OPG's DEEP GEOLOGIC

REPOSITORY

FOR LOW & INTERMEDIATE LEVEL WASTE

Supporting Technical Report

Phase I Regional Hydrogeochemistry, Southern Ontario

November 30, 2008

Prepared by:
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University of Waterloo

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EXECUTIVE SUMMARY

A geochemical database has been complied based on the chemical and isotopic compositions of waters collected from multilevel research wells and producing hydrocarbon wells across southern Ontario and in Michigan by researchers at the University of Waterloo, Ontario, Canada. Two geochemical systems are recognized at the regional scale: i) a shallow system (<200 m below ground surface) containing fresh through brackish waters classified as Na-Cl, Na-Mg-Ca-Cl, $Ca\text{-}SO_4$ or Ca-Na-Cl type based on major ion concentrations. Waters in this system have stable isotopic compositions of $\delta^{18}O$ and $\delta^{2}H$ consistent with mixing of dilute meteoric or cold-climate (glacial) waters with more saline waters; and ii) an intermediate to deep system (>200 m below ground surface) containing predominantly brines associated with hydrocarbons in reservoirs which are characterized by Na-Ca-Cl or Ca-Na-Cl type waters with elevated TDS values (200,000-400,000 mg/L). The stable oxygen and hydrogen values of these waters are typical of sedimentary basin brines (TDS > 100,000 mg/L) in that they are enriched relative to the Global Meteoric Water Line ($\delta^{18}O$ values between -6 and +3 ‰ and $\delta^{2}H$ values between -55 and +20 ‰).

Through an assessment of the geochemical database in the context of the geology, diagenetic and thermal history and hydrogeology of the sedimentary sequence, the following lines of evidence relevant to the geochemical stability of the intermediate to deep system on geologic time scales were established:

- The maximum depth at which waters with isotopic signatures indicative of a meteoric origin are observed in the database (with two exceptions that are attributed to drill water mixing) is 140 m below ground surface. In Ontario, the maximum depths at which glacial waters have been observed are 130 m in shallow bedrock aquifers and 125 m below ground surface in the till deposits of the Alliston aquifer.
- Along the northern and western margins of the Michigan Basin and the northern margin of the Illinois Basin, the maximum reported depth for glacial recharge is 300 m below the subcrop of the Antrim (MB) or New Albany (IB) shale formations in waters associated with microbial methane gas reservoirs. At the eastern edge of the Michigan Basin, there is no evidence for significant dilution of formation fluids within the Antrim Shale (or the Kettle Point Formation in Ontario) by meteoric recharge or for microbial methanogenesis.
- The presence of methane gas in many of the hydrocarbon reservoirs suggests that the reduction-oxidation conditions are reducing in the intermediate to deep system.
- The major ion composition of waters within the intermediate to deep system strongly suggests that these waters evolved from seawater by evaporation past halite saturation. Increased Ca concentrations and decreased Mg concentrations relative to seawater are consistent with dolomitization reactions between these waters and calcite within the carbonate formations.
- The stable isotopic signatures ($\delta^{18}O$ and $\delta^{2}H$) of waters from reservoirs from formations of different ages and lithologies (e.g., carbonate versus sandstone) are observed to cluster in distinct ranges. The persistence of these distinct isotopic signatures at a regional scale suggests that the waters and associated hydrocarbons have remained isolated from one another over geologic time frames.

- The presence of Cambrian-Ordovician oils in two Silurian reservoirs suggests that at a local-scale, some cross-formational flow of hydrocarbons occurred between reservoirs.

- Waters associated with hydrocarbons are interpreted to be diagenetic in origin. These waters may have formed in-situ as the result of extensive seawater evaporation in the basin, which led to entrapment of waters in the rocks during sedimentation and compaction during burial; or they may be remnants of hydrothermal fluids which formed deeper within the sedimentary basin(s) and then migrated into the stratigraphic or structural traps along permeable pathways.

- Based on evidence from fluid inclusions, the fluids involved in dolomitization in Silurian and Ordovician formations are $NaCl-MgCl_2-CaCl_2$ or Na-Ca-Mg-Cl type fluids, with salinities in the range of 14 to 41 wt. % NaCl. The temperatures of between 65 and 220°C determined for primary fluid inclusions indicate that these fluids were hydrothermal (i.e., temperatures > 100°C). Fluid inclusions in fluorite from the Silurian-aged Lockport formation suggests that the mineralizing fluids associated with Mississippi Valley Type (MVT) deposits in southern Ontario were also hydrothermal (temperatures between 130 to 140°C). These temperatures are consistent with the upper range of temperatures reported for fluids associated with dolomitization in Silurian-aged formations. Elevated temperatures may have been generated in the basin due to deep burial by sediments which have since been eroded. At the basin margins, at least 1,000 m of sediment has been eroded. However, even burial depths of 2,000 m would have produced burial temperatures of <70 °C in southwestern Ontario. The interpretation that hydrothermal fluids were involved in both dolomitization in Ordovician-aged formations and the emplacement of MVT deposits in Silurian-aged formations is therefore considered more consistent with the thermal and burial history of the sedimentary sequence.

- The general similarity in the range of salinities and the composition of the fluids involved in dolomitization with the compositions of waters occurring in association with hydrocarbons in the subsurface supports the interpretation of these waters as diagenetic in origin.

- In the current scientific understanding of the emplacement of diagenetic fluids associated with dolomitization, MVT massive sulphide deposits and hydrocarbons, the presence of driving forces which are sufficient to transport dense brines from deep within the sedimentary basins to the margins along regional aquifers and other permeable pathways such as fractures or faults is a key constraint on the timing of fluid movement. In the different basin-scale flow models, the majority of the driving forces are associated with tectonic or orogenic events. A Late Paleozoic to Early Mesozoic (350 to 250 Ma BP) time-frame has been proposed for both the emplacment of MVT Pb-Zn deposits in Silurian strata in southern Ontario and for the formation of fracture-related dolomitization and hydrocarbon migration in the Michigan Basin in Ordovician formations, concurrent with deformation and thrusting events associated with the Alleghenian orogeny.

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1. INTRODUCTION

The regional hydrogeochemical synthesis is part of an overall synthesis of geoscientific knowledge on sub-surface conditions in southwestern Ontario conducted in support of Ontario Power Generation's Deep Geological Repository (DGR) proposal. The overall objective of this geosynthesis is to assess the integrity and long-term stability of the sedimentary sequence underlying southwestern Ontario in terms of the suitability of the geologic formations to isolate low and intermediate level waste (L & ILW) at timeframes of one million years and beyond.

This hydrogeochemical report is one of six supporting Technical Reports prepared as part of the Phase I Geosynthesis work program (Gartner Lee Limited, 2008a). The other Phase I supporting Technical Reports include: Regional Geology (Gartner Lee Limited, 2008b); Regional Hydrogeologic Modelling (Sykes et al., 2008); Long-term Climate Change (Peltier, 2008); Regional Geomechanics (Gartner Lee Limited, 2008c); and Long Term Cavern Stability (Itasca, 2008).

1.1 Objectives

The purpose of the regional hydrogeochemical study is to present i) the information currently available on the occurrence of groundwaters within the Paleozoic sedimentary sequence underlying southwestern Ontario, including their compositions and spatial distribution; and ii) the scientific understanding of the origin, evolution and timing of emplacement of these groundwaters within the sedimentary sequence.

The objectives of this study were to:

- Verify and expand the published geochemical database for formation waters from sedimentary formations underlying southwestern Ontario and eastern Michigan;
- Assess the origin of formation fluids based on their inorganic and isotopic geochemistry and on the geologic setting in which the fluids occur, documenting evidence for the relative age of the formation waters;
- Examine the geochemical signatures of the various formation waters on a three-dimensional, regional basis;
- Determine potential pathways of groundwater transport and mixing within the Paleozoic sequence, including an evaluation of cross-formational flow; and
- Evaluate the depth of penetration of modern recharge and glacial meltwaters into the Paleozoic sequence.

1.2 Methodology

The first task in the regional hydrogeochemical synthesis was to compile a comprehensive geochemical database of chemical and isotopic analyses for waters sampled throughout the sedimentary sequence. This database was assembled from published and previously unpublished research conducted over more than 25 years at the University of Waterloo. Section 5 of this report fully describes the procedures and quality assessment procedures used to verify the database.

The database, in conjunction with published geologic literature for southwestern Ontario, is used to evaluate the hydrogeochemical evidence relevant to the stability of the groundwater flow systems on geological time scales. The interpretations of the regional geochemical database presented in this report are consistent with published, current “best scientific” understanding of the evolution of highly saline groundwaters in sedimentary basins, as well as the processes and driving forces required for transport and entrapment of these fluids.

1.3 Hydrogeochemical Hypothesis

Hydrogeochemical lines of evidence indicate that waters from deep within the Paleozoic sedimentary formations underlying Southern Ontario have remained undisturbed over geologic times scales (Mazurek, 2004):

- With the exception of groundwaters collected from shallow levels within the sedimentary sequence, high salinities (200,000 to 300,000 mg/L Total Dissolved Solids) coupled with water and strontium isotopic signatures indicate long residence times;

- Groundwaters from different formations have distinct chemical and isotopic characteristics which argue against the occurrence of cross-formational flow in most areas since the time of burial diagenesis of the sedimentary formations.

These observations were based on a geochemical dataset obtained from 80 brine samples within southwestern Ontario and eastern Michigan and published by McNutt et al. (1987) and Frape et al. (1989). By examination of an extended geochemical database, which contains over 200 groundwater samples from throughout southwestern Ontario and eastern to central Michigan, this regional hydrogeochemical synthesis further tests these early hypotheses and expands on the concepts presented by Mazurek (2004).

There are two fundamental geoscientific tenets for the DGR Safety case as described by Gartner Lee Limited (2008a) to which the regional hydrogeochemical synthesis contributes scientific understanding:

- ➢ Contaminant Transport is Diffusion Dominated: deep groundwater regime is ancient showing no evidence of glacial perturbation or cross-formational flow

- ➢ Shallow Groundwater Resources are Isolated: near surface groundwater aquifers isolated

The hydrogeochemical evidence available at the regional scale which relates to these tenets is presented and interpreted in this report.

2. GEOLOGY AND HYDROGEOLOGY OF SOUTHWESTERN ONTARIO

To provide context for the interpretation of the geochemical database, a brief description of the geology and hydrogeology of southwestern Ontario are provided in the following sections. A detailed synthesis of the regional geology of southern Ontario is provided by Gartner Lee Limited (2008b) and the hydrogeological conceptual model and numerical simulations are described in Sykes et al. (2008).

2.1 Geology

Southern Ontario is located between the foreland Appalachian Basin and the intracratonic Michigan Basin in the interior platform of the North American Continent (Figure 1). The Algonquin Arch (Figure 1) is a Precambrian basement high which trends northeast-southwest, and is an extension of the Findlay arch to the southwest. These positive structural features were likely formed during the Late Precambrian, and then intermittently reactivated during the Paleozoic, creating a broad platform between the Michigan Basin to the west and the Appalachian Basin to the southeast (Sanford et al. 1985). The Algonquin and Findlay arches are separated by a major structural depression referred to as the Chatham sag. From the crest of the Algonquin arch in southwestern Ontario, sedimentary rocks dip into the Michigan Basin to the northwest and into the Allegheny Trough of the Appalachian Basin to the southeast (Figure 2). Regional dip of the sedimentary rocks flanking the Algonquin Arch is about 5.5 m/km into the Michigan Basin and about 8.5 m/km into the Appalachian Basin (Winder and Sanford, 1972). Palaeozoic strata in the Chatham Sag are essentially horizontal.

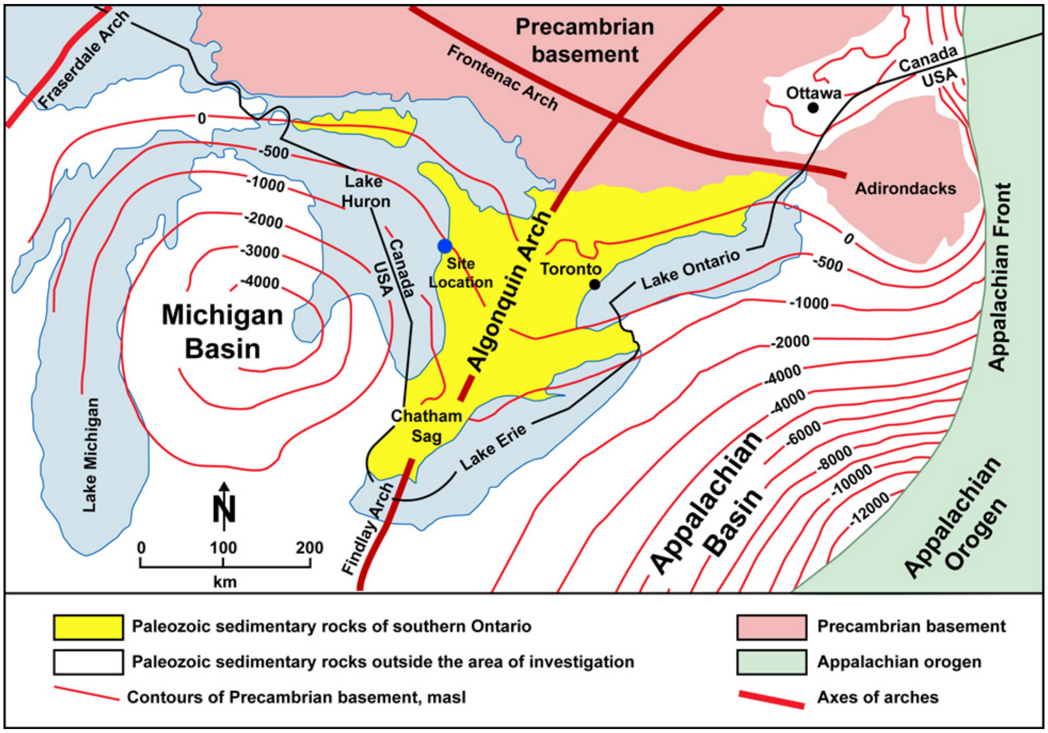


Figure 1: Large-scale tectonic elements in southern Ontario and definition of study area, adapted from Johnson et al. 1992 (from Mazurek 2004).

