteoric water line indicate that leakage of moderately saline, recently recharged meteoric water has occurred since petroleum production began in the last century.

The geochemical data presented here support a model involving cross-formational fluid flow from depth occurring vertically on the scale of several hundred meters since glaciation. The hydrogeologic regime in this shallow basinal system must, therefore, be viewed as dynamic, rather than static, to depths of at least 500 m over a time frame of <10 000 yr.

INTRODUCTION

Oil-bearing Devonian, carbonate-rich formations in the shallow eastern Michigan Basin host saline ground water at depths of <150 m. Clayton et al. (1966) and Dollar et al. (1991) showed that total dissolved solids (TDS) in ground water from these formations ranged up to 30 g/L and that the dominant ions were Na^+ and Cl^-. This composition contrasts with that of ground water in other shallow (<200 m depth), low-temperature (<25 °C) carbonate-rich environments. Ground-water samples from the Pahapsa Limestone in South Dakota and Wyoming (Back et al., 1983) and Cambrian and Ordovician carbonate rocks in western Pennsylvania (Langmuir, 1971) have TDS contents of ~0.5 g/L and are typically Ca-HCO_3 or Ca-Mg-HCO_3 waters. By contrast, ground water with TDS contents similar to, or greater than, those in the Devonian carbonate rocks of the eastern Michigan Basin is typical of deeper basinal systems. This research identifies possible sources of the saline fluids present in these oil-bearing formations and mechanisms by which these fluids could have been emplaced.

Proposed sources of salinity in ground water in sedimentary basins include original "marine" salinity or recharged evaporated sea water remaining in the system for long periods (Hitchon and Friedman, 1969; Carpenter and Trout, 1978; Connolly et al., 1990a, 1990b; Walter et al., 1990; Wilson and Long, 1993), mixing of ground water from sources with different salinities (Clay-

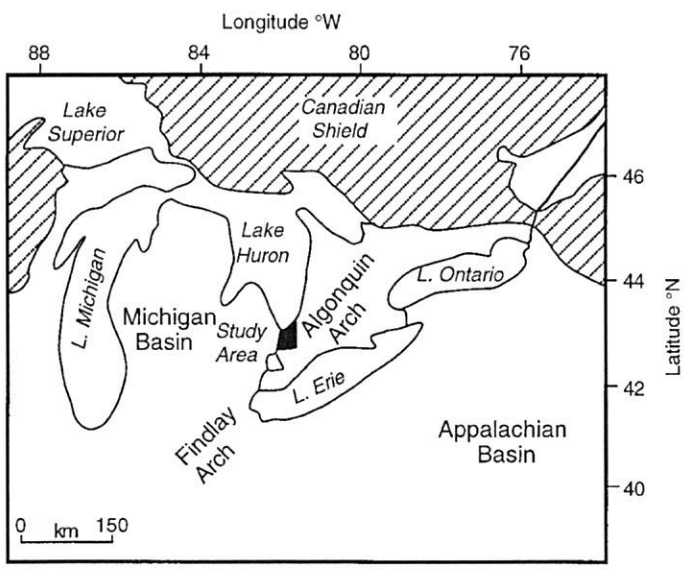

Figure 1. Location and structural setting of study area in southwestern Ontario, eastern Michigan Basin (after Ells, 1969).

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ton et al., 1966; Land and Prezbindowski, 1981; Hanor, 1988; Banner et al., 1989), and mineral dissolution. These mechanisms are discussed in this research.

The study area is in southern Ontario, where Devonian shale and carbonate rocks of the easternmost Michigan Basin underlie a thick glacial till sequence. Long et al. (1988) described the presence of ground water with anomalously high salinities in shallow, unconsolidated sequences in the Saginaw Bay region of eastern Michigan and suggested that the salinity was derived by molecular diffusion from saline fluids in the underlying Devonian carbonate rocks of the Michigan Basin. Long et al. (1988), however, did not identify the origin or source of these deeper saline fluids. We present stable-isotope and major-ion data that have allowed identification of the processes controlling the sources of both water and its dissolved species in the oil-bearing Devonian formations in the study area. We also identify potential mechanisms and timing for these processes.

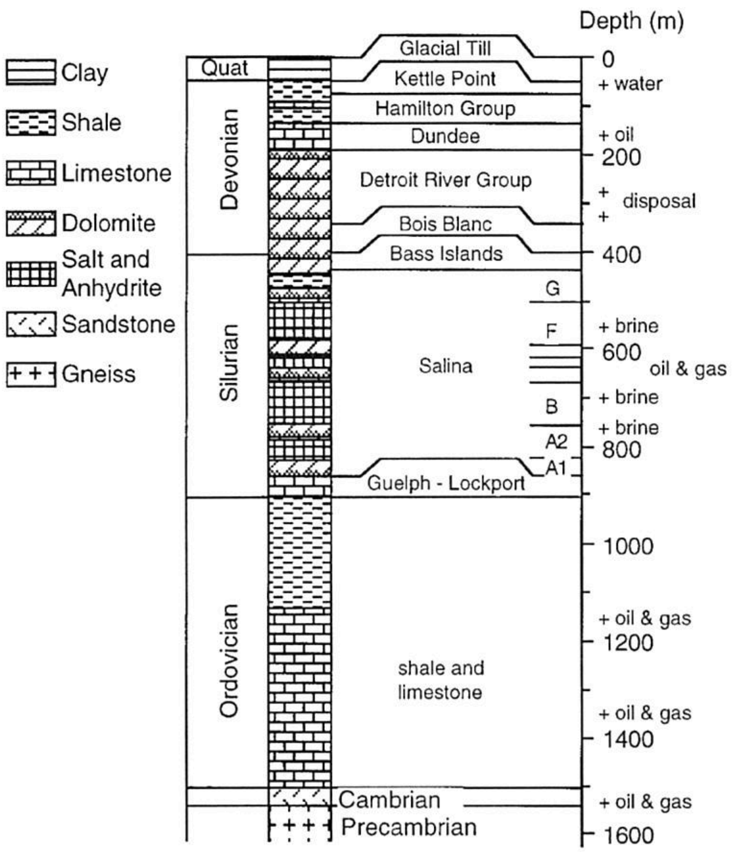

Figure 2A. Simplified stratigraphic section and major resource use of Paleozoic sequence and overlying glacial formations in southwestern Ontario (after O'Shea et al., 1988).

GEOLOGIC SETTING AND HISTORIC BACKGROUND

The study area is in southwestern Ontario on the easternmost flank of the Michigan Basin. The Findlay and Algonquin arches in the Precambrian basement to the east form the boundary between Paleozoic sedimentary rocks of the Appalachian and Michigan Basins (Fig. 1). The Devonian formations in this region are part of a thick, gently westward-dipping Paleozoic sequence that extends from the Precambrian basement and includes Cambrian sandstone, Ordovician shale and carbonate rocks, Silurian carbonate rocks and evaporites, and Devonian limestones, dolomites, and shales (Fig. 2A). Petroleum in the Devonian Dundee Formation and uppermost Detroit River Group is found in structural traps where the carbon-

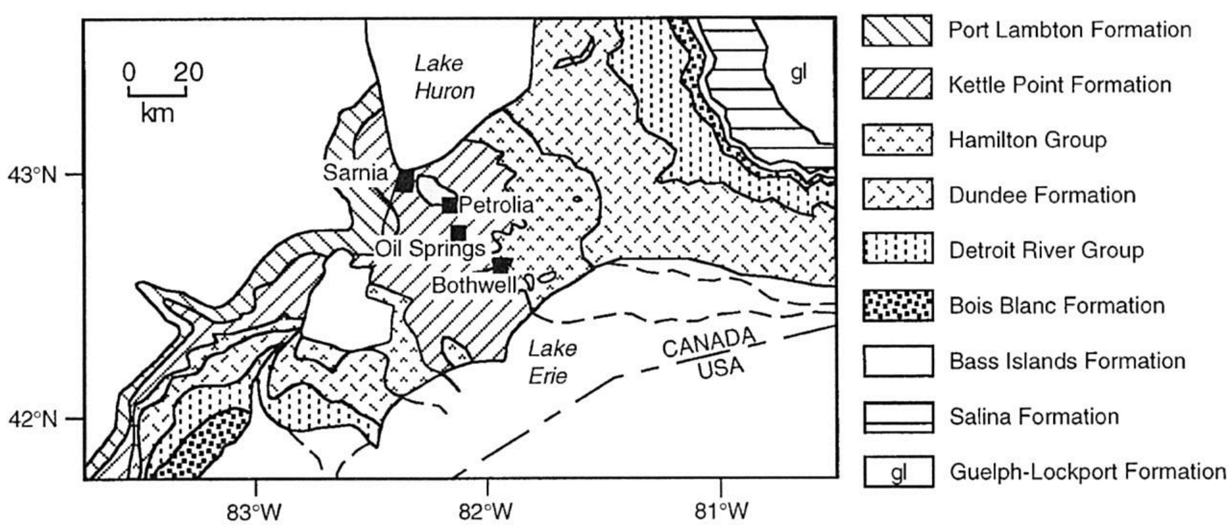

Figure 2B. Subcrop map and sampling locations in southwestern Ontario (after Brigham, 1971).

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ate rocks have been fractured due to variable dissolution and karstic collapse of underlying Silurian evaporites (Brigham, 1971; Bailey Geochemical Services and Cochrane, 1985). Throughout the study area, the Dundee Formation is overlain by the Hamilton Group and Kettle Point Formation (Fig. 2B), a thick sequence of Devonian shale and shaly limestone dominated by low hydraulic conductivities of $\sim 10^{-10}$–10^{-8} m/s (Raven et al., 1989; Weaver, 1994). The shale, in turn, is overlain by 15–40 m of glacial clay till that is characterized by hydraulic conductivities of 10^{-10}–10^{-9} m/s (Desaulniers et al., 1981; Weaver, 1994).

Karstic dissolution of Silurian evaporites and the presence of oil and gas throughout Cambrian-Devonian sequences indicate that several major episodes of fluid movement have occurred in the region during the geologic past. The extent of dissolution in the Silurian evaporites varies across the region and may be related to regional-scale lineaments or fractures that developed during the Paleozoic, and are oriented predominantly northeast-southwest and northwest-southeast (Fig. 3), cutting across the Paleozoic sequence (Sanford et al., 1985). Differential collapse of overlying Devonian formations occurred sporadically throughout the Late Devonian Period (Brigham, 1971; Bailey Geochemical Services and Cochrane, 1985), and the regional fractures could have provided pathways for the large volume of fluids required to dissolve sufficient amounts of halite and anhydrite from the Silurian formations to promote collapse. This fracture network may also have provided the pathways necessary for the migration of petroleum and associated fluids into the overlying structural traps in the Dundee Formation. The chemistry of the oil produced from these reservoirs indicates a common source for the petroleum (Powell et al., 1984); however, Powell et al. (1984) were unable to identify the source or to specify the time of emplacement of the oil. Major episodes of fluid movement involving the oil-bearing Dundee Formation and Detroit River Group occurred during the Middle–Late Devonian and during later petroleum migration. Additionally, large volumes of petroleum and saline fluids migrated through the Pleistocene clay-rich till overlying the Devonian sequence. Large-scale diffusion-dominated transport (Desaulniers et al., 1981, 1986; Weaver, 1994) and the limited occurrence of petroleum deposits in the till indicate that advective movement of petroleum and saline fluids in the till was probably limited to localized areas in the oil-producing regions.

SAMPLING AND ANALYTICAL TECHNIQUES

Ground-water samples were collected from 32 operating oil wells in Lambton County, southwestern Ontario, to determine the major-ion and isotopic composition of saline ground water in the shallow Devonian oil-bearing formations. These wells are open to the Dundee Formation and the uppermost Detroit River Group at depths of ~100–120 m, are completed with packers that isolate the oil-producing zone, and are cased through the till to the bottom of the Hamilton Group, cutting off overlying water-bearing zones. The integrity of the packers and casings is tested regularly. The sampled wells are located in eight separate oil fields in three carbonate-hosted Devonian oil-producing regions: Bothwell, Petrolia, and Oil Springs. These regions lie along a trend coincident with lineaments described by Sanford et al. (1985) (Fig. 3). Oil in the Petrolia, Oil Springs, and Bothwell regions was discovered in the glacial till and Devonian bedrock units in the 1860s and continues to be produced from the Dundee Formation and the uppermost Detroit River Group at depths of ~90–140 m (Fairbank, 1953; Bailey Geochemical Services and Cochrane, 1985).

Where possible, ground-water samples were collected at the well head; otherwise, they were collected from individual lines where they entered collection and separation tanks. The aqueous component was separated from the oil using methods based on those described by Lico et al. (1982). Water samples were separated, filtered, and preserved as necessary, and pH, temperature, bicarbonate alkalinity, and specific conductivity were measured in the field.

Ground-water samples were analyzed for major ions in the Water Quality Laboratory at the University of Waterloo. Cations and silica were analyzed by atomic absorption, and chloride, sulfate, and bromide were analyzed by ion chromatography. Detection limits for major-ion analyses were 0.01 mg/L for Cl^-, Br^-, and SO_4^{2-}, 7 mg/L for HCO_3^- (from alkalinity), 0.02 mg/L for Na^+ and K^+, 0.05 mg/L for Ca^{2+}, 0.10 mg/L for Sr^{2+}, 0.005 mg/L for Mg^{2+}, and 2 mg/L for Si^{4+}. Dissolved organic carbon (DOC) was analyzed by the Organic Geochemistry Laboratory at the University of Waterloo. A comparison of DOC with alkalinity indicated that organic acids did not contribute significantly to alkalinity in these samples.

Samples for $\delta^{18}O$ and δ^2H analyses were filtered and heated under paraffin wax prior to analysis to remove any remaining organic compounds from the aqueous phase. $\delta^{18}O$ and δ^2H analyses were performed using methods for the analysis of saline fluids described by Fritz et al. (1986). Precision, based on internal standards, is better than ±0.2‰ for $\delta^{18}O$ and better than ±2.0‰ for δ^2H. $\delta^{18}O$ values in sulfate were deter-

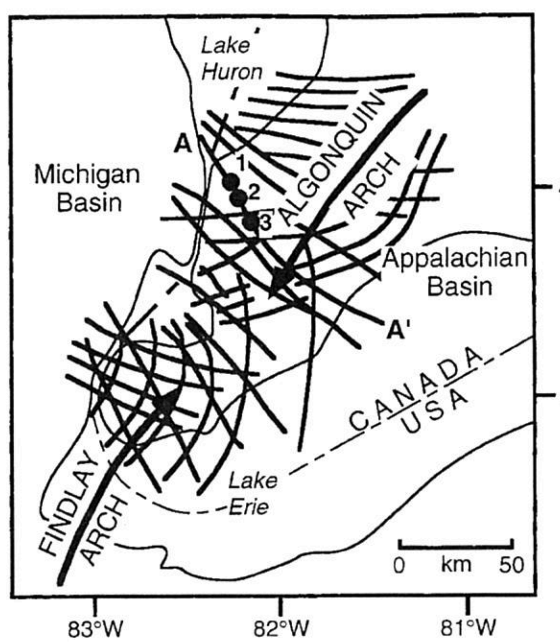

Figure 3. Fracture and fault system across southwestern Ontario, proposed by Sanford et al. (1985). Fracture trend A–A′ is parallel and close to trend along which the four oil-producing areas sampled in this study are located. Oil-producing regions sampled during this research are (1) Petrolia, (2) Oil Springs, and (3) Bothwell.

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TABLE 1. MAJOR-ION AND STABLE-ISOTOPE GROUND-WATER CHEMISTRY OF DEVONIAN AND UPPER DETROIT RIVER GROUP OIL-BEARING FORMATIONS