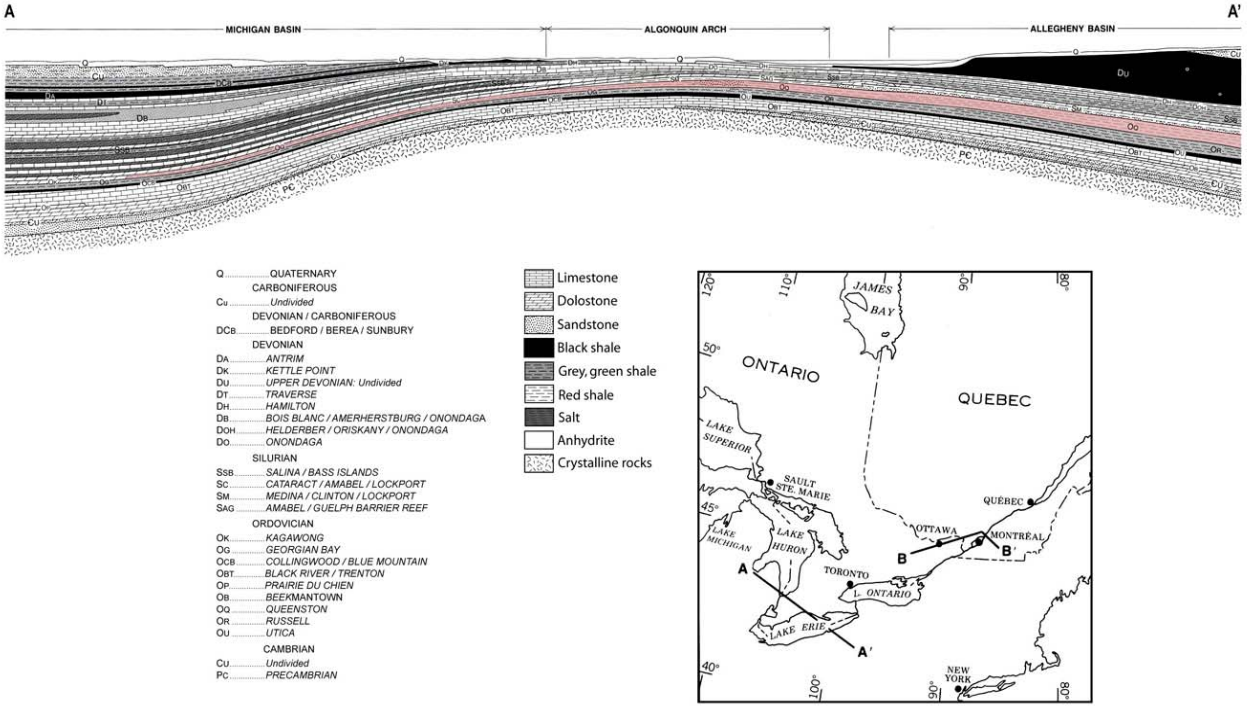


Figure 2: Cross-section across the Algonquin Arch in southwestern Ontario (A – A' as shown in the insert) (from Sanford et al. 1993).

Southwestern Ontario is underlain by a sedimentary succession that is tectonically undisturbed, and which rests unconformably on Precambrian basement rocks (Figure 2). The maximum recorded thickness of the Palaeozoic sedimentary sequence within the province is 1,525 m (Winder and Sanford, 1972). The formations either thin or pinch-out, or have been partially eroded over the crest of the Algonquin arch to the northeast. The oldest bedrock outcrop is Ordovician in age and occurs in the northeastern part of the study area (Figure 3). Bedrock outcrops are successively younger toward the southwest along the Algonquin Arch. Over much of the study area, outcrops are obscured by Pleistocene glacial drift.

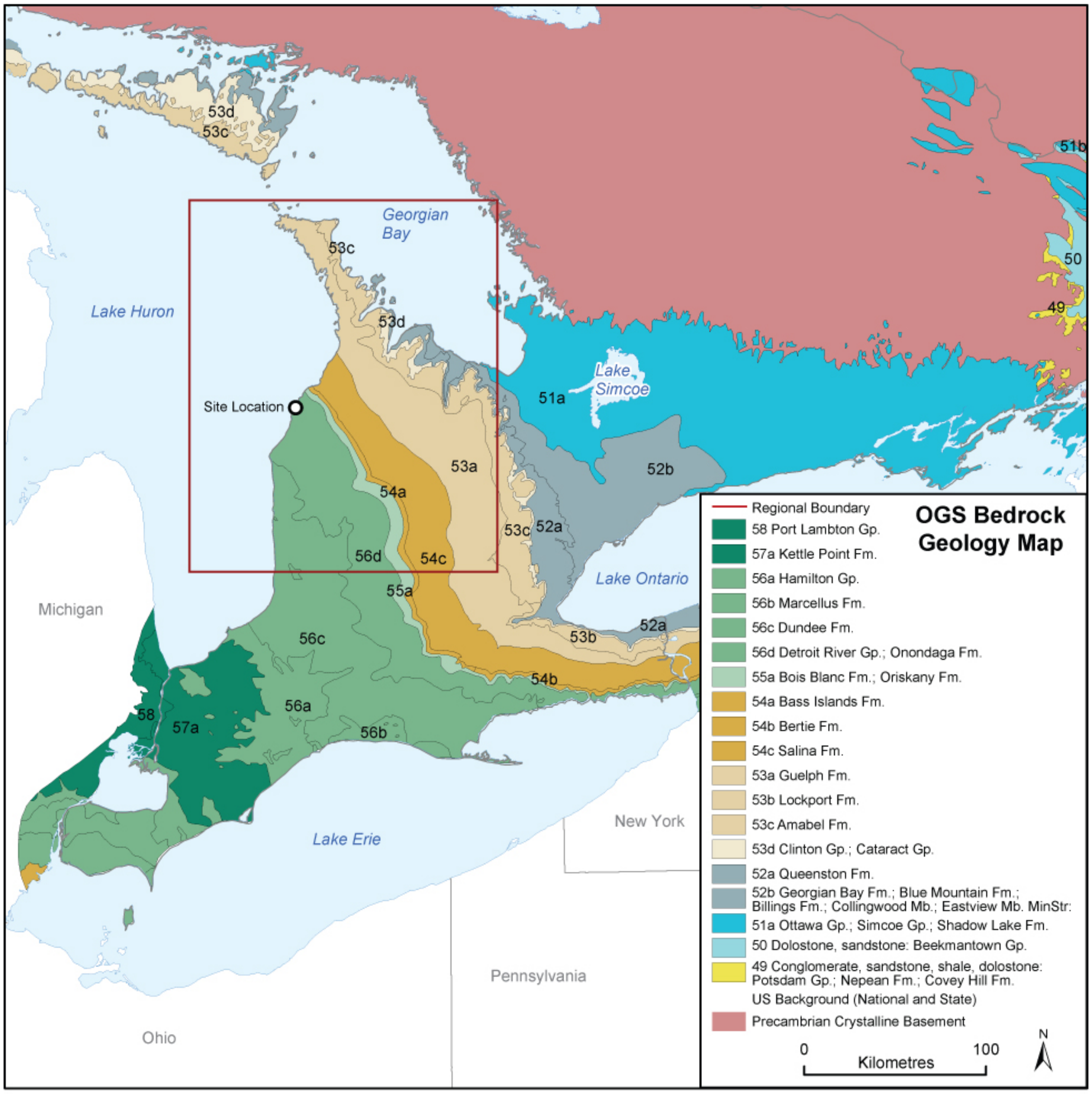
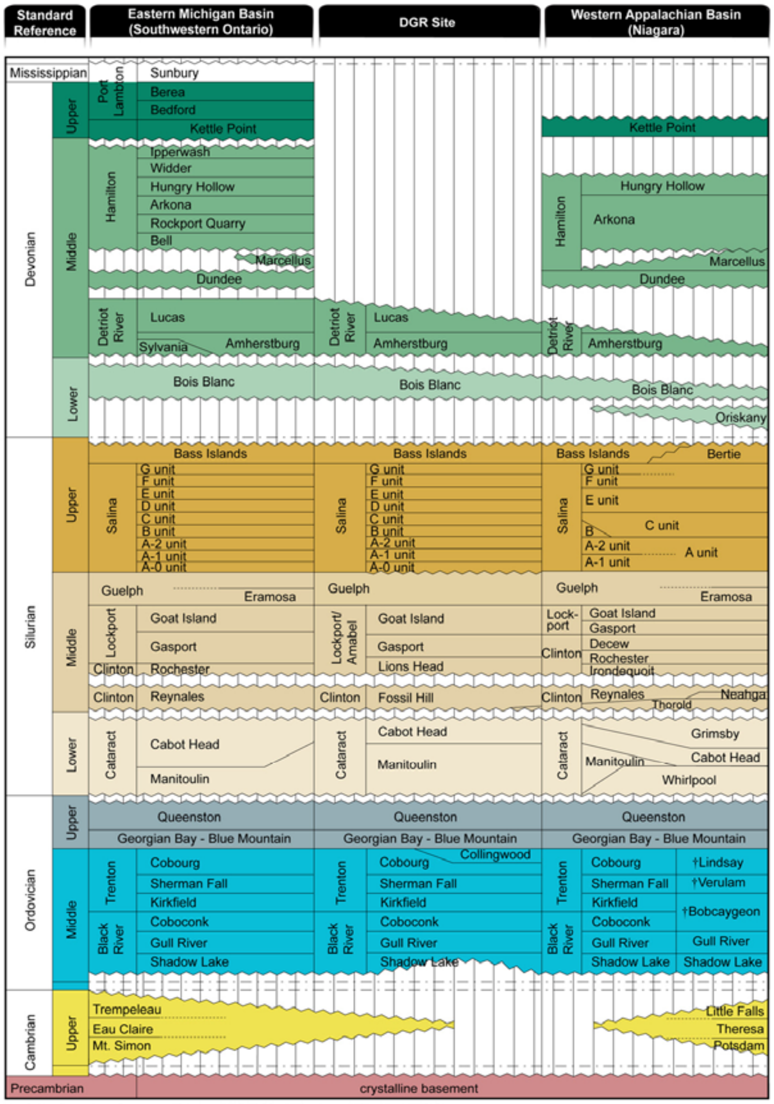


Figure 3: **Geologic map of southern Ontario, redrawn from Ontario Geological Survey (1991) showing the site location and the boundaries of the Regional Study Area (red box). Map from Gartner Lee Limited (2008b).**

2.1.1 Formations Sampled for Groundwaters

The stratigraphy of the sedimentary formations underlying southwestern Ontario is illustrated in Figure 4. The nomenclature used for the sedimentary formations where they occur in southwestern Ontario as part of the eastern Michigan Basin, at the DGR site and in the Niagara region of Ontario at the western margin of the Applachian Basin is given.



*modified from Armstrong and Carter (2006) after Winder and Sanford (1972)
†outcrop nomenclature for Southern and Eastern Ontario

Figure 4: **Stratigraphy and nomenclature of the sedimentary formations in Ontario to the west where they form the eastern edge of Michigan Basin, and to the east where the formations occur as part of the western edge of the Appalachian Basin. From Gartner Lee Limited (2008b).**

Figure 5 is a map of southwestern Ontario and central Michigan showing the sampling locations for the datasets included in the regional geochemical data base. Over 90 percent of all samples in the database are from producing oil and gas wells.

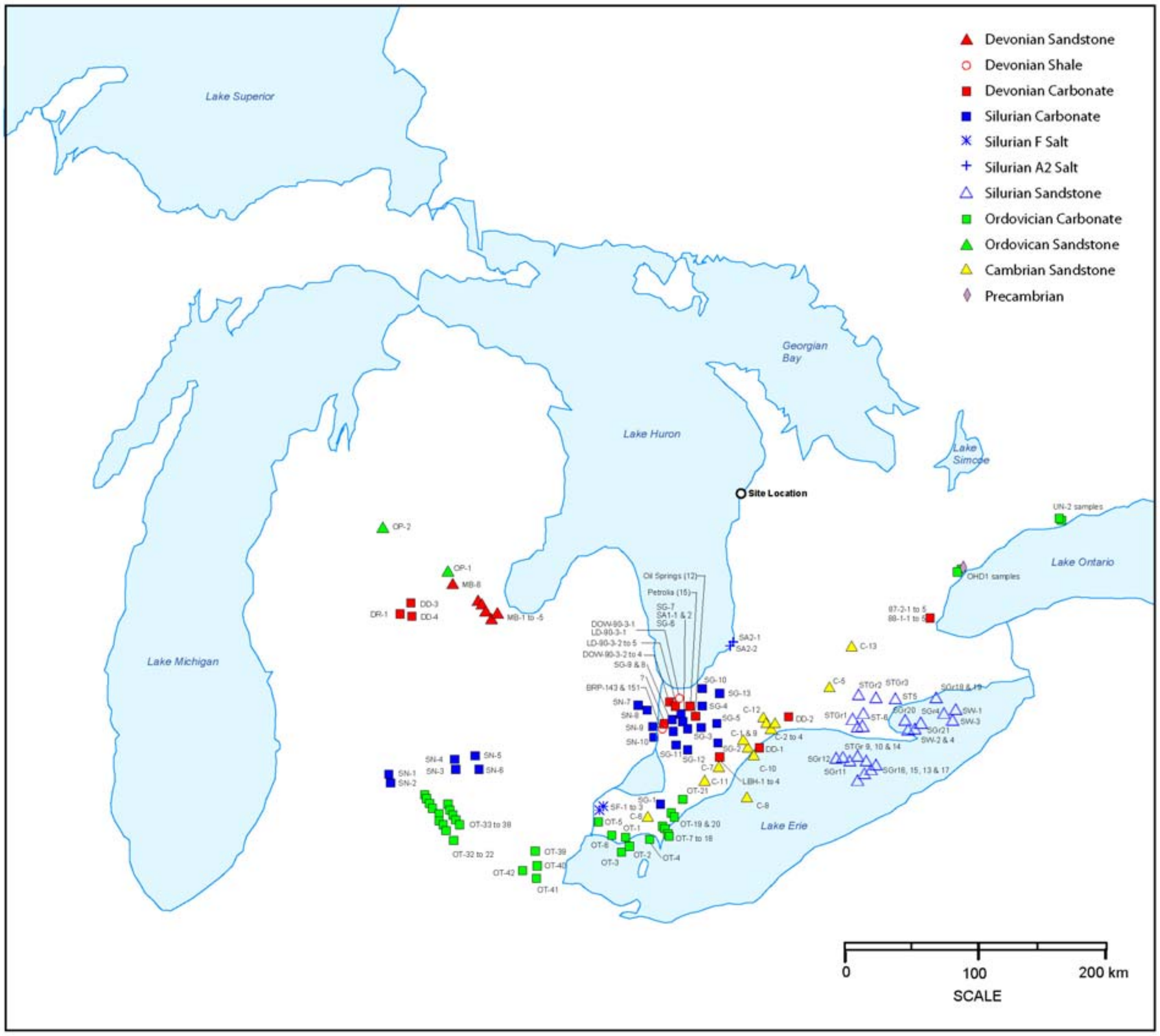


Figure 5: **Map showing the sampling locations for fluids collected from the sedimentary formations in southwestern Ontario and in central and eastern Michigan, USA. Modified from Frape et al. (1989).**

In southwestern Ontario, groundwater samples were collected from formations ranging in age from Cambrian to Devonian. Groundwater samples were collected from the following formations:

- Cambrian-aged Mount Simon and Eau Claire formations. These samples are referred to as Cambrian sandstones within the database (Dollar et al., 1991; Dollar 1988);
- Middle Ordovician carbonates of Trenton and Black River Groups (Dollar et al., 1991; Sherwood Lollar and Frape, 1989; Dollar 1988);
- Late Ordovician shales of the Blue Mountain Formation (Sherwood Lollar and Frape, 1989);

- Early Silurian (Whirlpool, Grimsby) formations and Middle Silurian (Thorold Formation) which are predominantly sandstones (Dollar et al., 1991; Dollar, 1988);
- Middle Silurian carbonates (Guelph Formation in Ontario; Niagaran refers to the Guelph and Lockport formations where they occur in Michigan), and Salina A1) and salts (Salina F and A2) formations (Hanratty, 1996; Dollar, 1988);
- Middle Devonian-aged Detroit River Group and Dundee Formation carbonates (Weaver, 1994; Cloutier 1994); and
- Late Devonian Hamilton Group and Kettle Point (Antrim) shale formations (Husain, 1996; Cloutier, 1994).