Well name	Formation	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Sr^{2+} (mg/L)	Si^{4+} (mg/L)	Cl^- (mg/L)	Br^- (mg/L)	SO_4^{2-} (mg/L)	HCO_3^- (mg/L)	TDS (mg/L)	% Error	pH	$\delta^{18}O$ (‰ SMOW)*	δ^2H (‰ SMOW)*	$\delta^{34}S(SO_4^{2-})$ (‰ CDT)†	$\delta^{18}O(SO_4^{2-})$ (‰ CDT)†	$\delta^{34}S(H_2S)$ (‰ CDT)†	^3H (TU)§
Petrolia																				
PD-COCH	Dundee	1 180	715	3 470	91	22.7	3.98	8 650	57.7	1 700	264	16 200	−2.33	6.50	−7.47	−47.6	31.3	17.1	−11.0	
PD-NORTH	Dundee	1 580	898	4 830	115	29.1	4.63	12 000	90.9	2 200	325	22 100	−3.21	6.40	−6.85	−41.4	29.4	17.5	−14.9	
PD-RAL	Dundee	1 580	908	4 390	117	30.0	4.58	10 900	78.3	2 000	158	20 200	−0.64	6.50	−6.84	−42.5	29.8	17.7	−16.7	2.4
PD-WEST	Dundee	1 400	793	3 870	105	26.4	4.39	9 920	82.4	1 940	258	18 400	−2.97	6.50	−7.11	−46.2	31.9	17.4	−15.9	
RA-N	Dundee	1 140	675	3 420	85	24.3	4.08	8 870	62.0	1 380	348	16 000	−3.92	6.50	−7.58	−48.8	31.7	17.0	−7.3	7.1
RA-NE	Dundee	1 410	808	4 360	105	27.9	3.95	11 300	73.6	1 810	247	20 100	−4.57	6.45	−6.83	−45.6	31.8	17.1	−11.7	
RA-SE	Dundee	1 490	858	4 530	111	27.9	4.20	11 500	78.5	1 920	320	20 800	−3.51	6.35	−7.20	−44.7	31.5	17.4	−13.1	
RA-SW	Dundee	1 320	758	3 970	100	24.5	4.51	10 100	66.9	1 690	308	18 300	−3.48	6.50	−7.32	−48.7	30.1	17.5	−13.3	
LAI-1	Dundee	1 270	818	3 670	103	25.4	3.42	9 500	58.5	1 790	589	17 800	−3.63	6.35	−6.60	−36.4	29.6	16.7	−8.8	
LAI-2	Dundee	1 300	803	3 520	102	25.5	3.53	8 980	53.8	2 010	548	17 300	−2.97	6.40	−6.54	−43.2	27.6	16.2	−13.3	
LAI-3	Dundee	1 220	773	3 430	107	22.9	4.30	8 240	43.7	2 110	651	16 500	−1.63	6.35	−6.43	−37.2	28.5	15.7	−11.6	<0.8
WB-11	Dundee	736	450	2 100	62	51.4	4.11	5 700	43.3	751	572	10 500	−5.22	6.70	−8.48	−55.2	29.0	16.4	−12.9	
WB-2	Dundee	918	593	2 620	76	20.8	3.78	7 190	20.5	787	599	12 800	−4.15	6.55	−8.22	−48.8	30.5	17.9	−9.4	7.2
WB-7	Dundee	1 100	688	3 090	88	21.8	3.58	8 450	60.1	1 320	512	15 300	−5.03	6.55	−7.57	−48.0	29.7	16.7	−11.4	
WB-8	Dundee	1 240	843	3 590	111	26.8	4.02	9 750	56.5	1 230	536	17 400	−3.21	6.40	−6.94	−41.8	33.7	18.0	−15.7	
N. Oil Springs																				
LBO-2	U. DRG#	1 530	940	4 030	131	33.8	4.20	11 300	99.1	448	40	18 600	0.47	6.65	−7.46	−52.6			−7.9	
LBO-3	U. DRG	1 640	920	3 130	125	35.1	3.20	10 400	69.4	630	113	17 000	−1.90	7.05	−7.16	−54.0			−11.6	
CFN-14	U. DRG	1 310	608	2 390	85	29.0	3.66	7 990	66.1	796	219	13 500	−5.16	6.05	−9.47	−63.3	30.8	17.7	−10.8	
CFN-A	U. DRG	1 570	830	3 170	123	35.0	4.16	9 460	85.9	916	171	16 400	−0.23	6.30	−8.99	−59.7	29.9	16.9	−12.6	
CFN-B	U. DRG	1 190	673	2 590	98	27.1	3.91	7 810	60.5	398	297	13 100	−0.79	6.40	−9.13	−59.8	31.5	17.6	−2.7	37.7
S. Oil Springs																				
CFN-161	U. DRG	5 990	2 750	10 900	445	99.9	3.34	31 400	277	1 240	328	53 400	4.79	5.95	−6.31	−83.5	24.5	15.3	−14.7	1.1
CFN-C	U. DRG	3 830	2 430	8 690	307	69.5	3.66	27 400	200	7 601	221	43 900	−1.04	6.10	−6.34	−38.4	36.2	17.6	−10.2	<0.8
CFN-E	U. DRG	4 020	2 270	8 090	288	67.1	4.00	26 800	216	1 220	328	43 300	−2.69	5.95	−5.89	−56.0	28.6	15.4	−17.6	
CFS-A	U. DRG	4 320	2 330	9 330	311	69.5	3.71	30 300	294	1 390	345	48 700	−4.10	6.00	−6.01	−76.2	26.0	16.2	−16.7	
CFS-B	U. DRG	4 240	2 270	9 700	325	66.6	2.71	25 500	202	1 350	148	43 800	4.91	5.95	−6.26	−48.8	26.4	15.4	−18.7	<0.8
CFS-C	U. DRG	3 800	2 160	8 910	309	66.6	3.57	26 600	195	941	206	43 200	−0.74	6.10	−6.37	−48.4	28.2	15.2	−17.5	
CFS-D	U. DRG	3 500	2 150	8 320	299	66.6	3.54	25 700	187	808	421	41 500	−1.93	6.05	−6.26	−68.0	28.5	15.3	−13.3	
Bothwell																				
LBH-1	Dundee	1 700	1 170	4 450	152	32.0	5.11	13 200	47.0	1 400	157	22 300	−3.24	6.75	−8.66	−59.0	33.8	16.7	0.1	
LBH-2	Dundee	2 000	1 320	4 950	156	33.5	3.49	14 300	86.0	2 340	5	25 200	−2.81	6.90	−8.78	−62.0	31.9	16.1	−3.7	
LBH-3	Dundee	1 940	1 340	4 900	169	35.7	4.14	14 100	96.8	2 140	5	24 700	−2.10	6.65	−8.15	−58.6	32.8	15.9	−2.4	<0.8
LBH-4	Dundee	1 760	1 300	5 150	171	36.1	4.08	15 000	86.0	1 220	112	24 800	−3.14	6.75	−8.08	−57.3	29.8	18.4	1.4	
Aquifer																				
R-AQ1	Lower till	59.5	33.3	189	3.65	2.74	9.07	351	3.44	1.64	289	945	−1.90	6.00	−17.12	−120.9				<0.8

*SMOW = standard mean ocean water.
†CDT = Canyon Diablo troilite.
§TU = tritium units.
#U. DRG = upper Detroit River Group.

mined based on the method of Sakai and Krouse (1971). $\delta^{34}S$ of aqueous sulfate was determined according to the method described by Yanagisawa and Sakai (1983). Reproduction of an internal $BaSO_4$ standard is better than ±0.3‰. $\delta^{34}S$ values for $\delta^{34}S$ in sulfide were determined by analysis of Ag_2S after aqueous sulfide was fixed in the field by the addition of excess Cd-acetate. $\delta^{18}O$ and δ^2H values are expressed relative to Vienna–standard mean ocean water (V-SMOW), and $\delta^{34}S$ values are expressed relative to Canyon Diablo troilite. Enriched-^3H analyses were performed on ground-water samples from 10 wells according to methods described by Taylor (1977). All isotopic analyses were performed by the Environmental Isotope Laboratory at the University of Waterloo. Results of analyses of ground water sampled during this research are presented in Table 1.

Core samples from the upper Dundee Formation and the overlying Hamilton Group and Kettle Point Formation were used to estimate the interstitial salt content of the matrix of these units (Thurston, 1991). Samples were ground to clay size, sieved, divided into two 100 g batches, and leached in 50 mL of deionized water at 25 or 60 °C for 10 days (Thurston, 1991). The equivalent concentrations of "readily soluble" salts that would be present in interstitial fluid within each formation were estimated from the water:rock ratio, formation porosity, and bulk density.

MAJOR-ION AND STABLE-ISOTOPE GROUND-WATER CHEMISTRY

The major-ion and stable-isotope chemistry of ground water from the oil-bearing zones in the Petrolia, Bothwell, and northern Oil Springs regions is relatively uniform, with TDS ranging from 10–25 g/L (Table 1). Chloride is the dominant anion, which increases as TDS increases, and sodium is the dominant cation. $\delta^{18}O$ and δ^2H values of ground water from these regions range from −9.5‰ to −6.4‰ and −63‰ to −37‰, respectively (Table 1).

Ground-water samples from seven oil wells in southern Oil Springs, however, have distinct solute and stable-isotope compositions (Table 1). Like the wells in the Petrolia, northern Oil Springs, and Bothwell regions, these wells are completed in the lower Dundee Formation and upper Detroit River Group. Ground water in this region is up to twice as saline as that in the rest of the area and, unlike ground water from the other producing regions, δ^2H values decrease markedly with increasing TDS (Fig. 4).

To explain trends in the major-ion and stable-isotope data in the ground water from the Devonian oil-bearing formations, the following features of the data must be accounted for: (1) the spread of data along the meteoric water line from $\delta^{18}O$ = −9‰ to −6‰ and the high TDS (~10–25 g/L) of these samples; (2) the depletion in ^2H in the southern Oil Springs samples with respect to both other ground-water samples from the local Paleozoic sequence and ground water from other basinal systems; and (3) the trend of decreasing δ^2H values with increasing salinity in the southern Oil Springs samples.

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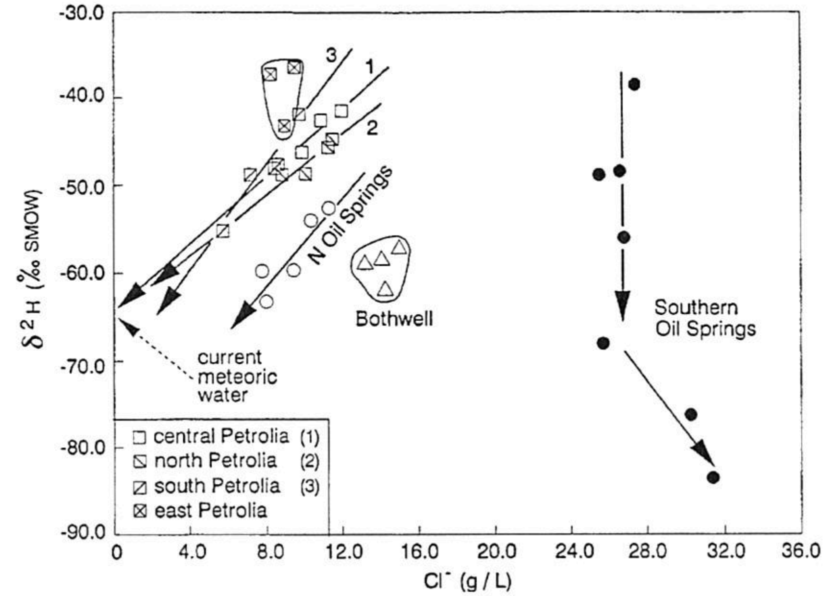

Figure 4. Cl$^-$ (g/L) versus δ^2H (‰ standard mean ocean water) for individual oil fields indicating dilution by meteoric water probably as a result of petroleum production practices, and distinct ground-water chemistry in southern Oil Springs.

samples tend to have positive slopes (Clayton et al., 1966; Hitchon and Friedman, 1969; Frape et al., 1989; Walter et al., 1990; Connolly et al., 1991b). In this study, however, the line between the most saline sample (region X; Fig. 6) and lower salinity ground water from the same oil field (region Y; Fig. 6) is approximately vertical, distinctly different from stable isotope versus salinity trends in ground water from other sedimentary basins.

A two-stage mixing model based on stable-isotope ratios in ground water could produce the trend in δ^2H values and Cl$^-$ concentrations observed in ground water from southern Oil Springs. The first stage involves mixing a saline and ^{2}H- and ^{18}O-enriched fluid initially with ^{2}H- and ^{18}O-depleted, low-salinity fluids (stage 1; Fig. 6). The isotopic signature of the most saline and ^{2}H-depleted ground water sampled during this study was reproduced by mixing ground water with an isotopic signature similar to brine from the underlying Silurian A-2 salt (Dollar et al., 1991) (region S; Fig. 6) with ground water recharged under glacial conditions (region G; Fig. 6). Mixing these end members to produce the isotopic composition of ground-water X (Fig. 6) requires 45% A-2 brine (S) and 55% dilute, glacially recharged ground water (G).

MODELS BASED ON STABLE ISOTOPES

The influence of mechanisms such as water-rock interaction on brine development in several sedimentary basins has been evaluated using oxygen- and hydrogen-isotope data (Clayton et al., 1966; Hitchon and Friedman, 1969; Long et al., 1988; Banner et al., 1989; Connolly et al., 1990b; Stueber and Walter, 1991; Wilson and Long, 1993). Our study uses a similar approach to evaluate the degree to which mixing and water-rock interaction have affected ground-water chemistry in the oil-bearing Devonian formations of the shallow Michigan Basin in southwestern Ontario (Fig. 5). δ^2H and δ^{18}O values act as conservative tracers of water in low-temperature environments, whereas major ions, other than Cl$^-$ and Br$^-$, are less likely to behave conservatively. Consequently, stable-isotope data were initially used to develop a model of mixing episodes and water-rock interaction. The extent to which the chemical compositions predicted using this model correlate with measured major-ion compositions was then assessed.

The isotopic signatures of ground water from southern Oil Springs plot significantly below the local meteoric water line described by Fritz et al. (1987) (Fig. 6). These samples have low δ^2H values and relatively constant δ^{18}O values, and Cl$^-$ concentrations tend to increase with decreasing δ^2H (Fig. 4 and Table 1). In the Michigan, Illinois, and Alberta Basins, δ^{18}O versus δ^2H trends between the most and least saline

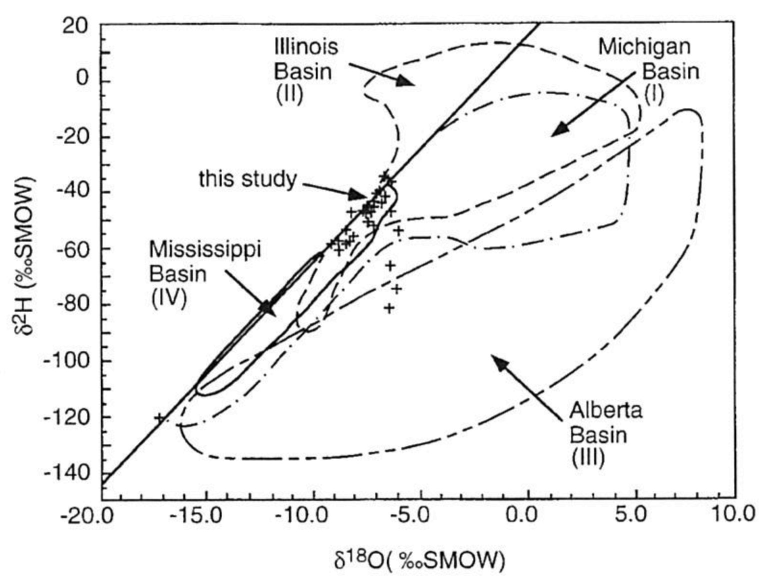

Figure 5. Stable-isotope compositions of basin brines, and ground water sampled during this research. Data, other than those collected during this study, are taken from Clayton et al. (1966) (I, II, III), Hitchon and Friedman (1969) (III), McNutt et al. (1987) (I), Stueber and Walter (1991) (II), Banner et al. (1989) (IV), Connolly et al. (1990b) (III), Dollar et al. (1991) (I), and Wilson and Long (1993) (I). The most saline ground-water samples analyzed during this research are deuterium depleted. In the other studies, salinity typically increases with increasing δ^2H and δ^{18}O.

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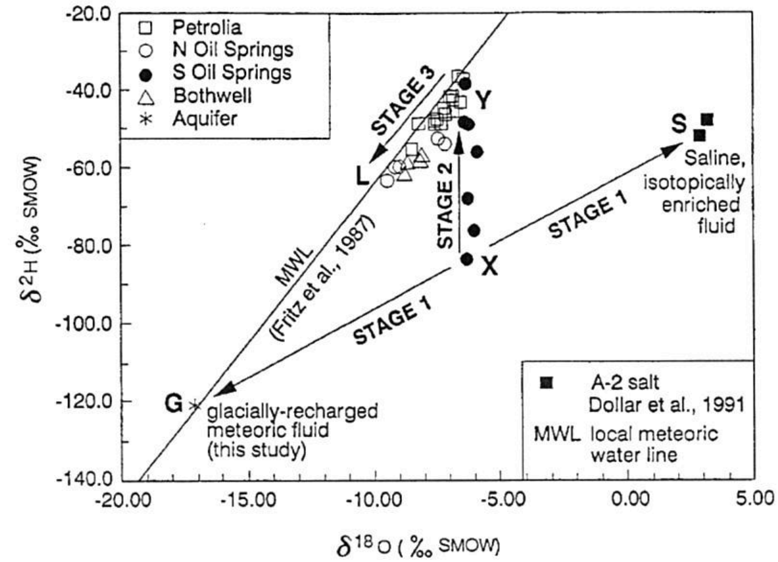

Figure 6. Multistage mixing model. Deeper, more saline basinal fluids initially mixing with ^{2}H-depleted, low-salinity fluids, and later mixing with local, recently recharged meteoric water. Isotopic composition of the most ^{2}H-depleted sample from oil-bearing formations (X) (CFN-161, this study) may be reproduced by mixing fluid with an isotopic signature similar to that of brine from the A-2 salt (S) (Dollar et al., 1991) with ground water recharged during glacial conditions (G) (similar to sample R-AQ1, this study) along line in stage 1. This ground water then mixed with "formation" water in the oil-bearing formations (Y), producing a vertical mixing line (stage 2) between X and Y. Stage 3 represents dilution of ground water with water recharged under similar climatic conditions to the present (L). This could have resulted from petroleum production practices such as oil-field flooding, or from leakage through abandoned boreholes.

Other saline end members that could be involved in this mixing process include the Devonian Richfield Formation (Dollar et al., 1991; Wilson and Long, 1993) and the Detroit River Group (Wilson and Long, 1993) in central Michigan, which are at depths of >1.5 km in the Michigan Basin. Although the isotopic signatures of brines from these units are similar to those of the A-2 salt, the Richfield Formation is absent from the study area. Isotopic values of brines from the Detroit River Group in the study area were not determined, because waste fluids were injected to this group in southwestern Ontario from the 1950s to the 1970s. It is unlikely that dense fluids from the central Michigan Basin were transported several hundred kilometers up dip into the study area, and it seems more feasible that locally derived fluids were involved in this mixing. Unless both a glacial component and a high-δ^{18}O, intermediate-δ^2H fluid are included in this model, the much lower ^{2}H value of from well CFN-161 (region X; Fig. 6) cannot be duplicated by mixing fluids sampled from the shallow Michigan Basin in southwestern Ontario.

In the second stage of mixing (stage 2; Fig. 6), we consider that the fluid from stage 1 (X) mixes with fluid already present in the Dundee Formation. This stage involves the migration of saline-glacial fluid into the oil-bearing shallow Dundee Formation and Detroit River Group. Variations in the amount of mixing between the Dundee Formation water and the more saline, low-δ^2H water could result in the spread of isotopic data identified in samples from this area. Major-ion and stable-isotope data from this research and data from previous researchers (Clayton et al., 1966; Dollar et al., 1991) indicate that the fluid in the Dundee Formation prior to stage 2 mixing may be a diluted "formation" water (region Y; Fig. 6). The isotopic composition of ground water sampled from the Dundee Formation during this research falls within the field of Michigan Basin data (Fig. 5).

Most of the isotopic values of ground water sampled during this study plot on the local meteoric water line from $\delta^{18}O$ = -6‰ to -9‰ (stage 3; Fig. 6). Current meteoric water in the region has an isotopic composition similar to that of region L (Fig. 6) (Fritz et al., 1987). We attribute the spread of data along the meteoric water line (from $\delta^{18}O$ = -6‰ to -9‰) to mixing with varying amounts of meteoric water recharged to the Devonian oil-bearing formations after petroleum production began during the 1860s. This mixing could have resulted from intentional oil-field flooding, from leakage between the surface or intermediate formations along fractures, or from leakage in poorly sealed or corroded wells. Stable-isotope and major-ion data for ground water from individual fields other than southern Oil Springs support the model of simple dilution by meteoric water (Fig. 4).

^{3}H values above zero in several wells outside of northern Oil Springs (Table 1) indicate that some leakage of meteoric water to the oil-bearing formations has occurred in the past. If substantial leakage of meteoric water continued to the present, however, ^{3}H values more similar to current meteoric water (~50 tritium units [TU]) would be expected. A ^{3}H value of 37.7 TU in northern Oil Springs (from well CFN-14) indicates that leakage of meteoric water into the Dundee Formation has occurred in the vicinity of this well since the 1960s.