Figure 6 illustrates locations that are referenced frequently throughout this report.

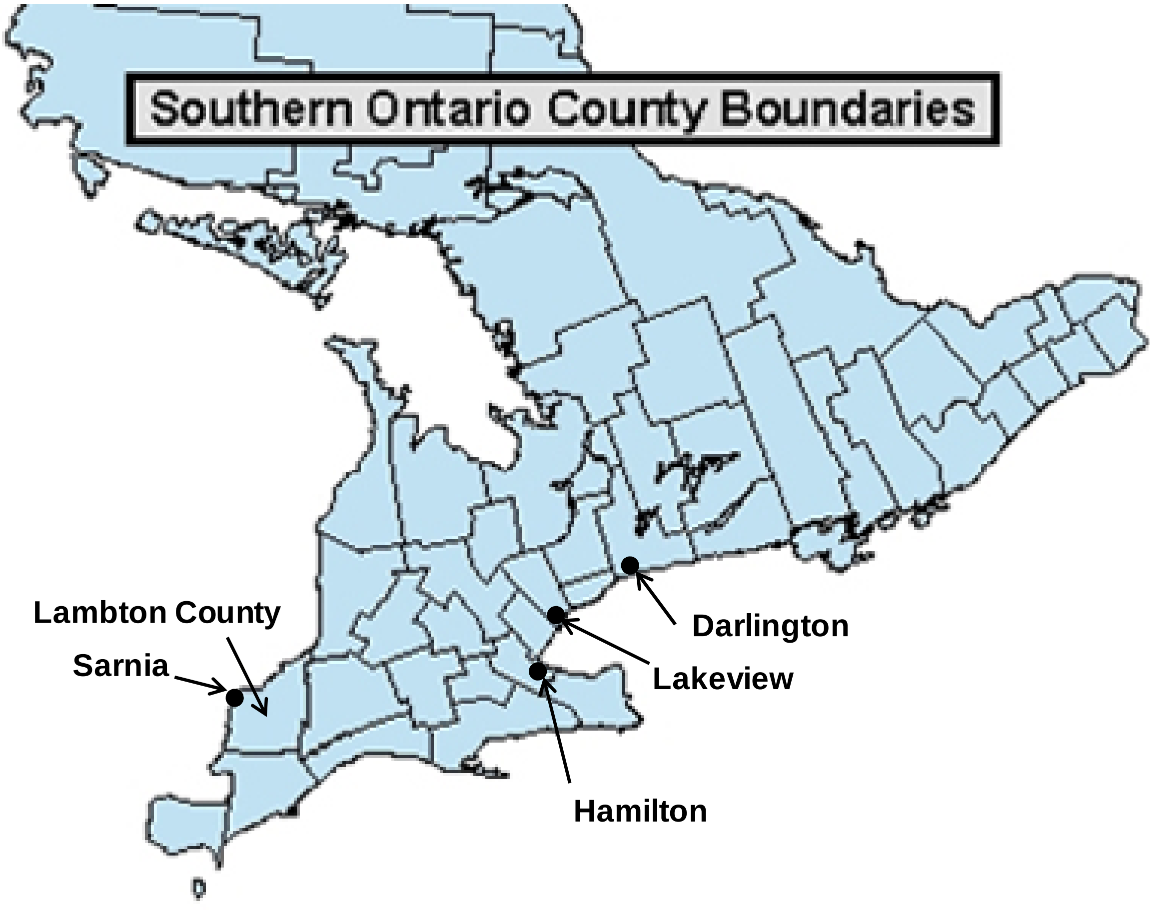


Figure 6: Map showing locations in southwestern Ontario which are referenced frequently.

In Michigan, water samples were collected from the Prairie du Chien sandstone (Early Ordovician) in the central portion of the Michigan Basin and from the Middle Ordovician carbonates of the Trenton-Black River in southeastern Michigan. Six of the seven samples collected from Devonian formations were collected from the central part of the basin, with one sample from the northern margin of the basin. The samples are from the Middle Devonian

Richfield Member and Dundee Formation (carbonate), and the Late Devonian Antrim (shale) Formation (equivalent to the Kettle Point Formation in Ontario). Waters sampled from the Berea Formation in central Michigan are referred as Devonian in age; In earlier research (e.g., Dollar, 1988; Dollar et al., 1991, Martini et al., 1998; McIntosh et al., 2002), the Berea formation was considered to be Mississippian in age. All waters from the Berea Formation examined in this study are from the central part of the Michigan Basin.

2.1.2 Potential Structural Controls on Fluid Transport

There is evidence to suggest that faults and fractures in the Precambrian basement have provided conduits for fluid movement into the overlying Palaeozoic sedimentary sequence within southern Ontario in the geologic past, including fluids associated with i) clay alteration in the uppermost Precambrian basement and overlying Cambrian sandstones (Ziegler and Longstaffe, 2000a; 2000b); ii) dolomitization of carbonates (e.g. Congilio et al., 1994; Middleton et al., 1993; Carter, 1991; Sanford et al., 1985); iii) Mississippi Valley Type (MVT) lead-zinc mineralization in Silurian-aged formations (Farquar et al., 1987); and iv) dissolution of Silurian salt-bearing strata (Sanford et al., 1985). In addition, a close association has been observed between the locations of dolomitized faults and fractures and the occurrence of the oil and gas pools in southern Ontario, particularly for reservoirs occurring in Ordovician and Cambrian-aged formations (Sanford et al., 1985). Detailed descriptions of the diagenetic processes which influenced the sedimentary sequence are presented in Gartner Lee Limited (2008b). A brief overview of the major structural features is provided in this section; a more detailed synthesis of the regional structural geology is provided in Gartner Lee Limited (2008b).

The crystalline Precambrian basement underlying southern Ontario is composed of deformed and metamorphosed gneisses of the Grenville Province. The structural subdivisions of the Precambrian basement and the locations of previously mapped major faults and aeromagnetic lineaments are shown in Figure 7. The two major structures in the basement are also shown; the Grenville Front Tectonic Zone (GFTZ) and the Central Metasedimentary Belt Boundary Zone. The GFTZ is a 50 kilometre-wide, east-dipping shear zone which rises from mid-crustal depths to the base of the Paleozoic cover (Culotta et al., 1990). As shown in Figure 8, the Precambrian basement east of the Grenville Front is segmented into a number of lithotectonic terranes and domains, which are distinguished on the basis of differences in lithology, internal structure and metamorphic grade, and geophysical signature (Carter et al., 1996). To the east, a western-dipping shear zone (the Coshocton zone) was identified beneath the Appalachain basin in eastern Ohio (Culotta et al., 1990).

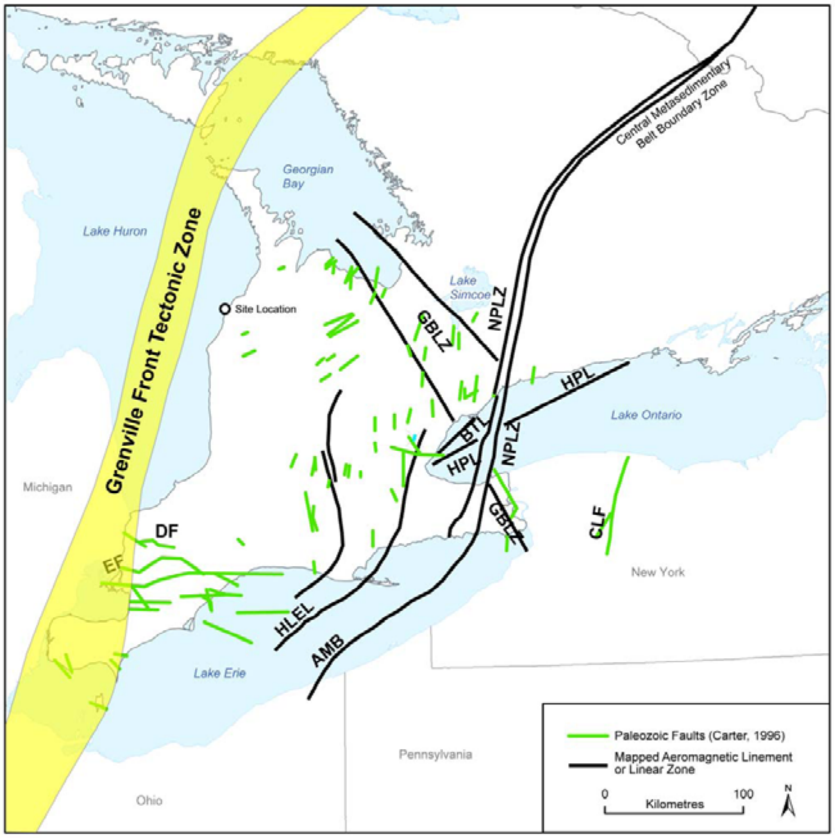


Figure 7: **Structural Subdivisions of Precambrian Basement with faults (Carter et al., 1996, and Carter, 2006), aeromagnetic lineaments and lithotectonic domain boundaries (after Carter and Easton, 1990; Easton and Carter, 1995; Wallach et al., 1998; Jacobi and Fountain,1993). CMBBZ: Central Metasedimentary Belt Boundary Zone; AMB: Akron Magnetic Boundary; NPLZ: Niagara– Pickering Linear Zone; HLEL: Hamilton– Lake Erie Lineament; BTL: Burlington–Toronto Lineament; HPL: Hamilton– Presqu'ile Lineament; GBLZ: Georgian Bay Linear Zone; EF: Electric fault; DF: Dawn fault; CLF: Clarendon–Linden fault (Boyce and Morris, 2002). From Gartner Lee Limited (2008b).**

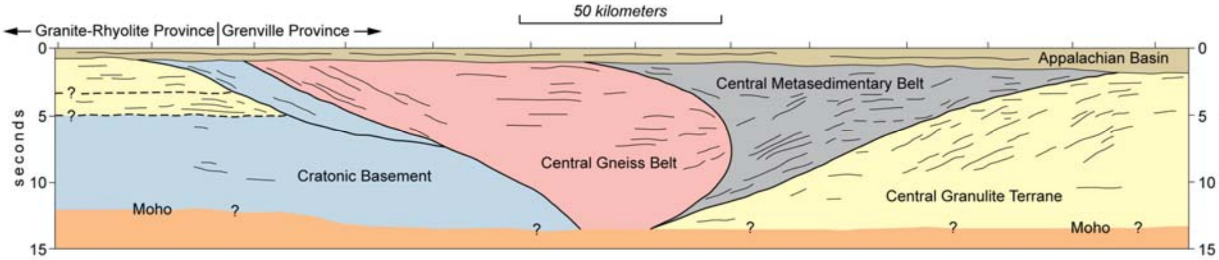


Figure 8: **Speculative interpretation of two of COCORP's deep seismic lines of the Grenville province (adapted from Culotta et al., 1990).**

2.2 Hydrogeology

In the following section, the current understanding of the groundwater flow systems within the formations underlying southwestern Ontario is presented, based on the regional hydrogeologial modelling report of Sykes et al. (2008). Reviews of published literature providing evidence for the discharge of groundwaters into the Great Lakes and for the depth of penetration of glacial recharge into the sedimentary formations within the Michigan and Appalachian Basins are then summarized.

2.2.1 Hydrogeologic Conceptual Model

A hydrogeologic conceptual model for southwestern Ontario was developed by Sykes et al. (2008) in the context of regional-scale groundwater modelling within a portion of southwestern Ontario centred on the Bruce DGR site. Three groundwater domains are identified in this model: a shallow zone characterized by Devonian-aged formations which have a higher permeability and contain groundwaters with a relatively low Total Dissolved Soilds (TDS) content; an intermediate zone which consists of Silurian formations, including low permeability shales and evaporate units; and a deep groundwater zone within the Ordovician shales and limestones, Cambrian sandstones, where present, and the Precambrian basement (Sykes et al., 2008). Figure 9 illustrates the boundaries considered in the regional-scale modelling for the DGR.