The trends in isotopic data from this study could also be produced by several other mechanisms, if a fluid similar to other Michigan Basin fluids (region Y; Fig. 6) had been diluted by local meteoric water and, in southern Oil Springs, is undergoing a process where increased mineral dissolution is accompanied by continued loss of ^{2}H from the fluid. Processes such as the generation of hydrogen-bearing gases including methane or H_2S, however, would increase rather than decrease the δ^2H value of the remaining fluid. If the original ground water present in the Dundee Formation were similar in composition to that sampled in southern Oil Springs (region X; Fig. 6), ground water sampled from other areas would have been derived from this water. It is unlikely that this fluid would remain only in a very local area of the formation. This fluid would also be isotopically distinct when compared with other Michigan Basin fluids (Clayton et al., 1966; Dollar et al., 1991; Wilson and Long, 1993) with an isotopic signature resembling fluids from the Alberta Basin. A model simultaneously incorporating all end-member fluid compositions in the multistage mixing model (glacially derived dilute water, isotopically enriched brine, and Devonian formation water) may also apply in this area; however, this would probably produce a

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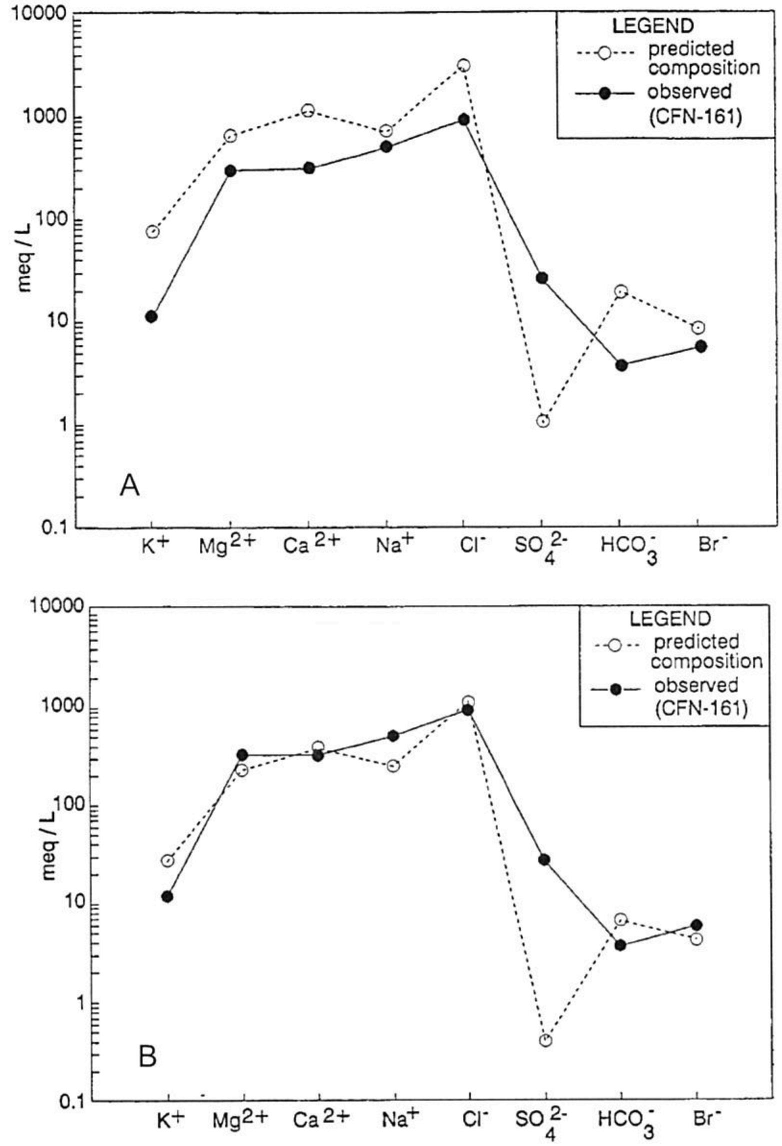

Figure 7. (A) Stage 1 mixing model with A-2 brine. Observed versus predicted ground-water composition. (B) Stage 1 mixing model with hypothetical fluid (diluted A-2 brine). Observed versus predicted ground-water composition.

more diverse range of stable-isotope signatures in the southern Oil Springs region than is indicated in this research.

Major-Ion Ground-Water Chemistry

The feasibility of the multistage mixing model determined from stable-isotope compositions was tested by comparing major-ion ground-water chemistry data from the area with results predicted from the mixing model. We focused on the more conservative components of ground water, Cl^- and Br^-. The thermodynamically based model PHRQPITZ (Plummer et al., 1988) was used to model mixing scenarios involving less conservative ions such as Ca^{2+}, Mg^{2+}, and SO_4^{2-}.

Glacial-Brine Mixing. When low-salinity glacial fluid (e.g., sample R-AQ1) and a Silurian brine with a composition similar to the A-2 brine were mixed in the ratio indicated by the stable-isotope data, the resulting water was significantly more saline than sample CFN-161 (Fig. 7A; predicted Cl^- = 3 mol/kg versus CFN-161 Cl^- = 0.9 mol/kg). A less-saline fluid with a similar isotopic composition to the A-2 salt, Richfield Formation, or central-Michigan Detroit River Group could be present in the Silurian or deeper Devonian formations in the study area but may not have been sampled. Mixing a fluid with a similar isotopic composition to the Silurian A-2 brine and a similar but less-saline major-ion composition, with a glacially recharged low-salinity meteoric water (PHRQPITZ; Plummer et al., 1988) produced concentrations of Cl^-, Mg^{2+}, and Ca^{2+} within 15% of the concentrations measured in sample CFN-161 (Fig. 7B).

Compared with samples from Petrolia, northern Oil Springs, and Bothwell, the Br^- versus Cl^- and Na^+ versus Ca^{2+} ratios of ground water from southern Oil Springs are offset from a simple dilution trend (Figs. 8A and 8B). Trajectories to ground water from both the A-2 and the F salts of the Salina Formation are shown in Figures 8A and 8B. The change in slope in the conservative ions Br^- and Cl^- in ground water from southern Oil Springs result from mixing with a fluid with a major-ion composition similar to the A-2 salt. A break in slope between the same samples is also apparent in the δ^2H/Cl^- ratios (Fig. 4). The change in slope occurs between different samples on the Na^+ versus Ca^{2+} plot, probably reflecting the less conservative behaviour of these ions. The major-ion geochemical modeling and trends in major-ion ratios further support a multistage mixing model which involves the migration of saline, δ^2H-depleted fluids into shallow Devonian formations.

Vertical Mixing with Deep Saline Brines. Stable-isotope and major-ion data indicate that mixing occurred between saline, low-δ^2H water and significantly less saline, higher-δ^2H water already present in the Devonian oil-bearing formations. The mixing ratios required to reproduce the isotopic ratios measured in ground water from southern Oil Springs were determined from linear mixing between the most saline sample (CFN-161) and less saline fluids in that area. Unless a moderately saline fluid (TDS similar to CFN-C) is involved in this mixing model, the predicted solution chemistries are too dilute. We consider that water in the oil-bearing regions of the shallow Devonian formations was similar to CFN-C in composition before extensive dilution occurred as a result of petroleum production.

Stable isotopes of sulfates and sulfides also provide a comparison of fluid sources between the regions where water has entered the system from depth and regions where sulfate may have been derived from the host Devonian formations. Sulfur iso-

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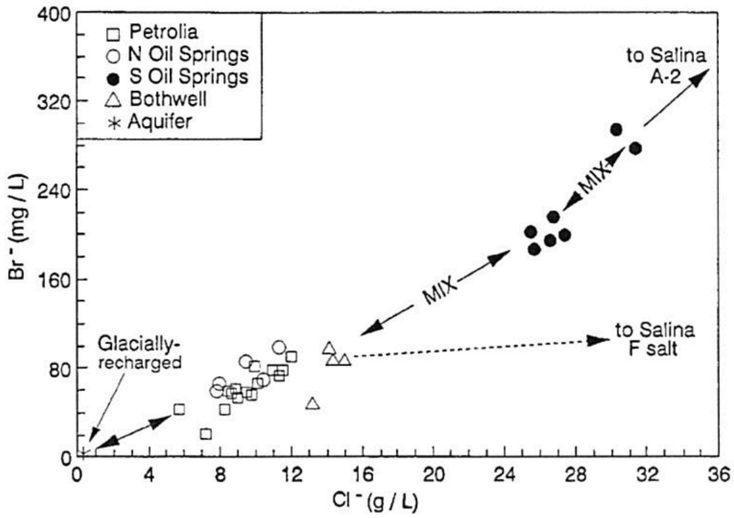

Figure 8A. Br$^-$ (mg/L) versus Cl$^-$ (g/L) indicating multistage mixing between less-saline ground water (Petrolia and northern Oil Springs) and saline ground water with a composition similar to that of A-2 brine (Dollar et al., 1991). Brine from the F-salt does not appear to contribute salinity to saline ground water in southern Oil Springs.

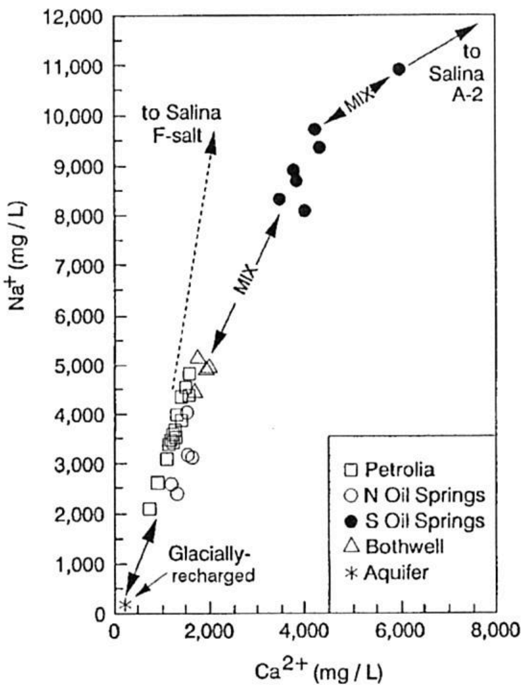

Figure 8B. Na$^+$ (mg/L) versus Ca^{2+} (mg/L) indicating multistage mixing between less-saline ground water (Petrolia and northern Oil Springs) and saline ground water with a composition similar to that of A-2 brine (Dollar et al., 1991).

topes of sulfate in ground water from Petrolia, northern Oil Springs, and Bothwell are consistent with dissolution of gypsum from host Devonian formations (Fritz et al., 1988; Fritz et al., 1989) accompanied by bacterial sulfate reduction. Sulfate in ground water from southern Oil Springs tends to be depleted in ^{34}S and ^{18}O with respect to ground water from Petrolia, northern Oil Springs, and Bothwell (average $\delta^{34}S_{(SO_4^{2-})}$ = 28.3‰ [southern Oil Springs] versus 31.1‰ [other areas], and average $\delta^{18}O_{(SO_4^{2-})}$ = 15.8‰ [southern Oil Springs] versus 17.1‰ [other areas]; Table 1). If sulfate reduction has occurred in these fluids, these values would be within the range expected for Silurian sulfates (Claypool et al., 1980); therefore, the stable-isotope ratios of sulfates in ground water from the southern Oil Springs region also indicate that both ground water and solutes have been emplaced into this area of the Dundee Formation from a different, probably Silurian formation.

Dilution with Moderately Saline Meteoric Water. The moderate salinity of samples along the meteoric water line, ranging from 10–25 g/L, and the Cl$^-$ concentrations of 2–6 g/L inferred for water from northern Oil Springs and south Petrolia with a δ^2H value similar to that of recent meteoric water (Fig. 4) indicate that the meteoric water that diluted these samples contained significant concentrations of solutes including Na$^+$ and Cl$^-$ (Table 1). Possible sources for these solutes include mineral dissolution occurring along flow paths between the surface and the oil-bearing formations (e.g. Banner et al., 1989), diffusion of salts from the matrix of the Dundee Formation or the Hamilton Group into ground water in the oil-bearing formations, and dissolution of salts evaporated from oil-field water that was disposed of at surface in the oil-producing regions from 1860 to 1990. This water may have subsequently leaked into the Devonian oil-bearing formations.

Assuming a formation porosity (n) of 0.1 and a bulk density of 2.0 for the Hamilton Group shale, leaching of ground Hamilton Group shale samples (Thurston, 1991) indicates that Cl$^-$ concentrations in the interstitial fluids in these shales would be about 5–11 g/L. Lower interstitial fluid concentrations of 2–4 g/L were indicated from the results of the leached Dundee samples. These concentrations are only estimates; interstitial fluid concentrations would be expected to decrease in zones of higher flow and at the temperature of 11 °C in the shallow Devonian formation (compared with the laboratory temperature of 25 °C).

A two-dimensional, numerical solute-transport model representing flow in fractured and unfractured porous media (FRACTRAN; Sudicky and McLaren, 1992) was used to evaluate the extent to which diffusion of salts from the rock matrix could contribute salinity to meteoric water leaking through fractures in the Hamilton Group shale units. The parameters used in this model were an effective Cl$^-$ diffusion coefficient (D*) of 5.9×10^{-10} m^2/s (Desaulniers et al., 1986); a matrix porosity (φ) of 0.1; a matrix hydraulic conductivity of 1×10^{-11} m/s (Weaver, 1994); vertical hydraulic

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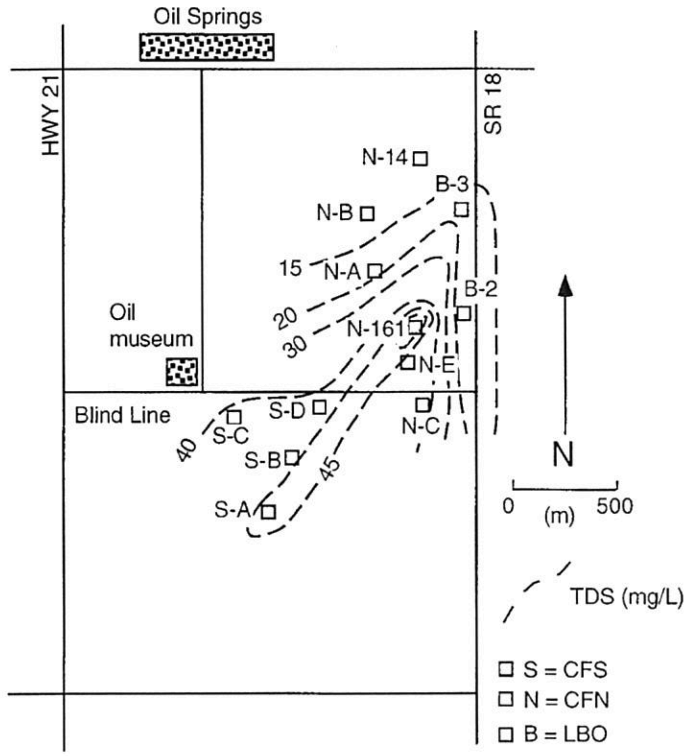

Figure 9. Contour map of total dissolved solids (TDS) (g/L) in southern Oil Springs.

gradients ranging from 0.5 to 0.7 (Raven et al., 1989; Weaver, 1994); an estimated fracture aperture (2b) of 2×10^{-4} m; a fracture spacing of 20 m; a free-ion diffusion coefficient (D°) of 17.1×10^{-10} m^2/s (Li and Gregory, 1974); and a dispersivity value (α) of 0.1 m in the fractures.

The model was run for a time (t) of 100 yr, which represents the time since petroleum production started. Historical records indicate that wells that were initially gushers ceased to flow at the surface shortly after oil production began; therefore, the direction of hydraulic gradients probably reversed from upward to downward during the late 1800s (Weaver, 1994). When matrix diffusion was modeled with fresh water entering the vertical fracture network at the top of the Hamilton Group at t = 0 and an assumed initial Cl^- concentration in the matrix of 8 g/L (Hamilton Group shale units), the resulting Cl^- concentrations in meteoric water in the fractures and entering the Dundee Formation were on the order of 4–7 g/L. This is similar to the estimated range of Cl^- concentrations (2–6 g/L) in meteoric water recharging the system (Fig. 4).

MECHANISMS AND TIMING OF FLUID MIXING

The presence of petroleum and saline water in glacial till in the Petrolia and Oil Springs regions (Harkness, 1951; Fairbank, 1953) indicates that these fluids were emplaced during, or after, the Wisconsinan glacial retreat at ca. 10 ka; therefore, upward hydraulic gradients between the oil-bearing Devonian formations and the surface would have existed at that time. Reports of newly drilled wells coming in as gushers during the 1860s at the start of the development of the petroleum industry (Harkness, 1951) indicate that, in the oil-producing regions, high fluid pressures and upward hydraulic gradients persisted in the shallow Devonian oil-bearing formations until petroleum production began. As drilling continued, upward hydraulic gradients dissipated, and downward, rather than upward, hydraulic gradients dominated the flow regime between the surface and the oil-bearing Devonian formations (Weaver, 1994).

In this research, stable and radiogenic isotopes, the major-ion composition of ground water, and historical information are used to constrain the mechanisms and timing of fluid mixing and transport involving the Devonian oil-bearing formations. Geochemical data indicate that Silurian or Lower Devonian brines mixed with glacially recharged ground water and were then emplaced into the oil-bearing Devonian formations during or after deglaciation (Figs. 6, 8A, 8B). The limited occurrence of these low-δ^2H, high-TDS fluids (Fig. 9) implies that migration of the mixed brine/glacial fluid probably occurred along discrete fractures. Parallel studies by Coniglio et al. (1994) and Middleton et al. (1993) of the Ordovician strata of southwestern Ontario show that large-scale fluid flow in fractures and associated dolomitization dominated the area. Sanford et al. (1985) provide further evidence of a large-scale, predominantly vertical fracture network (Fig. 3) across the Paleozoic sequence.

Because glacially derived fluids were involved in mixing prior to their emplacement in the oil-bearing Devonian formations of the southern Oil Springs region, cross-formational movement of saline fluids into these formations must have occurred during, or after, the last glaciation. Lower $\delta^{34}S$ values, low δ^2H values, high Cl^- contents, lower pH values, and more negative saturation indices (PHRQPITZ; Plummer et al., 1988) for ground water with respect to the host mineralogy in this area indicate that this localized influx of saline (possibly Silurian) fluids from depth may have continued since glaciation in this region. Mechanisms leading to mixing could have included diffusion due to chemical gradients (Long et al., 1988) or flow through fractures and higher-permeability porous media during periods of stress release such as deglaciation (Siegel and Mandle, 1984; Siegel, 1991; Raven et al., 1992). The localized occurrence of these anomalous fluids within the oil-bearing Devonian formations further indicates that saline fluid moved along fractures rather than by diffusion alone.