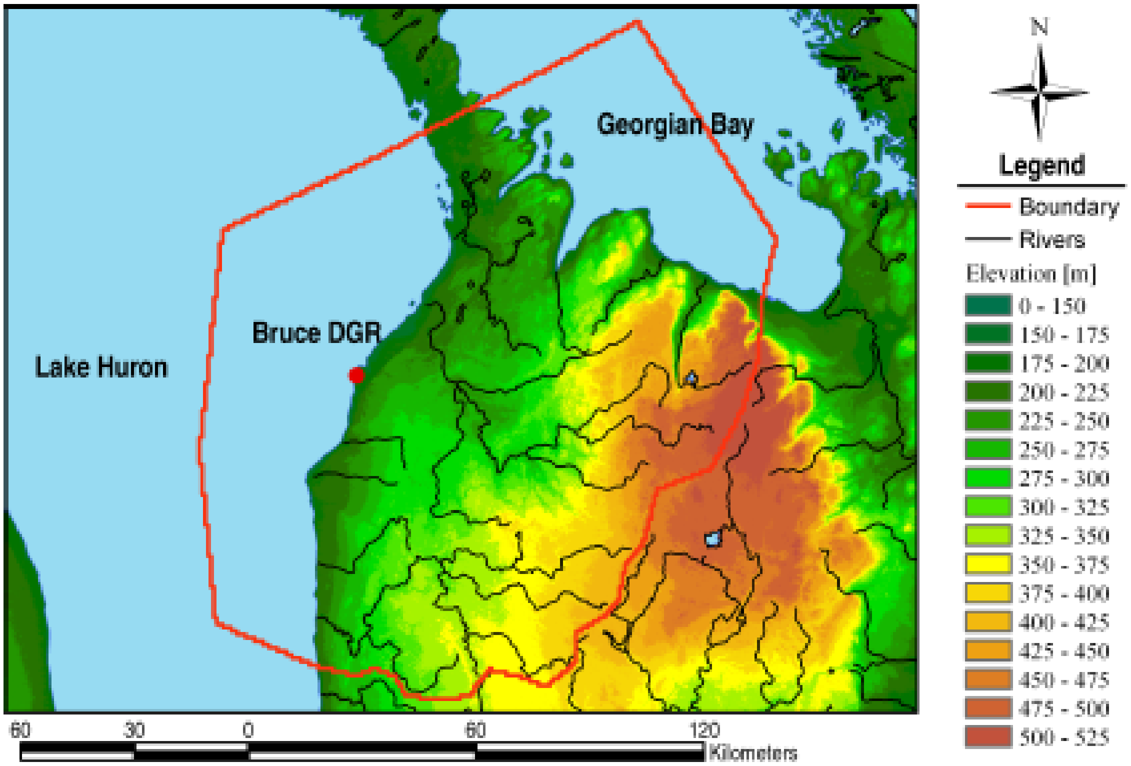


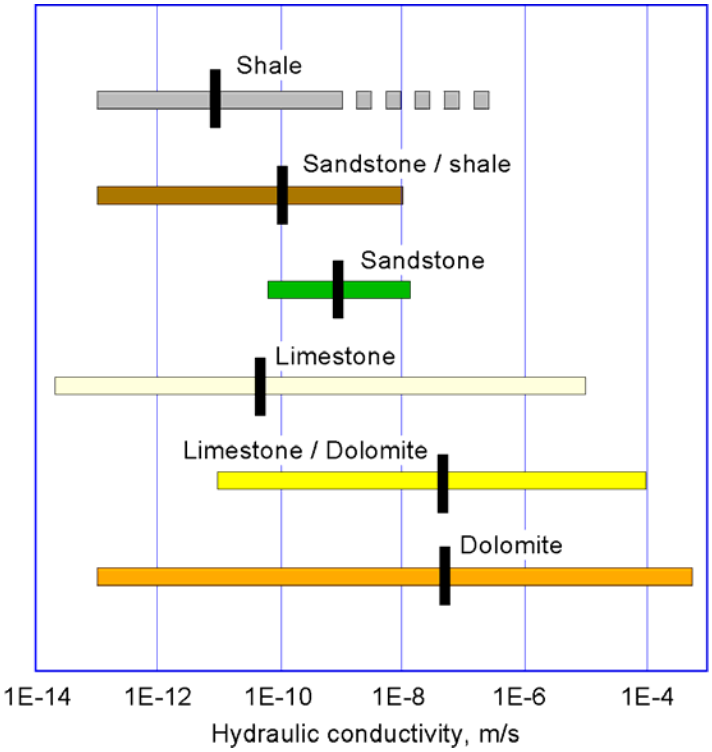
Figure 9: The boundaries of the conceptual model used in regional-scale groundwater modelling, showing river courses (from Sykes et al., 2008).

The shallow aquifer system represented by unconfined, semi-confined and confined aquifers present in the Quaternary glacial drift sediments can also be considered to be part of the shallow flow system as defined by Sykes et al. (2008). Glacial aquifers typically consist of sands and gravels that comprise outwash deposits or discontinuous lenses of ice-contact stratified drift within ground and end-moraine deposits. In general, modern recharge infiltrates topographic highs, such as glacial moraines and the spine of the Algonquin Arch, and migrates through glacial drift and shallow bedrock aquifers, to ultimately discharge into topographic lows, such as streams and lakes. Modern groundwater flow in the Great Lakes region is primarily restricted to the shallow unconfined glacial drift aquifers (McIntosh and Walter, 2006).

The direction of groundwater flow in the shallow Devonian bedrock and glacial aquifers is gravity-driven and topographically controlled (Sykes et al., 2008; Vugrinovich, 1987). However, the low topographic gradients and the presence of high salinity waters in underlying sedimentary formations inhibit deep circulation of meteoric waters. In this report, the term “meteoric” refers to waters in or derived from the atmosphere (Bates and Jackson, 1984). In the intermediate and deep groundwater zones, the only potential location for groundwater recharge or discharge is along the bands where these formations outcrop (Figure 3). Fresh water infiltrating into these aquifers is expected to have a major component of flow parallel to the strike of the formations because i) the density of the shallow waters in the bedrock are substantially higher than that of fresh water and are therefore not easily displaced; and ii) there is an absence of discharge areas in the basin, and therefore very low hydraulic gradients (Sykes et al., 2008; Mazurek, 2004).

Based on a compilation of the available hydraulic conductivity (K) data for the Paleozoic sedimentary bedrock underlying southern Ontario, Mazurek (2004) observed a good correlation between rock type and hydraulic conductivity (Figure 10). Dolomites and dolomitic limestones are observed to have the highest hydraulic conductivities, representing potential regional aquifers. Shales and dolomite-free (often argillaceous) limestones have the lowest hydraulic conductivities.

Figure 10: Hydraulic conductivity of Paleozoic formations in southern Ontario as a function of rock type, based on *in situ* packer tests in boreholes. Black bars are geometric means, coloured bars show the full range of individual measurements. For shale, all data indicate K <1E-9 m/s, with the exception of one outlier in Rochester Shale (52 m overburden). The outlier is shown by stippling and was also included in the calculation of the geometric mean (From Mazurek, 2004).



On the basis of the vertical distribution of hydraulic conductivity and lithology alone, Mazurek (2004) subdivided the sedimentary sequence into 8 hydrogeologic units. Sykes et al. (2008) developed a more detailed hydrostratigraphic model with 31 layers, in which each layer corresponds to a geologic unit within the stratigraphic section. The hydraulic conductivites and porosities assigned to each of these layers in the base-case of the numerical model are given in Table 1.

Table 1: Hydrostratigraphic values for the 31 layers in the regional-scale conceptual model, showing the hydraulic conductivity (K) and porosity value assigned to each layer (from Sykes et al., 2008). Note that Niagaran includes both the Guelph and Lockport formations.

Period	Geology	K_H [m/s]	K_V [m/s]	K_V/K_H	Porosity	Specific Stor.
Quaternary	Drift	1.0×10^{-7}	2.0×10^{-8}	0.2	0.10	9.9×10^{-5}
Devonian	Traverse Group	1.0×10^{-7}	1.0×10^{-8}	0.1	0.10	9.9×10^{-5}
	Dundee	1.0×10^{-7}	1.0×10^{-8}	0.1	0.10	9.9×10^{-5}
	Detroit River Group	1.0×10^{-7}	1.0×10^{-8}	0.1	0.10	1.4×10^{-6}
	Bois Blanc	1.0×10^{-7}	1.0×10^{-8}	0.1	0.10	1.4×10^{-6}
Silurian	Bass Islands	1.0×10^{-7}	1.0×10^{-8}	0.1	0.10	1.4×10^{-6}
	G-Unit	1.0×10^{-7}	1.0×10^{-8}	0.1	0.08	1.3×10^{-6}
	F-Unit	4.0×10^{-12}	4.0×10^{-13}	0.1	0.03	1.2×10^{-4}
	F-Salt	1.0×10^{-13}	1.0×10^{-13}	1.0	0.08	1.6×10^{-6}
	E-Unit	4.0×10^{-12}	4.0×10^{-13}	0.1	0.08	1.6×10^{-6}
	D-Unit	1.0×10^{-10}	1.0×10^{-11}	0.1	0.03	1.3×10^{-6}
	B&C Units	4.0×10^{-12}	4.0×10^{-13}	0.1	0.08	1.2×10^{-4}
	B Anhydrite-Salt	1.0×10^{-13}	1.0×10^{-13}	1.0	0.08	1.6×10^{-6}
	A2-Carbonate	1.0×10^{-10}	1.0×10^{-11}	0.1	0.08	1.6×10^{-6}
	A2 Anhydrite-Salt	1.0×10^{-13}	1.0×10^{-13}	1.0	0.08	1.6×10^{-6}
	A1-Carbonate	2.0×10^{-12}	2.0×10^{-13}	0.1	0.08	1.6×10^{-6}
	A1-Evaporite	1.0×10^{-13}	1.0×10^{-13}	1.0	0.08	1.6×10^{-6}
	Niagaran	1.0×10^{-7}	1.0×10^{-8}	0.1	0.08	1.6×10^{-6}
	Fossil Hill	2.0×10^{-11}	2.0×10^{-12}	0.1	0.08	1.6×10^{-6}
	Cabot Head	2.0×10^{-12}	2.0×10^{-13}	0.1	0.03	1.2×10^{-4}
	Manitoulin	1.5×10^{-12}	1.5×10^{-13}	0.1	0.01	1.2×10^{-6}
Ordovician	Queenston	1.3×10^{-11}	1.3×10^{-12}	0.1	0.11	1.2×10^{-4}
	Georgian Bay/Blue Mtn.	9.1×10^{-12}	9.1×10^{-13}	0.1	0.11	1.2×10^{-4}
	Cobourg	9.6×10^{-12}	9.6×10^{-13}	0.1	0.02	1.3×10^{-6}
	Sherman Falls	9.0×10^{-12}	9.0×10^{-13}	0.1	0.02	1.3×10^{-6}
	Kirkfield	1.4×10^{-11}	1.4×10^{-12}	0.1	0.02	1.3×10^{-6}
	Coboconk	5.2×10^{-11}	5.2×10^{-12}	0.1	0.02	1.3×10^{-6}
	Gull River	3.6×10^{-11}	3.6×10^{-12}	0.1	0.02	1.3×10^{-6}
	Shadow Lake	8.0×10^{-12}	8.0×10^{-13}	0.1	0.01	1.2×10^{-6}
Cambrian	Cambrian	3.0×10^{-6}	3.0×10^{-7}	0.1	0.01	1.2×10^{-6}
Precambrian	Precambrian	8.0×10^{-12}	8.0×10^{-13}	0.1	0.01	1.2×10^{-6}

Within the Silurian-aged formations, the Guelph Formation is more permeable with a hydraulic conductivity of approximately 10^{-6} m/s, and was identified as a potential aquifer by Mazurek

(2004). The underlying Ordovician shales and limestones have among the lowest measured hydraulic conductivities of approximately 1.0 x 10^{-11} m/s, which is close to the detection limit of field measurements. Dollar et al. (1991) suggested that Cambrian sandstone formations had both a high porosity and permeability based on the large outflows of brine (>100,000 mg/L TDS) frequently observed in wells that penetrate them. Although hydraulic conductivities measured for the Cambrian sandstone of up to 1.0 x 10^{-6} m/s suggest that this could be a potential aquifer, the Cambrian is discontinuous, pinching out against the Algoniquin Arch and is confined by overlying lower permeability Ordovician argillaceous limestone and shale formations. On this basis, the Cambrian is considered unlikely to represent a transport pathway (Sykes et al., 2008).

2.2.2 Groundwater-Surface Water Interaction in the Great Lakes

Based on the topography of the Great Lakes region from Lakes Erie, Ontario and Huron, the water bodies within the Great Lakes Watershed are considered to be discharge zones for shallow regional groundwater flow systems. A summary of research undertaken in the Great Lakes region to investigate groundwater-lake water interactions using physical hydrogeological and geochemical techniques is given in the following sections.

2.2.2.1 Hydrogeologic Evidence

Harvey et al. (1997) measured in-situ sediment pore-pressures as a means to determine local groundwater flow gradients within Hamilton harbour near the western end of Lake Ontario. Pore-pressures were measured using a tethered pore pressure probe at 10 locations within the harbour, and all sites but one showed positive gradients ranging from 0.010 to 0.425. Using this method, the exact measurement depth cannot be known, however, it likely varies between a few centimetres to a maximum of 2 metres below the sediment-water interface. A negative gradient (-0.015) was observed at the Stelco site, which lies at the harbour mouth to Lake Ontario (Figure 11). Harvey et al. (1997) suggested that i) a well may be pumping at the Stelco site, which generates a drawdown cone in the vicinity of the sampling location; or ii) the hydraulic connection between the harbour and Lake Ontario may be influencing groundwater flow at the Stelco location, and the gradients shift between positive and negative depending on the water levels of Lake Ontario. The Stelco site is also known to be close to the location of a reef feature in the bedrock which outcrops under Hamilton harbour. The direction of the vertical gradients was confirmed by measurements made using mini-piezometers installed near 6 of the sites, at depths of 3 to 7 m below the zone penetrated by the pore pressure probes.

Hydraulic gradients within the same study site in Hamilton harbour were measured by Harvey et al. (2000) in order to assess discharge from groundwater to the harbour. Fifteen drive-point piezometers were installed in pairs with one piezometer installed at 1 to 2 m and the other at 2 to 5 m depth below the sediment-water interface. Mini-piezometers were installed in deeper water at depths of up to 24 m in silty-mud, clays, and in the sand aquifer that underlies the harbour-bottom sediments. Similar to the results from Harvey et al. (1997), the measured hydraulic gradients ranged from -0.333 to 0.430 and the majority of values were positive, indicating groundwater discharge conditions. As is typical in lake environments, the hydraulic gradients were observed to decrease away from shore but remain predominantly positive over the entire study area. Based on the piezometer data, Harvey et al. (2000) estimated groundwater influx into the harbour in both the deep and shallow zones of varying sedimentary structure (clay, sand, silt) to be 2.1×10^7 m^3/year. In comparison with other hydrogeological components, groundwater is roughly equal to the yearly input from precipitation, constituting approximately 8% of total surface inflows to the harbour.