Isostatic rebound due to ice retreat at 10 ka occurred over ~8 000 yr (Fulton et al., 1984) and would have affected the formation pressures and consolidation states of the Paleozoic sequence and the overlying Quaternary deposits (e.g., Neuzil and Pollock, 1983; Neuzil, 1985) (Table 2). At the glacial maximum, the ice sheet covering the study area is assumed to have been 2–3.5 km thick (Paterson, 1972). Clark et al. (1990) indicate that, at 18 ka, the ground surface in the Port Huron area could have been depressed by as much as 450 m below its present surface elevation. Current vertical rebound rates are ~7 cm/100 yr (Clark et al.,

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TABLE 2. SUMMARY OF MECHANISMS DURING GLACIATION AND DEGLACIATION RESULTING IN CHANGES IN HYDRAULIC PARAMETERS AND FLOW RATES

Event and timing	Effect	Result	Hydraulic conductivity
Glacial loading (>10 ka)	Varying amounts of compaction. Increased compaction in shale, clay, and highly fractured formations.	Closed fractures. Decreased porosity. Fluid expulsion or increased fluid pressure.	Decreased bulk hydraulic conductivity (K_{bulk}).
Deglaciation (10–8 ka)	Differential expansion on ice removal. Increased expansion in shale and clay.	Reactivated or new fractures formed. Increased porosity. Possible decrease in fluid pressure.	Increased bulk hydraulic conductivity (K_{bulk}).

Note: Mechanisms such as gas generation which may contribute to overpressured conditions at depth are assumed to be consistent throughout glaciation and deglaciation.

1990; Tushingham, 1992). In addition to vertical rebound, James and Morgan (1990) suggested that horizontal rebound has occurred after deglaciation, and they calculated present-day horizontal rebound rates of ≤2 cm/100 yr in the Great Lakes region.

Upon deglaciation, bedrock and overburden sequences would have expanded at differential rates because of different formation compressibility values. In the lithified Paleozoic sequence, this expansion may have created new fractures or reactivated or enlarged existing fractures. In the unlithified overburden, the expansion could have led to an increase in matrix porosity. In both cases, the bulk hydraulic conductivity of the previously ice-compressed formations would have increased, thereby resulting in increased ground-water flow rates within these formations. The changes in hydraulic parameters produced by deglaciation could have provided conditions under which cross-formational flow of saline fluids from depth could occur.

Meteoric water with low δ^2H and $\delta^{18}O$ values could have entered the bedrock formations where they subcropped under glacial deposits during glaciation or deglaciation and mixed with Silurian brines along fracture pathways. Reactivated fractures would have provided pathways for the glacial/saline fluid to enter the shallow oil-bearing Devonian formations (Fig. 10). Newly activated fracture pathways in the overlying Hamilton shales and increased permeability in localized areas of the glacial till could have enabled petroleum and saline fluids to migrate into these overlying units.

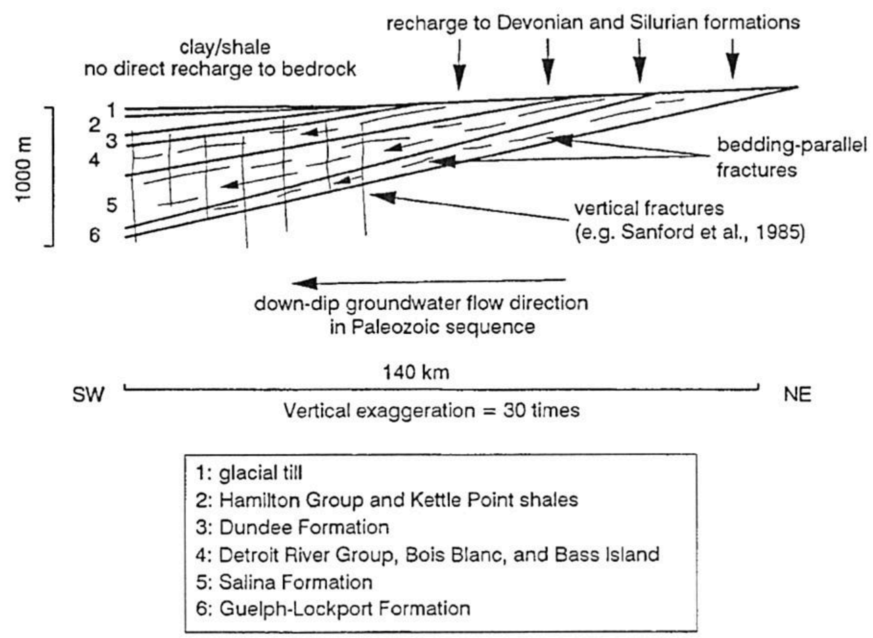

Figure 10. Conceptual model of fluid migration and mixing during and after glaciation. (1) Recharge of ^{2}H-depleted ground water to permeable Devonian and Silurian formations during and after glaciation (e.g., Siegel and Mandle, 1984). Down-gradient migration of ^{2}H-depleted ground water probably along bedding-parallel fractures. If transport occurred along fractures, this fluid would mix with fluid in formation matrix. (2) During deglaciation, horizontal and vertical fractures opened or were reactivated, allowing the vertical migration of fluid from depth. In the study area, a previously mixed glacial-brine fluid probably migrated from Silurian formations to the oil-bearing Devonian formations over vertical distances of about 400 m. (3) Continuing lateral migration of glacially recharged and more-recently recharged ground water down-gradient in Paleozoic units since glaciation.

SUMMARY

Major-ion and isotope data in ground water constrain the mechanisms and timing of the migration of saline fluids into Devonian oil-bearing formations in the shallow Michigan Basin. The earliest recognizable episode of fluid movement directly involving the Devonian sequence was the migration of petroleum into the region. Results of this research indicate that more recent cross-formational flow has occurred in the region. Saline, low-δ^2H fluids migrated vertically along fracture networks from depths of several hundreds of meters into the oil-bearing Devonian formations. This migration probably occurred during, or after, deglaciation. Consequently, the shallow Michigan Basin in this area should be viewed as a hydrogeologically active rather than static system.

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REFERENCES CITED

Back, W., Hanshaw, B. B., Plummer, L. N., Rahn, P. H., Rightmire, C. T., and Rubin, M., 1983, Process and rate of dedolomitization: Mass transfer and ^{14}C dating in a regional

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carbonate aquifer: Geological Society of America Bulletin, v. 94, p. 1415–1429.
Bailey Geochemical Services Ltd. and Cochrane, R. O., 1985, Evaluation of the conventional and potential oil and gas reserves of the Devonian of Ontario: Ontario Geological Survey Open File Report 5555, 9 vol., 178 p.
Banner, J. L., Wasserburg, G. J., Dobson, P. F., Carpenter, A. B., and Moore, C. H., 1989, Isotopic and trace element constraints on the origin and evolution of saline groundwaters from central Missouri: Geochimica et Cosmochimica Acta, v. 53, p. 383–398.
Brigham, R. J., 1971, Structural geology of southwestern Ontario and southeastern Michigan: Ontario Department of Mines and Northern Affairs, Petroleum Resource Section, Paper 71-2, 110 p.
Carpenter, A. B., and Trout, M. L., 1978, Geochemistry of bromide-rich brines of the Dead Sea and southern Arkansas: Oklahoma Geological Survey Circular 79, p. 78–88.
Clark, J. A., Pranger, H. S., II, Walsh, J. K., and Primus, J. A., 1990, A numerical model of glacial isostasy in the Lake Michigan basin: Geological Society of America Special Paper 251, p. 111–123.
Claypool, G. E., Holser, W. T., Kaplan, R., Sakai, H., and Zak, I., 1980, The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation: Chemical Geology, v. 28, p. 199–260.
Clayton, R. N., Friedman, I., Graf, D. L., Mayeda, T. K., Meents, W. F., and Shimp, N. F., 1966, The origin of saline formation waters, 1. Isotopic Composition: Journal of Geophysical Research, v. 71, no. 16, p. 3869–3882.
Coniglio, M., Sherlock, R., Middleton, K., Williams-Jones, A. E., and Frape, S. K., 1994, Burial and hydrothermal diagenesis of Ordovician carbonates from the Michigan Basin, Ontario, Canada: International Association of Sedimentologists Special Publications, v. 21, p. 231–254.
Connolly, C. A., Walter, L. M., Baadsgaard, H., and Longstaffe, F. J., 1990a, Origin and evolution of formation waters, Alberta Basin, western Canada sedimentary basin. I. Chemistry: Applied Geochemistry, v. 5, p. 375–395.
Connolly, C. A., Walter, L. M., Baadsgaard, H., and Longstaffe, F. J., 1990b, Origin and evolution of formation waters, Alberta Basin, western Canada sedimentary basin. II. Isotope systematics and water mixing: Applied Geochemistry, v. 5, p. 397–413.
Desaulniers, D. E., Cherry, J. A., and Fritz, P., 1981, Origin, age and movement of pore water in argillaceous Quaternary deposits at four sites in southwestern Ontario: Journal of Hydrology, v. 50, p. 231–257.
Desaulniers, D. E., Kaufmann, R. S., Cherry, J. A., and Bentley, H. W., 1986, ^{37}Cl-^{35}Cl variations in a diffusion-controlled groundwater system: Geochimica et Cosmochimica Acta, v. 50, p. 1757–1764.
Dollar, P., Frape, S. K., and McNutt, R. H., 1991, Geochemistry of formation waters, southwestern Ontario, Canada and southern Michigan, U.S.A. Implications for origin and evolution: Ontario Geological Survey Open File Report 5743, 72 p.
Ells, G. D., 1969, Architecture of the Michigan Basin, *in* Stonehouse, H. B., ed., Studies of the Precambrian of the Michigan Basin: Michigan Basin Geological Society Annual Field Excursion Guidebook, p. 60–80.
Fairbank, C. O., II, 1953, The Petrolia story: Edmonton. Alberta, Northwest Oil Journal, v. 2, no. 1, p. 5–13.
Frape, S. K., Dollar, P., Lollar, B. S., and McNutt, R. H., 1989, Mixing of saline basinal fluids in southern Ontario: Implications of rock-water interaction, hydrocarbon emplacement and Canadian Shield brines *in* Miles, D. L., ed., Proceedings, Water-Rock Interaction, WRI-6, Malvern, U.K., 1989: Balkhema, Rotterdam, Netherlands, p. 223–226.
Fritz, P., Basharmal, G. M., Drimmie, R. J., Ibsen, J., and Qureshi, R. M., 1989, Oxygen isotope exchange between sulfate and water during bacterial redaction of sulfate: Chemical Geology (Isotope Geoscience Section), v. 79, p. 99–105.
Fritz, P., Drimmie, R. J., Frape, S. K., and O'Shea, K., 1987, The isotopic composition of precipitation and groundwater in Canada: Vienna, Austria, International Atomic Energy Agency, International Symposium on the Use of Isotope Techniques in Water Resources Development, Vienna, 1987, IAEA-SM-299/017, p. 539–550.
Fritz, P., Frape, S. K., Drimmie, R. J., and Heemskerk, A. R., 1986, Reply to comments by Grabczak et al. on "Water-rock interaction and chemistry of groundwaters from the Canadian Shield": Geochimica et Cosmochimica Acta, v. 50, p. 1561–1563.
Fritz, P., Lapcevic, P. A., Miles, M., Frape, S. K., Lawson, D. E., and O'Shea, K. J., 1988, Stable isotopes in sulfate minerals from the Salina formation in southwestern Ontario: Canadian Journal of Earth Sciences, v. 25, p. 195–205.
Fulton, R. J., Karrow, P. F., LaSalle, D., and Grant, D. R., 1984, Summary of Quaternary stratigraphy and history, eastern Canada, *in* Fulton, R. J., ed., Quaternary stratigraphy of Canada—A Canadian contribution to IGCP Project 24: Geological Survey of Canada Paper 84-10, p. 193–210.
Hanor, J. S., 1988, Origin and migration of subsurface sedimentary brines: Tulsa, Oklahoma, SEPM Short Course 21, 247 p.
Harkness, R. B., 1951, Ontario's part in the petroleum industry: Canadian Oil and Gas Industries, February and March 1951, p. 1–8.
Hitchon, B., and Friedman, I., 1969, Geochemistry and origin of formation waters in the western Canada sedimentary basin—I. Stable isotopes of hydrogen and oxygen: Geochimica et Cosmochimica Acta, v. 33, p. 1321–1349.
James, T. S., and Morgan, W. J., 1990, Horizontal motions due to post-glacial rebound: Geophysical Research Letters, v. 17, no. 3, p. 957–960.
Langmuir, D., 1971, The geochemistry of some carbonate ground waters in central Pennsylvania: Geochimica et Cosmochimica Acta, v. 35, p. 1023–1045.
Land, L. S., and Prezbindowski, D. R., 1981, The origin and evolution of saline formation water, Lower Cretaceous carbonates, south-central Texas, U.S.A.: Journal of Hydrology, v. 54, p. 51–74.
Li, Y. H., and Gregory, S., 1974, Diffusion of ions in sea water and in deep sea sediments: Geochimica et Cosmochimica Acta, v. 38, p. 703–714.
Lico, M. S., Kharaka, Y. K., Carothers, W. W., and Wright, V. A., 1982, Methods for collection and analysis of geopressured geothermal and oil field waters: U.S. Geological Survey Water Supply Paper 2194, 20 p.
Long, D. T., Wilson, T. P., Takacs, M. J., and Rezabeck, D. H., 1988, Stable-isotope geochemistry of saline near-surface ground water: East-central Michigan Basin: Geological Society of America Bulletin, v. 100, p. 1568–1577.
McNutt, R. H., Frape, S. K., and Dollar, P., 1987, A strontium, oxygen and hydrogen isotopic composition of brines, Michigan and Appalachian Basins, Ontario and Michigan: Applied Geochemistry, v. 2, p. 495–505.
Middleton, K., Coniglio, M., Sherlock, R., and Frape, S. K., 1993, Dolomitization of Middle Ordovician carbonate reservoirs, southwestern Ontario: Bulletin of Canadian Petroleum Geologists, v. 41, p. 150–163.
Neuzil, C. E., 1985, Comment on "Possible effects of erosional changes of the topographic relief on pore pressures at depth" by J. Toth and R. F. Millar: Water Resources Research, v. 21, no. 6, p. 895–898.
Neuzil, C. E., and Pollock, D. W., 1983, Erosional unloading and fluid pressures in hydraulically "tight" rocks: Journal of Geology, v. 91, p. 179–193.
O'Shea, K. J., Miles, M. C., Fritz, P., Frape, S. K., and Lawson, D. E., 1988, Oxygen-18 and carbon-13 in the carbonates of the Salina Formation of southwestern Ontario: Canadian Journal of Earth Sciences, v. 25, p. 182–194.
Paterson, W. S. B., 1972, Laurentide ice sheet: Estimated volumes during late Wisconsin: Reviews of Geophysics and Space Physics, v. 10, no. 4, p. 885–917.
Plummer, L. N., Parkhurst, D. L., Fleming, G. W., and Dunkle, S. A., 1988, A computer program incorporating Pitzer's equations for calculation of geochemical reactions in brines: U.S. Geological Survey Water-Resource Investigations Report 88-4153, 310 p.
Powell, T. G., Macqueen, R. W., Barker, J. F., and Bree, D. G., 1984, Geochemical character and origin of Ontario oils: Bulletin Canadian Petroleum Geologists, v. 32, no. 3, p. 289–312.
Raven, K. G., Lafleur, D. W., and Sweezey, R. A., 1989, Monitoring well into abandoned deep-well disposal formations at Sarnia, Ontario: Canadian Geotechnical Journal, v. 27, p. 105–118.
Raven, K. G., Novakowski, K. S., Yager, R. M., and Heystee, R. J., 1992, Supernormal fluid pressures in sedimentary rocks of southern Ontario–western New York State: Canadian Geotechnical Journal, v. 29, p. 80–93.
Sakai, H., and Krouse, H. R., 1971, Elimination of memory effect in ^{18}O-^{16}O determinations in sulfates: Earth and Planetary Science Letters, v. 11, p. 369–373.
Sanford, B. V., Thompson, F. J., and McFall, G. H., 1985, Plate tectonics—A possible controlling mechanism in the development of hydrocarbon traps in southwestern Ontario: Bulletin Canadian Petroleum Geologists, v. 33, no. 1, p. 52–71.
Siegel, D. I., 1991, Evidence for dilution of deep, confined ground water by vertical recharge of isotopically heavy Pleistocene water: Geology, v. 19, p. 433–436.
Siegel, D. I., and Mandle, R. J., 1984, Isotopic evidence for glacial meltwater recharge to the Cambrian–Ordovician aquifer, north-central United States: Quaternary Research, v. 22, p. 328–335.
Stueber, A. M., and Walter, L. M., 1991, Origin and chemical evolution of formation waters from Silurian–Devonian strata in the Illinois basin, U.S.A.: Geochimica et Cosmochimica Acta, v. 55, p. 309–325.
Sudicky, E. A., and McLaren, R. G., 1992, The Laplace Transform Galerkin technique for large-scale simulation of mass transport in discretely fractured porous formations: Water Resources Research, v. 28, no. 2, p. 499–514.
Taylor, C. B., 1977, Tritium enrichment of environmental waters by electrolysis: Development of cathodes exhibiting high isotopic separation and precise measurement of tritium enrichment factors, *in* Proceedings, International Conference of Low-Radioactivity Measurements and Applications: Bratislava, Slovenski Pedagogicke Nakladatelstvo, p. 131–140.
Thurston, D. M., 1991, A geochemical analysis of rocks and their leachates from the Kettle Point, Hamilton Group and Dundee Formations, Sarnia, Ontario [B.Sc. thesis]: Waterloo, Ontario, University of Waterloo, Department of Earth Sciences, 77 p.
Tushingham, A. M., 1992, Postglacial uplift predictions and historical water levels of the Great Lakes: Journal of Great Lakes Research, v. 18, no. 3, p. 440–455.
Walter, L. M., Stueber, A. M., and Huston, T. J., 1990, Br-Cl-Na systematics in Illinois basin fluids: Constraints on fluid origin and evolution: Geology, v. 18, p. 315–318.
Weaver, T. R., 1994, Groundwater flow and solute transport in shallow Devonian bedrock formations and overlying Pleistocene units, Lambton County, southwestern Ontario [Ph.D. thesis]: Waterloo, Ontario, University of Waterloo, 401 p.
Wilson, T. P., and Long, D. T., 1993, Geochemistry and isotope chemistry of Michigan Basin brines: Devonian formations: Applied Geochemistry, v. 8, p. 81–100.
Yanagisawa, F., and Sakai, H., 1983, Thermal decomposition of barium sulfate–vanadium pentoxide silica glass mixtures for preparation of sulfur dioxide in sulfur ratio measurements: Analytical Chemistry, v. 55, p. 985.

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