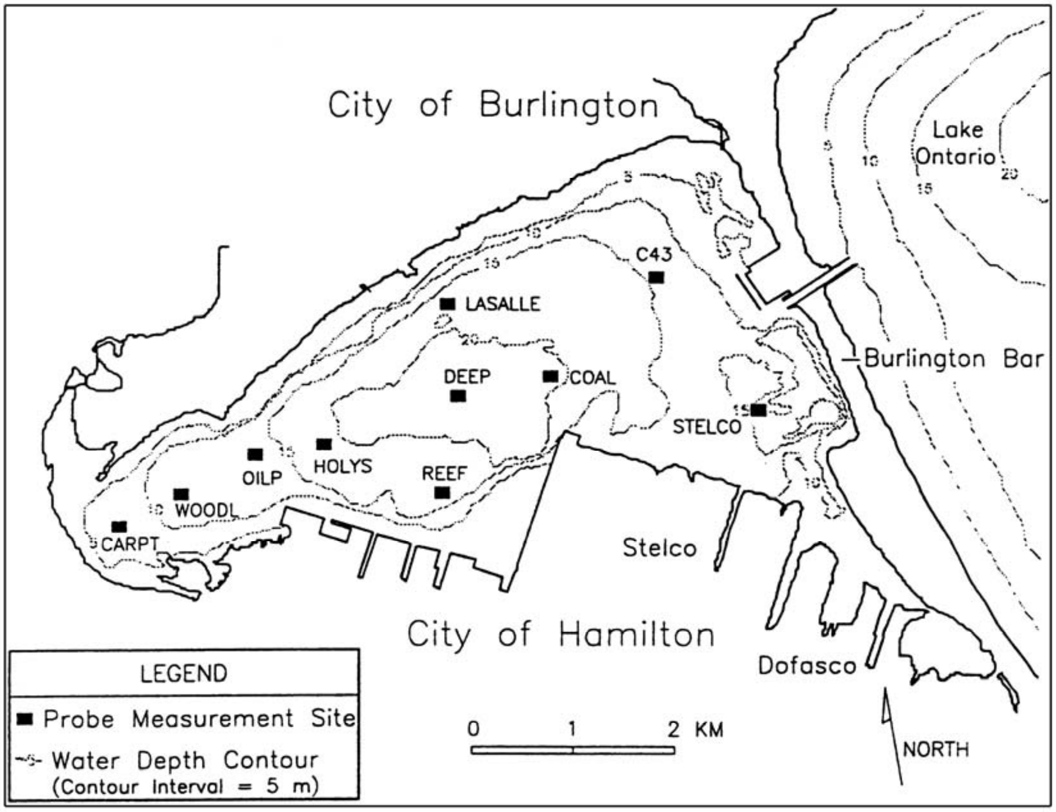


Figure 11: Locations in Hamilton harbour where measurements were made using a tethered pore pressure probe by Harvey et al. (1997).

Cartwright et al. (1979) reported similar values to Harvey et al. (1997; 2000) for upward gradients measured in southern Lake Michigan. In their study, 33 piezometers were installed in water depths ranging between from 5 - 15 m, and were placed an average of 3 m below the sediment-water interface. Hydraulic gradients in the shallow waters were upward and averaged 0.002. Hydraulic gradients at the base of the lake were determined in deeper waters using a differential-pressure transducer. The average hydraulic gradient for the deep water zones (48 - 140 m water depth) was 0.2. An apparent correlation was observed between the thickness and lithology of the unconsolidated sediments underlying and surrounding the lake, and the measured gradients which range from 0.18 to 0.35. The higher gradients are measured on the west side of the study site, where the underlying material is a Silurian limestone and dolostone aquifer, whereas the low gradients are measured on the eastern side of the study site where the underlying material is assumed to be Devonian-aged shale. However, at the extreme eastern margin of the study area, higher gradients are also observed, and this is presumed to reflect the progression from shale into younger, Mississippian sandstones and limestones that comprise shallow aquifers on the eastern shore of the lake.

Hoaglund et al. (2004) used numerical modelling to investigate the extent of modern interaction between groundwater and large lakes in the Saginaw Bay area. Although the groundwater flow model predicts that the hydraulic head in the Marschall Aquifer underlying Saginaw Bay exceeds the modern lake elevation, simulated groundwater discharge into the bay was only

0.028 m^3/s. The rate of groundwater discharge appeared to be controlled by the bedrock lithology. Hoaglund et al. (2004) conclude that modern groundwater discharge from a glaciofluvial aquifer to the lake shoreline is relatively low because of low gradients across the Saginaw lowlands area and because the bay is surrounded by clay-rich tills and glaciolacustrine clays with low hydraulic conductivities.

2.2.2.2 Geochemical Evidence

Porewaters in lakebottom sediments from various locations in Lake Ontario and Lake Erie have been examined in several studies to i) provide an improved understanding of the origin of saline pore fluids in shallow sediments in both lakes; and ii) determine the dominant transport mechanisms for solute migration from underlying bedrock formations. Murray-Morden (1994) and Murray-Morden et al. (1999) examined major and trace element concentrations, strontium concentrations and stable isotopes including $\delta^{18}O$, $\delta^{2}H$ and $^{87/86}Sr$ in porewaters; Drimmie and Frape (1996) report on measured Na and Cl concentrations and $\delta^{37}Cl$; Harvey (1995) measured major elements and tritium; and Drimmie et al. (1993) examined major elements and stable water isotopes ($\delta^{18}O$, $\delta^{2}H$). In the majority of these studies, cores of sediment were collected from the lake bottom at sites selected on sediment availability and proximity to linear, structural features in lake sediments, as described by Thomas (1993). Most of the sediment cores were collected on the south side of Lake Ontario (Figure 12) or in Hamilton Harbour (Harvey, 1995). Porewaters were extracted from cores up to 20 m in length using coring and squeezing techniques developed and described by Patterson et al. (1978).

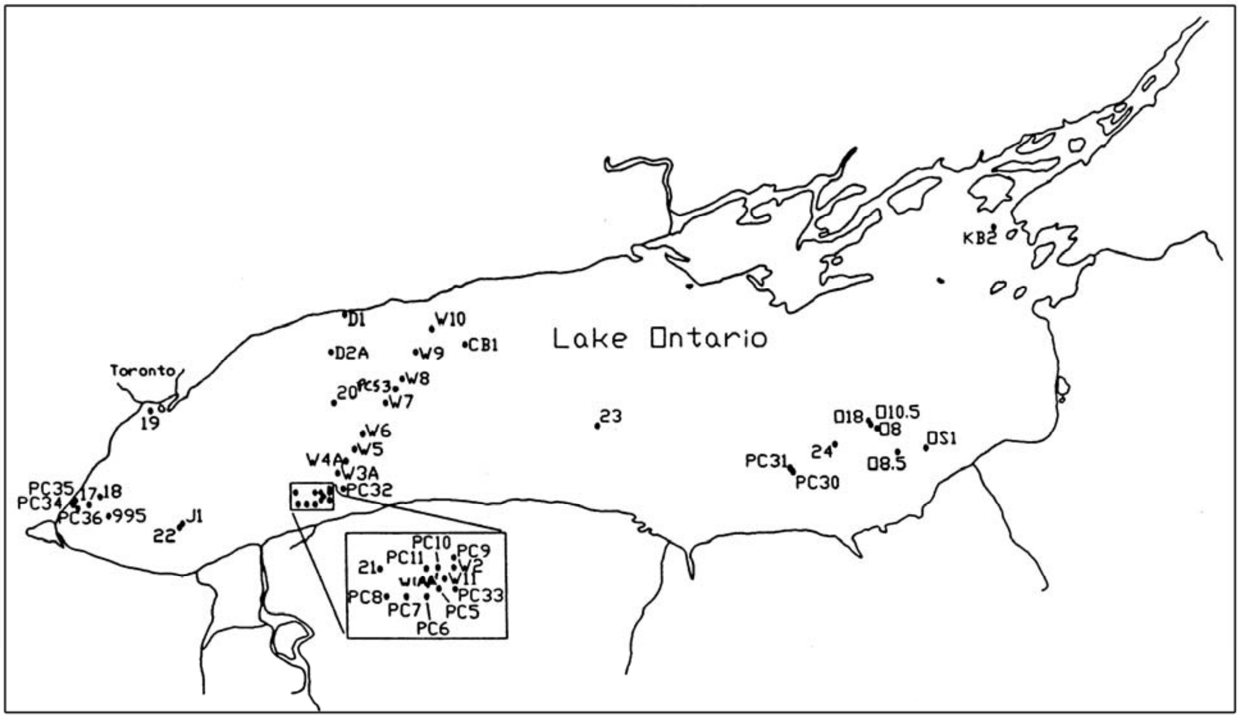


Figure 12: Map showing location of bottom sediment cores examined by Drimmie and Frape, 1996; Murray-Morden et al., 1999; and Murray-Morden, 1994. Map from Murray-Morden (1994).

Similar sediment porewater studies in areas of Lake Michigan and Lake Huron are also reported in the literature. Cartwright et al. (1979) compared the distribution of major ions and trace elements in waters sampled from piezometers installed in the bottom sediment on the southwestern shore of Lake Michigan. In Lake Huron, the chemical and isotopic compositions (Cl, Br, and $\delta^{18}O$) of porewaters in lake-bottom sediments from the Saginaw Bay area and in terrestrial sediments from the Saginaw lowland area were examined by Kolak et al. (1999). Terrestrial samples were taken from depths ranging between 5 and 30 m below land surface; bottom sediments in Saginaw Bay were sampled between approximately 0.05 and 2.5 m below the sediment-water interface.

There are several observations which are common to the porewater studies in Lakes Ontario, Erie, Michigan and Huron. For depths of up to 20 m investigated in these studies, increasing Cl concentrations were consistently observed as a function of depth in the lake sediment cores (Cartwright et al., 1979; Murray-Morden et al., 1999; Drimmie and Frape, 1996; Harvey, 1995; Drimmie et al., 1993). Sodium concentrations were also found to increase with depth in all cores (Drimmie and Frape, 1996). Kolak et al. (1999) also observed strong vertical gradients in Cl concentration in cores from lake-bottom sediments from Lake Huron, with nearly all cores exhibited increasing Cl concentrations with depth. The only exception noted to the trend of increasing solute porewater concentrations with depth was in cores collected from locations along the axis of Lake Erie. These cores had virtually no Cl in the porewater and in most locations, the $\delta^{18}O$ composition of the porewaters were found to be in isotopic equilibrium with shells within the glacial muds (Drimmie et al., 1993). These glacial muds would have been in equilibrium with the lake waters at the time of deposition. The persistence of the isotopic signatures in the sediment porewaters indicates that over large areas of Lake Erie, the sediment porewaters have not been exchanged with waters from lake or the underlying bedrock formation waters since deposition over 10,000 years ago.

In the study by Cartwright et al. (1979), the presence of trace metals in the bottom sediments was attributed to anthropogenic activities. However, in more recent studies, elevated porewater solute concentrations have been attributed to migration from underlying bedrock formations. For example, Harvey (1995) reported that anthropogenic Cl sources (i.e., road salt) are not likely responsible for the high Cl concentrations observed in sediments underlying Hamilton Harbour based on the lack of tritium in the waters, the measured Cl:Br ratios and on the elevated Cl and Br concentrations in the piston core samples. In general, several lines of evidence are given in the literature to support the interpretation that the solutes, and Cl in particular, observed in the sediment porewaters are derived from the underlying bedrock formations:

- Consistency of this interpretation with the occurrence of highly saline groundwaters in association with oil and gas in reservoirs within the bedrock formations underlying southwestern Ontario (e.g. McNutt et al., 1987);

- An examination of the Cl:Br mass ratios of porewater samples by Kolak et al. (1999) as a function of Cl concentration showed that although the Cl:Br mass ratios initially increase as a function of Cl concentration, the ratios plateau at a value of approximately 500. This value is within the range of 400-600 observed for Michigan Basin fluids, and suggests that formation brine is the source of chloride. Halite dissolution was ruled out as the source of Cl, because the Cl:Br mass ratios would be expected to continue up to a maximum value of ~3000 as Cl concentration increased, which was not observed;

- In the study by Murray-Morden (1994), high Cl concentrations were often found to be associated with elevated Li concentrations. High Li, Cl, and trace element concentrations are typical of formation brine fluids.

- Stable chlorine isotopic signatures (δ^{37}Cl) for sediment porewaters ranged from 0 to +2.65 ‰, with an average value of +1.2‰ (Drimmie and Frape, 1996). The values are at the high end of the δ^{37}Cl values reported for the saline groundwaters sampled from oil and gas reservoirs underlying southwestern Ontario and eastern Michigan, which range from 1.31 ‰ and +1.82 ‰ relative to SMOC (Shouakar-Stash, 2008).

Another observation common to the studies of sediment porewaters is variation in Cl concentrations between cores sampled at different depths and locations (e.g. Drimmie and Frape, 1996; Harvey, 1995; Murray-Morden, 1994). Drimmie and Frape (1996) and Harvey (1995) reported variations in Cl concentration between cores, indicating that Cl input is not uniform across the lake-bottom. Kolak et al. (1999) and Drimmie and Frape (1996) suggest that these variations in the porewater solute concentrations between sediments from different locations provide further evidence that Cl and other solutes are transported upwards into the lake-bottom sediments from the sedimentary formations which sub-crop below the lakes.

Using 1-D transport modelling, and considering the measured porewater profiles of Cl concentrations and δ^{18}O values in the terrestrial cores, Kolak et al. (1999) concluded that the profiles could be generated over a period of 5000 to 10,000 yr, with an upward advective flux of 0.0016 m/a from the underlying shallow groundwater regime. The Mississippian Marshall Aquifer subcrops below Saginaw Bay, and saline groundwater in the Marshall Aquifer discharges in the Saginaw Bay area (Ma et al., 2005), representing a possible explanation for an upward advective velocity in this region.

Kolak et al. (1999) also modelled chloride profiles from four of the bay cores. The results suggest that diffusion is the dominant transport mechanism for chloride and that these profiles could have developed over much shorter time periods (~300 yr). This is consistent with the conclusion of Drimmie and F47rape (1996) that diffusion is the dominant transport mechanism for ions into lakebottom sediments in Lake Ontario and at several locations in Lake Erie. Long et al. (1988) conclude that diffusive flow dominates over advective flow in the east-central Michigan Basin region, in agreement with the study of Desaulniers (1981) in Quaternary deposits in southwestern Ontario. As a result of concentration gradients between dilute, glacial waters and underlying salt-rich waters, Cl from these saline waters diffuses upwards into the more dilute glacial waters. Diffusion of δ^{18}O and δ^{2}H also occurs between the glacial waters and the saline waters due to differences in their isotopic compositions.

Discharge of groundwater through the bottom sediments into the Great Lakes has been detected using both hydrogeological and geochemical measurements, as described above. However, the regional impact of such discharge on either the hydrogeologic or geochemical budget has not been quantified (Kolak et al. 1999). The rate of exchange between saline formation waters in the underlying bedrock or sediments and overlying water column in lakes is also unknown (Hoagland et al., 2004). In Lake Michigan, groundwater discharge into the lake is estimated to constitute between 3 and 10% of the hydrologic budget for the lake (Hoaglund et al., 2004), with the majority of active groundwater circulation occurring predominantly in glacial-drift aquifers and shallow fractured bedrock aquifers (see also section 2.2.1 and section 2.2.3).

In all studies of groundwater-surface water interactions presented, a saline source is detected at depth. Solute transport is inferred to occur from depth towards the surface. The juxtaposition of highly saline brine in the rocks of the Michigan and Appalachian Basins with the overlying dilute meteoric water in the Great Lakes represents a large contrast in composition. Even under conditions where the dense brine is stagnant due to density stratification, upward diffusive fluxes of solutes from the basin into the bottom sediments are expected in response to the steep concentration gradient.

Advective, cross-formational flow of brines from deep within the Michigan Basin to the surface has not been documented. However, Ma et al. (2005) studied the geochemical characteristics of the Marshall Aquifer in northern Michigan and they describe increases in salinity (TDS < 500 mg/L to > 200,000 mg/L) and He concentrations versus time and distance along the northward flow path. In this case, freshwater recharges the aquifer in the south, and solutes accumulate in the groundwater during the residence time of the water in the aquifer (tens of thousands of years). Ma et al. (2005) infer upward cross-formational flow as a source for the solutes in the Marshall Aquifer based on application of a simple advection-dispersion model that is used to match observed He concentrations in the aquifer versus depth and time. The model requires assignment of a steady upward flux of solute from the underlying formations into the Marshall Aquifer. The authors refer to this flux as "cross-formational flow" but the flux could also arise as a result of diffusion. In fact, an upward diffusive flux of solutes is expected in this situation where freshwater flows horizontally in a confined aquifer that overlies brine-saturated sedimentary rocks.

2.3 Evidence for Recharge of Cold Climate Waters

In sedimentary basins, groundwater circulation occurs predominantly in glacial-drift aquifers and shallow, fractured bedrock at depths of less than 100 m (McIntosh and Walter, 2005; Person et al., 2007). Currently, the two predominant controls on the depth of circulation are i) the topographic relief in many sedimentary basins, which is insufficient to drive groundwater flow to depths of greater than 100 m (McIntosh and Walter, 2005); and ii) at depths below 100 m, the bedrock formations generally contain highly saline groundwaters and the resulting density gradient further inhibits flow (Mazurek, 2004). However, during past glaciations, recharge of glacial waters may have occurred as a result of ice-induced hydraulic loading and basal melting of ice sheets.

Evidence for recharge of Pleistocene waters in the intercratonic sedimentary basins in North America, including the Michigan, Illinois, Appalachian and Forest City basins was recently reviewed by Person et al. (2007). The evidence for glacial recharge within the Michigan and Appalachian basins is reviewed here in greater detail, because the sedimentary formations underlying southwestern Ontario straddle the eastern and northern edges of these two basins. Recharge of cold-climate waters is identified based on the stable oxygen and hydrogen isotopic signatures of groundwaters. Whereas modern recharge in southwestern Ontario have $\delta^{18}O$ values which range between -11 and -9‰ (e.g., Husain et al. 2004), glacial meltwater in the Great Lakes region is estimated to have had $\delta^{18}O$ values between -25 and -11‰ and corresponding $\delta^{2}H$ values of between -190 to -80‰ (e.g. Clayton et al., 1966; McNutt et al., 1987; Long et al., 1988). Radiocarbon ages of dissolved inorganic carbon (DIC) in groundwaters are also often used to support the interpretation of recharge under glacial conditions.

In southwestern Ontario, the area between Lake Erie, Lake Huron and Lake St. Clair is overlain by clay-rich glacial tills which extend into southeastern Michigan, and form an aquitard. Desauliers et al. (1981) examined porewaters in glacial tills from three sites within this region, and a fourth in the Haldimand clay plain, which lies between Lake Erie and the Niagara escarpment. A distinctive shift in $\delta^{18}O$ signatures of the porewaters was observed with depth, from -9 to -10‰ at the water table, to $\delta^{18}O$ values ranging from -14 to -17‰ at depths of 20 to 40 m below ground surface. Taken together with the corrected ^{14}C ages of the groundwater, which were greater than 8000 years B.P., this suggests that the porewaters were incorporated into the till deposits during or shortly after formation between 11,000 and 14,000 years ago (Desaulniers et al., 1981).

Similar trends in porewater $\delta^{18}O$ signatures through the Quaternary tills were observed by Husain et al. (2004). Husain et al. (2004) reported $\delta^{18}O$ values between -17.5 and -16.0‰ for a thin, regional “interface” aquifer which occurs at the interface between the overlying Quaternary clay aquitard and the underlying bedrock shale of the Kettle Point Formation, indicating that the water was emplaced during the Late Pleistocene. These authors determined that Pleistocene groundwater persists in the aquifer-aquitard system due to the flow pattern within the aquifer, and because the low yield and poor quality of groundwater in this zone has limited its use as a resource. Slightly less negative $\delta^{18}O$ values of between -13.9 and -16.3‰ were reported by Sklash et al. (1986) for groundwaters collected from a freshwater aquifer in wells adjacent to the St. Clair River.

Depleted stable isotopic signatures ($\delta^{18}O$ = -14.7 to -13.5‰ ; $\delta^{2}H$ = -101 to -95‰) measured in four groundwaters sampled from domestic and municipal wells at depths between 63 and 125 m from the regional, confined Alliston Aquifer in southern Ontario also suggest recharge of waters formed under cold-climate conditions (Aravena et al., 1995). The aquifer is comprised of sand and gravel lenses and is confined above by a thick glacial till and below by Ordovician bedrock or glacial till. Five domestic wells screened within bedrock at depths between 47 and 129 m were also sampled. Two of these wells (BR-14 and BR3 in Table 1 of Aravena et al., 1995) also had depleted $\delta^{18}O$ and $\delta^{2}H$ signatures, suggesting that these waters were recharge under cold climate conditions. Generally, the underlying bedrock, which is very low permeability limestone, dolomite and shale, is not considered an important source of groundwater in this region (Aravena et al., 1995; after Sibul and Choo-Ying, 1971).

McNutt et al. (1987) and Dollar et al. (1991) reported the occurrence of waters in the shallow (<100 m) bedrock subsurface from the Devonian-aged Dundee formation with $\delta^{18}O$ and $\delta^{2}H$ signatures which suggest a component of water recharged under cooler climatic conditions. Although glacial waters may have recharged directly into the formation (e.g., Clayton et al., 1966), the possibility that these waters originated in the overlying Pleistocene “interface” aquifer (e.g., as described by Husain et al., 2004) and that an interconnection via casing leaks in the well resulted in a mixture of formation waters and glacial waters from this overlying aquifer can not be ruled out (Dollar et al., 1991). Mixing of glacial waters with brines has also been proposed by Weaver et al. (1995) to explain isotopic signatures of waters from within Devonian-aged formations (see Chapter 6, section 6.1.2.2 for a detailed discussion).

Further to the west in the Michigan Basin, Long et al. (1988) and Kolak et al. (1999) report the presence of near-surface (<100 m) groundwater with depleted $\delta^{18}O$ and $\delta^{2}H$ signatures in the glacial aquifers in the Saginaw Bay lowland area of Lake Huron (east-central Michigan Basin), as a result of glacial loading effects during the advance of the Laurentide Ice Sheet (21-10 ka). Hoagland et al. (2004) used a model to investigate the extent of Pleistocene interaction between groundwater and large lakes in the Saginaw Bay. The results support the interpretation that glacial loading, and the resulting over-pressures, could have resulted in gradient reversals in the underlying bedrock, causing fluid to flow downward into the bedrock and the shallow underlying aquifers.

Several studies have examined the occurrence of microbial methane gas and associated groundwaters within the Devonian-aged Antrim Shale on the northern and western margins of the Michigan Basin (Martini et al., 1996; Martini et al., 1998, McIntosh et al., 2002; McIntosh and Walter, 2005). Radiogenic (^{14}C and ^{3}H) and stable water isotope analyses of shallow Antrim Shale formation waters and glacial drift groundwaters indicate recharge times from modern to 20,000 BP (Martini et al., 1998). In the case of the Antrim Shale at these locations, a well-developed fracture network within the Antrim shale provides a conduit for gas and water mass transport within the shale, and allows recharge of meteoric water from overlying aquifers in the glacial drift (Martini et al., 1998). Evidence for glacial recharge has been observed at depths of up to 300 m below the shale sub-crop (McIntosh et al., 2005). In contrast to the northern and western margins of the Michigan Basin, fluids within the Antrim Shale from the central Michigan Basin and the eastern margin were found to be similar to brines within the underlying Devonian-aged carbonates, which evolved from evaporated seawater via water-rock interactions (McIntosh et al., 2004). To date, no evidence for significant dilution by meteoric recharge or for microbial methanogenesis has been observed in these areas (McIntosh et al., 2004).

McIntosh and Walter (2006) examined the chemical and isotopic compositions of groundwaters within confined glacial drift and Silurian and Devonian-aged carbonate aquifers along the northern and southern margins of the Michigan and Illinois Basins. Using a combination of the radiocarbon ages and the range of $\delta^{18}O$ (-15 to -13‰) and $\delta^{2}H$ values of groundwaters in the Silurian-Devonian carbonates, recharge was estimated to have occurred between 14 and 50 ka BP, when the area lay beneath the Laurentide Ice Sheets.

Within the Appalachian Basin, the only known evidence for cold-climate recharge is from western New York. Bartos et al. (2000) reported groundwaters in the Silurian-aged Lockport Dolomite with $\delta^{18}O$ values of -13.5‰, which is at the low end of the range of values estimated for proglacial Lake Tonawanda (-13.5 to -11‰), which covered the carbonate escarpment (Bartos et al., 2000). However, the sampling depths for these waters are not known.

In summary, evidence for glacial recharge in the Michigan Basin is most often identified in shallow (<100 m) environments including porewaters within Quaternary-aged till deposits and within glacial drift or bedrock aquifers. In southern Ontario, the maximum depth at which glacial waters have been observed is 130 m below ground surface in shallow bedrock wells (Aravena et al., 1995). However, along the northern and western margins of the Michigan Basin and the northern margin of the Illinois Basin, glacial recharge has been observed to depths of 300 m below the subcrop of the Antrim (MB) or New Albany (IB) Shales in groundwaters associated with microbial methane gas reservoirs. To date, no evidence for significant dilution of formation fluids within the Antrim Shale by meteoric recharge or for microbial methanogenesis has been observed in central Michigan or at the eastern margin of the basin (McIntosh et al., 2004).

3. FORMATION WATERS IN SEDIMENTARY BASINS

In sedimentary basins, brackish to fresh waters are predominant in shallow flow systems. However, many authors have observed a trend to more concentrated fluids, including saline waters and brines with greater depth in sedimentary basins (e.g., Collins, 1975; Hanor, 1987; Land, 1997; Kharaka and Hanor, 2005). These brines and saline waters are most commonly sampled where they are associated with hydrocarbons. The purpose of this chapter is to review both the chemical and physical processes through which formation waters in sedimentary basins have evolved.

3.1 Origin of Salinity

Numerous geochemical processes have been proposed to account for the high salinity of brines, including i) the evaporation of seawater (e.g., Carpenter, 1978; Kharaka et al., 1987); ii) the dissolution of halite or other evaporites such as potash or gypsum (e.g., Rittenhouse 1967; Land and Prezbindowski, 1981); iii) membrane filtration (Bredenhoeft et al., 1963; Berry, 1969; Kharaka and Berry, 1973; Graf, 1982); iv) boiling and subsequent evaporation which removes water from the system (Ranganathan and Hanor, 1987); v) freezing of water during which solutes are concentrated in the residual, unfrozen water phase; vi) hydration of silicates (clays) during diagenesis (Hanor, 1987); or vii) ingress of concentrated brines from crystalline shield-type rocks (e.g., Land, 1997 proposed such an origin for some of the salinity observed in deep Gulf Coast fluids). It is generally agreed that most chloride in sedimentary basin brines has been derived from some combination of entrapped or infiltrated evaporated seawater and dissolved, subsurface evaporites (e.g., Kharaka and Hanor 2005; Hanor 2001).

The sediments comprising the Paleozoic rocks underlying southern Ontario were mainly deposited in shallow inland seas during the Cambrian through to the Devonian (543 – 354 Ma B. P.). For sediments deposited in marine environments, the original porewater is assumed to have been similar in composition and concentration to sea water. However, seawater contains approximately 19,000 mg/L of chloride and most subsurface brines have up to an order of magnitude more chloride. In order to trace the evolution of brines in the subsurface (e.g., diagenetic processes), the proportions of a number of inorganic ions are used as indicators of brine evolution, diagenetic reactions, and mixing of various subsurface fluids. Various stable isotopes can also be used as indicators of reactions, or as labels of the origin of the solid phases, as described in the following sections. Variations in strontium isotopic ratios over the past 400 Ma are also discussed.

3.1.1 Seawater Evaporation

3.1.1.1 Major Ions

To evaluate the evolution of brines, the major ion ratios are most often compared to those measured during the evaporation of present-day seawater. The changes in elements with progressive concentration are examined, providing a basic starting point to evaluate the possible origins for subsurface brines (i.e., seawater, modified seawater, etc.). Bromide is most often used as the ion against which all other ions are compared, because it forms few compounds with cations and has limited substitution in most chloride compounds. Therefore, even at very high ionic strengths, Br partitions predominantly into solution. The use of the Br-Cl plot and other plots such as Na-Br or Na-Cl have been well documented as a means of determining mixing, evolution and water-rock interaction in sedimentary basins (Carpenter, 1978; Rittenhouse, 1967; Collins, 1975; Connolly et al., 1990; Hanor, 1987; Kharaka et al., 1987; Land, 1997; Kharaka and Hanor, 2005).

Figure 13 shows the evolutionary paths of most major ions during the subaerial evaporation of seawater. Before the onset of mineral precipitation, the evaporation of seawater is essentially a concentration process. All ions show increasing concentrations with progressive seawater evaporation, until calcite ($CaCO_3$) and then gypsum ($CaSO_4$) begin to precipitate as these mineral phases reach saturation in solution. At this point, the calcium concentration decreases substantially and sulphate concentration also decreases. With progressive evaporation, halite (NaCl) is the next mineral phase to precipitate, causing a change in the concentrations of both Na and Cl. Changes in potassium and magnesium concentrations are observed during the final stages of evaporation due to the formation of K- and Mg-bearing salts.

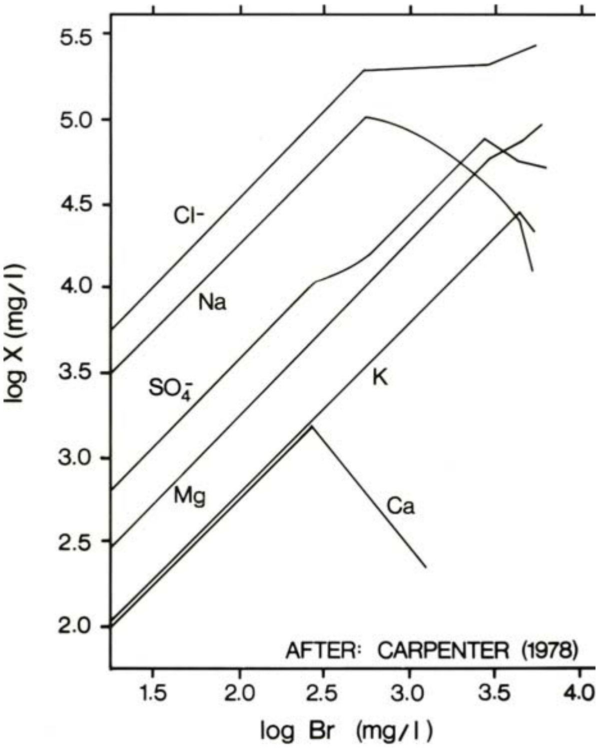


Figure 13: Concentration trends of a number of cations and anions in evaporating seawater (From Kharaka et al., 1987, after Carpenter, 1978).

The increase in chloride observed as a function of bromide concentration during the progressive evaporation and concentration of seawater is shown in Figure 14. The concentrations at which the various mineral phases first precipitate are also shown. A linear relationship is observed between the concentrations of Cl and Br until halite precipitation begins. The Cl concentration levels off during the precipitation of halite, until epsomite begins to precipitate. The Cl concentration then increases gradually with Br during precipitation of sylvite, carnalite and bischofite. Figure 14 also illustrates the evolution of the Cl and Br concentrations in brines formed by the evaporation of seawater which have been subsequently diluted by either fresh meteoric water or seawater. With increasing dilution, the brine would follow a path as shown in Figure 14, eventually curving toward the composition of meteoric composition (not shown), or towards seawater, if mixing with seawater was involved in dilution of the brine.

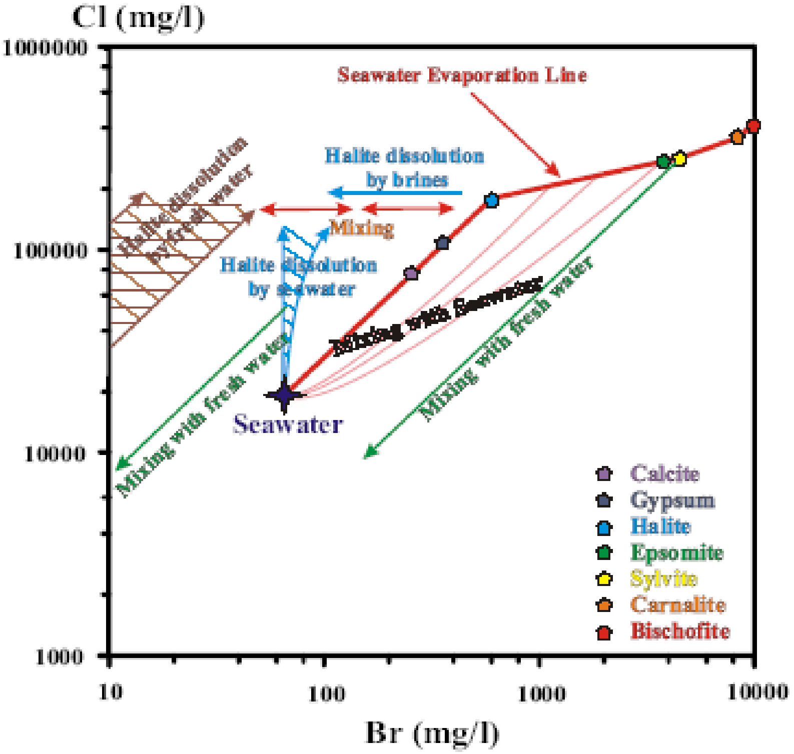


Figure 14: Progressive concentration of bromine and chloride during the evaporation of seawater, showing the initial point of precipitation of mineral phases. Data on seawater evaporation from McCaffrey et al. (1987); Point of precipitation of mineral phases from Matray (1988). Possible mixing scenarios after Rittenhouse (1967) are also shown, with different halite dissolution products and different end member waters (Carpenter, 1978). From Shouakar-Stash (2008).

The trends observed due to interaction of brines with halite (NaCl) are also shown in Figure 14. If the brine encountered halite beds, two trends are possible. First, the brine could dissolve halite congruently, while maintaining NaCl saturation, in which case its Br/Cl ratio would decrease because halite has a very low Br/Cl ratio (Rittenhouse, 1967; Hanor, 1987). However, a number of more recent studies (e.g., Land and Prezbindowski, 1981; Stoessell and Carpenter, 1986) have shown that brine could dissolve and then reprecipitate halite (i.e., incongruent dissolution). In this case, the brine will slowly accumulate additional Br. Finally, the brine could encounter bitter salts and take on a much higher Br/Cl ratio which would depend on congruent or incongruent dissolution of the solids. Organic compounds are another possible source of Br in waters from sedimentary formations (Kharaka and Hanor, 2005). Davis et al. (1998) note that while most solid materials contain Br concentrations in the range of 0.1 to 100 mg/kg, some organic materials have much higher concentrations of Br; organic-rich materials such as coal are the most enriched in Br relative to Cl (i.e. have the lowest Cl/Br ratios).

3.1.1.2 Oxygen and Hydrogen Stable Isotopes

The main processes which can modify the isotopic composition of water in sedimentary basins include i) exchange between water and minerals and the temperature at which exchange occurs; ii) evaporation and condensation; iii) isotopic fractionation as a result of membrane filtration of water; iv) release of water during burial diagenesis; and iv) exchange between water and other fluids (e.g., petroleum). Possible sources of water in sedimentary basins include original seawater trapped within the sediments during deposition, evaporated water trapped in precipitated salt (bittern water) or infiltrated into associated sediments, and modern (Holocene) or ancient (e.g., Pleistocene, cold-climate) meteoric water (Kharaka and Hanor, 2005). The $\delta^{18}O$ and $\delta^{2}H$ values of formation waters from sedimentary basins typically plot to the right of the Global Meteoric Water Line (GMWL). Determination of the evolutionary pathway of waters in sedimentary basins is further complicated by the fact that the seawater isotopic composition during the Paleozoic is not known.

Brines from most sedimentary basins display large enrichments in $\delta^{18}O$ and relatively small enrichments in $\delta^{2}H$ relative to the Global Meteoric Water Line (GMWL). The enrichment in $\delta^{18}O$ has been attributed to isotopic exchange reactions between waters and associated carbonate minerals (e.g., Clayton, 1966; Hitchon and Friedman, 1969). In this case, the exchange of deuterium is minimal, because the amount of water is large relative to hydrogen-bearing minerals in sedimentary rocks. Alternatively, Holser (1979) and Knauth and Beeunas (1986) proposed that the stable isotopic composition of formation waters may reflect evaporative processes (Figure 15). During evaporation, water becomes progressively more enriched in $\delta^{18}O$ and $\delta^{2}H$, until gypsum begins to precipitate, after which point the remaining water becomes progressively more depleted as a result of incorporation of the heavy isotopes into the mineral phase (Holser, 1979).

3.1.1.3 Strontium

The $^{87}Sr/^{86}Sr$ ratio is uniform throughout the world's oceans at any given time because strontium has a long residence time in the oceans (~4 Ma). Figure 16 shows the variations of $^{87}Sr/^{86}Sr$ in the ocean for the Phanerzoic based on analyses of brachiopods (normalized to NBS 987 of 0.710240) and literature data as reported by Veizer et al. (1999). The ratio has ranged from approximately 0.7076 - 0.7092 in the interval of interest for this study (Cambrian to Devonian), with a number of oscillations in between (Figure 16). The $^{87}Sr/^{86}Sr$ ratios of waters from within sedimentary basins can be compared to the seawater strontium curve through the Phanerozoic (e.g. Burke et al., 1982; Veizer et al., 1999).

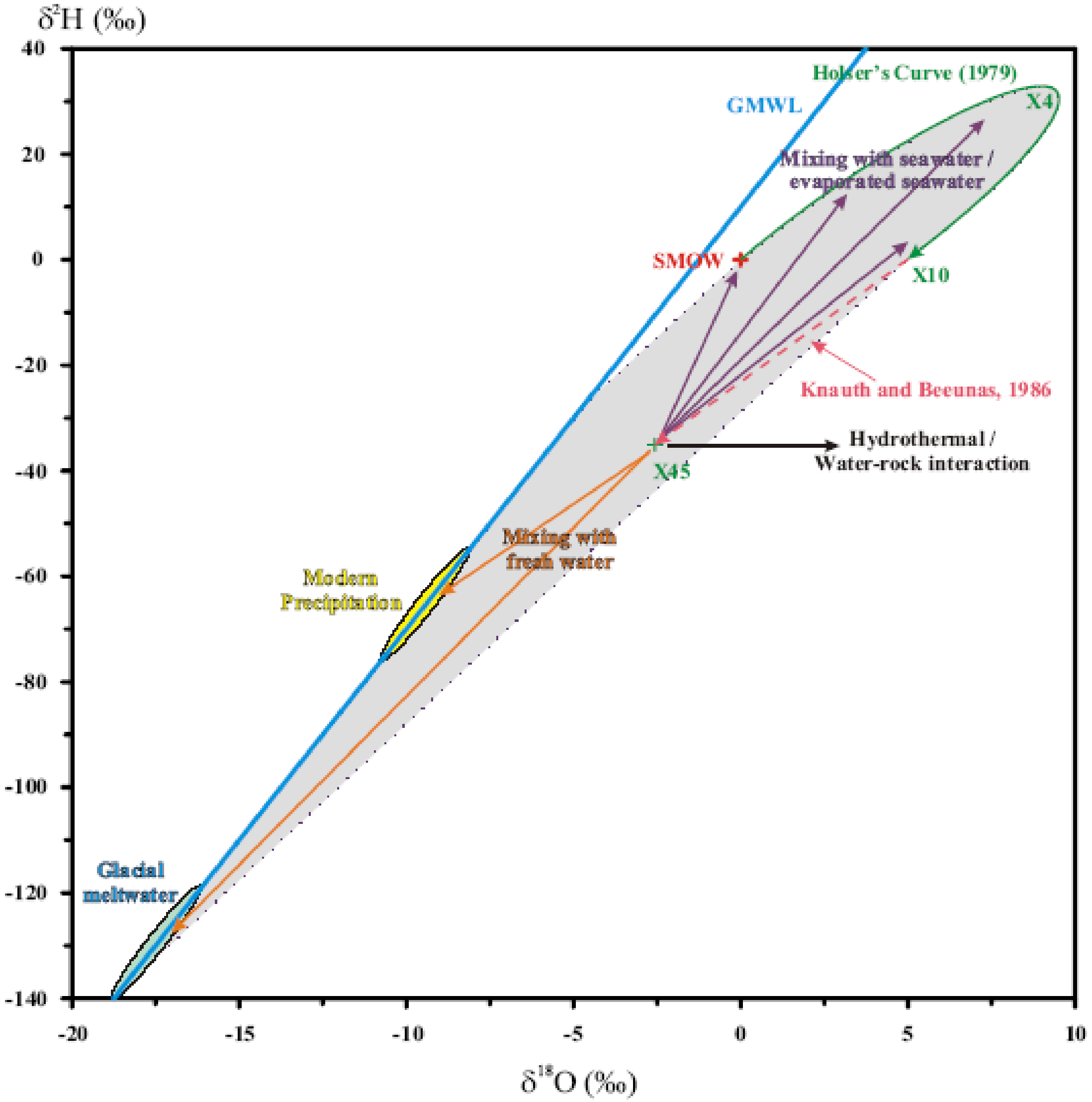


Figure 15: Different possible end members and processes controlling the oxygen and hydrogen isotopic compositions in sedimentary formation waters. The potential endmembers are seawater (SMOW), seawater which has undergone various degrees of evaporation, modern precipitation, and glacial melt-water. The major process influencing the evolution of the waters are mixing between various end members, seawater evaporation, hydrothermal activity, and water-rock interactions. The shaded area represents mixing between the main end members. The seawater evaporation curve of Holser (1979) is shown and indicates degree of evaporation (x4 and x10). Also shown is evaporation at x45 the concentration of seawater, as extrapolated by Knauth and Beeunas (1986). From Shouakar-Stash (2008).

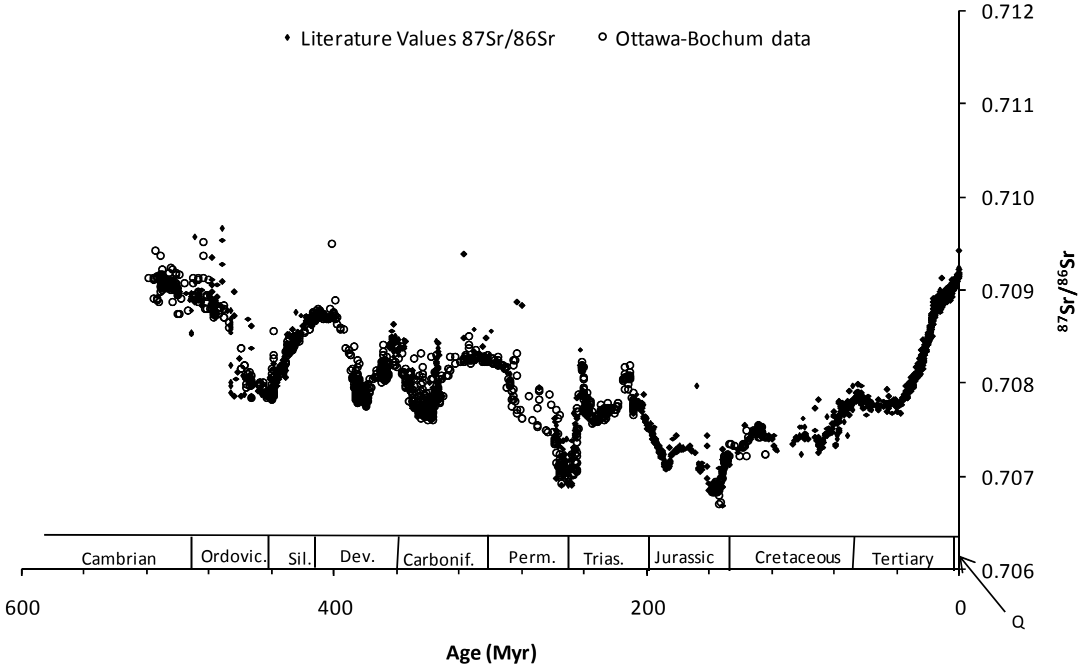


Figure 16: Plot showing the variations in the $^{87}Sr/^{86}Sr$ ratio of seawater during the Phanerozoic (after Veizer et al., 1999).

Fractionation of strontium does not occur under natural conditions. As a result, fractionation effects need not be considered as a potential mechanism for alteration of the strontium isotopic ratio in the fluids or rocks within sedimentary basin systems. Formations within sedimentary sequences deposited in marine environments will contain seawater trapped within the pores of the rock, and initially, this water will have the $^{87}Sr/^{86}Sr$ ratio of the marine system at the time of deposition. However, with time, reactions between water and rock may change the $^{87}Sr/^{86}Sr$ ratio in the water, depending on the mineralogy of the formation. Feldspars may contain relatively high Rb/Sr ratios and the $^{87}Sr/^{86}Sr$ ratio in these minerals is elevated by enrichment of ^{87}Sr from ^{87}Rb decay. The release of Sr from these minerals during diagenesis leads to an increase in the $^{87}Sr/^{86}Sr$ ratio of the waters within the rock matrix. Similarly, Rb that has substituted for K in clay-mineral assemblages decays to produce ^{87}Sr that may leach into solution and cause an increase in the $^{87}Sr/^{86}Sr$ ratio of the brine. In carbonate rocks, Sr^{2+} can substitute for Ca^{2+}, however Rb^{+} is excluded. Therefore, calcite has a very low Rb/Sr ratio and its $^{87}Sr/^{86}Sr$ ratio is not significantly altered by radioactive decay of ^{87}Rb to ^{87}Sr after deposition. On the basis that isotope fractionation does not occur and the production of radiogenic ^{87}Sr by decay of ^{87}Rb in carbonate rocks is negligible, Faure (1991) conclude that the isotopic composition of Sr in marine and non-marine carbonate rocks, in calcite cements and concretions reflects the composition of the fluid phase at the time of deposition.

Several authors have used Sr isotopes in various sedimentary basins to show the large contribution of Sr, and by analogy Ca, to the fluid phase as a result of diagenetic reactions such as feldspar dissolution (e.g., McNutt et al., 1987; Stueber et al., 1987). Stueber et al. (1997) demonstrated that in the Illinois Basin, clay minerals in shales and in quartz sandstone matrices represent the only significant source of radiogenic Sr for the waters. Based on mixing relationships between waters in Devonian- and Silurian-aged formations, Stueber et al. (1987) proposed an evolutionary model in which waters from the New Albany shales entered the Silurian-Devonian carbonate rocks and mixed with marine interstitial water in order to explain the radiogenic enrichment in these waters above the corresponding Paleozoic seawater values.

3.1.2 Water-Rock Interaction

The majority of sedimentary formation waters described in the literature have chemistries that vary considerably from what would be expected of evaporated meteoric or sea water. During the diagenetic evolution of the brines, calcium and strontium concentrations increase by up to an order of magnitude compared to evaporated seawater, whereas magnesium and potassium concentrations may decrease by as much as an order of magnitude (Kharaka and Hanor, 2005). Calcium is most often observed to be highly enriched compared to evaporated seawater. Collins (1975) and numerous other authors have described Ca enrichment, both with increasing depth and age, in most oil field-sedimentary environments. The proportion of Ca to TDS is also found to differ significantly from formation to formation, and even within oil fields from the same formation (e.g., Land, 1997). This would indicate that the concentration of many, if not all, cations and most anions are readily modified from conservative behaviour during seawater evaporation. Alternatively, Lowenstein et al. (2003) have suggested that $CaCl_2$ brines present in most sedimentary basins inherited their compositions and salinities from evaporated paleoseawaters that were rich in calcium and depleted in sulphate relative to modern day seawater (e.g., during the Silurian and Devonian). However, Hanor and McIntosh (2006) emphasize that the compositions of typical brines hosted by Silurian and Devonian-aged formations from the Illinois and Michigan basins do not show the same compositional trends of progressively evaporated $CaCl_2$-rich seawater. Significant diagenetic alteration is required to explain their compositions.

Variations in the chemistry of brines from that expected for evaporated seawater are often explained using several water-rock reactions, including 1) dissolution or precipitation of evaporite minerals, including halite and gypsum or anhydrite; 2) calcite precipitation or dissolution; 3) dolomitization; 4) dissolution or precipitation of aluminosilicates; and 5) ion exchange reactions with clays, which may also influence groundwater compositions (e.g. McIntosh and Walter, 2006). The possible effects of halite dissolution/precipitation on the evolution of Cl:Br ratios were described in the previous section (section 3.1.1.1).

Dolomitization reactions have been used to explain elevated calcium and decreased magnesium concentrations in brines, relative to those expected if evaporation of seawater was the only process involved. The dolomitization reaction can be described as:

$$2CaCO_3 + Mg^{2+} \rightarrow CaMg(CO_3)_2 + Ca^{2+} \tag{1}$$

where limestone ($CaCO_3$) reacts with magnesium to form dolomite, which results in the release of calcium to solution. Wilson and Long (1993a) developed a mass balance model to demonstrate the effects of dolomitization on brines. This model is based on the assumption that stoichiometric dolomitization is the only process affecting the concentrations of calcium and magnesium (as in equation 1). In this model, the Br concentrations measured in the brine are first compared to those in present day seawater, in order to determine the degree of concentration of the brine relative to seawater. The expected concentration of Mg in seawater which had undergone this degree of concentration is then calculated, and compared to the Mg concentration actually measured in the brine to determine the amount of Mg lost from solution.

The amount of Mg lost is attributed to dolomitization, and used to calculate the amount of calcium added to the brine. The total Ca concentration predicted for the brine is calculated by adding the amount of Ca from dolomitization to the Ca concentration expected from the evaporation of seawater. The predicted and measured Ca concentrations can then be compared in order to determine whether dolomitization reactions can reasonably account for the excess calcium measured in the brines.

The dissolution or precipitation of halite is a reversible reaction which results in either increases or decreases in Na and Cl concentrations:

$$\mathrm{NaCl_{(s)}} \Leftrightarrow \mathrm{Na^+} + \mathrm{Cl^-} \tag{2}$$

Reaction of brines with aluminosilicate minerals to form clays may also result in increased calcium concentrations in the residual brine. For example, the formation of albite from plagioclase feldspar increases Ca concentrations and lowers Na concentrations:

$$\underset{\text{(andesine)}}{\mathrm{Na_{0.7}Ca_{0.3}Al_{1.3}Si_{2.7}O_8}} + 0.6\mathrm{Na^+} + \underset{\text{(quartz)}}{1.2\mathrm{SiO_2}} \rightarrow \underset{\text{(albite)}}{1.3\mathrm{NaAlSi_3O_8}} + 0.3\mathrm{Ca^{2+}} \tag{3}$$

whereas the formation of kaolinite from albite increases Na concentrations:

$$\underset{\text{(albite)}}{2\mathrm{NaAlSi_3O_8}} + 11\mathrm{H_2O} + 2\mathrm{CO_2} \rightarrow \underset{\text{(kaolinite)}}{\mathrm{Al_2Si_2O_5(OH)_4}} + 2\mathrm{Na^+} + 2\mathrm{HCO_3^-} + 4\mathrm{H_4SiO_4} \tag{4}$$

The transformation of kaolinite to illite results in a decrease in K concentrations and increased Ca concentrations according to equation (5), while the conversion of smectite to illite (equation 6) decreases K concentrations and increases Na concentrations in the residual water.

$$2\mathrm{K^+} + \mathrm{CaCO_{3(s)}} + 3\mathrm{Al_2Si_2O_5(OH)_{4(s)}} \Rightarrow 2\mathrm{KAl_2(AlSi_3)O_{10}(OH)_{2(s)}} + \mathrm{Ca^{2+}} + 4\mathrm{H_2O} + \mathrm{CO_2} \tag{5}$$

Smectite to illite transformation: (6)

$$\begin{aligned} &3[\mathrm{Ca_{0.33}(Mg_{0.33}Al_{1.66})Si_4O_{10}(OH)_2 \cdot nH_2O}]_{(s)} + 2\mathrm{K^+} + \mathrm{Al^{3+}} + \mathrm{CaCO_{3(s)}} \Rightarrow \\ &\qquad 2[\mathrm{KAl_2(AlSi_3)O_{10}(OH)_2}]_{(s)} + 2\mathrm{Ca^{2+}} + \mathrm{Mg^{2+}} + \mathrm{CO_2} + 6\mathrm{SiO_{2(s)}} + (n+1)\mathrm{H_2O} \end{aligned}$$

Kaolinite is a commonly observed secondary mineral phase in clastic rocks. Under the correct temperature, solubility and $p\mathrm{CO_2}$ conditions, the excess silica may form quartz overgrowths. Similarly, formation of authigenic illite or potassium feldspar decreases potassium concentrations in the brine. For example, potassium in the brine reacts with smectite to form illite, chlorite and quartz, releasing Ca, Na and $\mathrm{Fe^{3+}}$ into solution (Kharaka and Hanor, 2005). With increasing temperatures, these reactions are important controls on brine compositions in many sedimentary basins (Kharaka and Hanor, 2005).

4. DIAGENTIC FLUIDS

Diagentic processes involving fluids which are known to have influenced the evolution of the sedimentary rocks in southern Ontario include clay alteration of the Upper Precambrian crystalline rocks and the overlying Cambrian and Ordovician formations, dolomitization, massive sulphide deposition, oil and gas generation and migration, dissolution of salts and precipitation of late-stage cements. The diagenetic history of the Michigan Basin is presented in detail in the Regional Geology Synthesis (Gartner Lee Limited, 2008b). In the following sections, the information currently available on the nature of fluids involved in these diagenetic processes and information which constrains their time of emplacement are described. This review provides a basis for comparison with the chemical and isotopic composition of the groundwaters within the geochemical database for southwestern Ontario.

4.1 Clay Alteration

Diagenetic alteration of the uppermost Precambrian rocks in southwestern Ontario below the Precambrian-Paleozoic boundary and in the overlying Cambrian and Ordovician sedimentary rocks has been investigated by Ziegler and Longstaffe (2000a; 2000b). The diagenetic mineralogy includes secondary K-feldspar and clay minerals (predominatly chlorite and illite with some kaolinite). The secondary clay minerals occur within fractures, as grain-coatings within the rock matrix and as in-filling minerals in the pore spaces between grains (Ziegler and Longstaffe, 2000b). Ziegler and Longstaffe (2000a; 2000b) determined the stable isotopic signatures of secondary chlorite and illite, and measured K-Ar dates for secondary K-feldspar and illite in an attempt to determine the nature and origin of the fluids and the timing of alteration.

For secondary chlorite occurring in both the Precambrian basement rocks and in the overlying Cambrian and Ordovician formations, the $\delta^{18}O$ signatures are consistent with precipitation from brines evolved from seawater, at temperatures greater than 150 °C (Ziegler and Longstaffe, 2000a, b). As the fluid cooled and possibly mixed with meteoric water, secondary potassium-rich feldspar precipitated. Radiometric dates for K-rich feldspar in the uppermost Precambrian rocks in southwestern Ontario range from 453 to 412 Ma, with an average of 444 million years B.P. (Harper et al., 1995). Ziegler and Longstaffe (2000a) proposed a conceptual model in which the regional migration of the brines from which secondary chlorite and K-rich feldspar were precipitated was induced by Taconic orogenic events to the east, which began in the Late Ordovician. In this model, westward migration of waters of marine origin trapped within Paleozoic formations within the Appalachian basin was focused along the unconformity between the Upper Precambrian crystalline basement and the overlying Paleozoic sedimentary rocks and was facilitated by faults within the lower part of the sedimentary section.

The available K-Ar dates and the $\delta^{2}H$ and $\delta^{18}O$ signatures of secondary illite suggest that it formed during a second event in the early to mid-Carboniferious from local meteoric waters at temperatures of between 40 and 55 °C. Beginning in the Late Devonian-Early Carboniferous (~350 Ma), the uplift of the Findlay-Algonquin Arch in response to the Acadian and Alleghanian orogenic activity along the eastern coast of North America resulted in the erosion of the Paleozoic formations across the top of the arch. Ziegler and Longstaffe (2000a) proposed a conceptual paleohydrogeogical model for illite formation in which local meteoric waters infiltrated into Paleozoic sandstone formations and reacted with the K-feldspar alteration assemblage near the unconformity, precipitating secondary illite.

Gross et al. (1992) proposed a similar conceptual model of active fluid circulation during the Acadian orogeny in southern Ontario and western New York to explain the orientation and spatial distribution of an east-northeast-trending systematic calcite vein set in the Lockport dolomite. The calcite vein set is prominent to the east of the Clarendon-Linden fault zone in western New York/southern Ontario, but rare to the west (Gross et al., 1992). Although calcites from only six sites were examined from the western side of the fault zone (sites 1-4 and 11-12 on Figure 17), reconnaissance fluid inclusion data indicated that these calcites precipitated at approximately 115 °C, which could suggest formation at depths ≥ 3 kilometers. Based on the stable oxygen isotopic signatures of the vein calcites ($\delta^{18}O_{PDB}$), calcites from the east of the Clarendon-Linden fault zone were precipitated from fluids which are isotopically lighter (+5.3 to +7.2‰) than those to the west (+8.5‰).

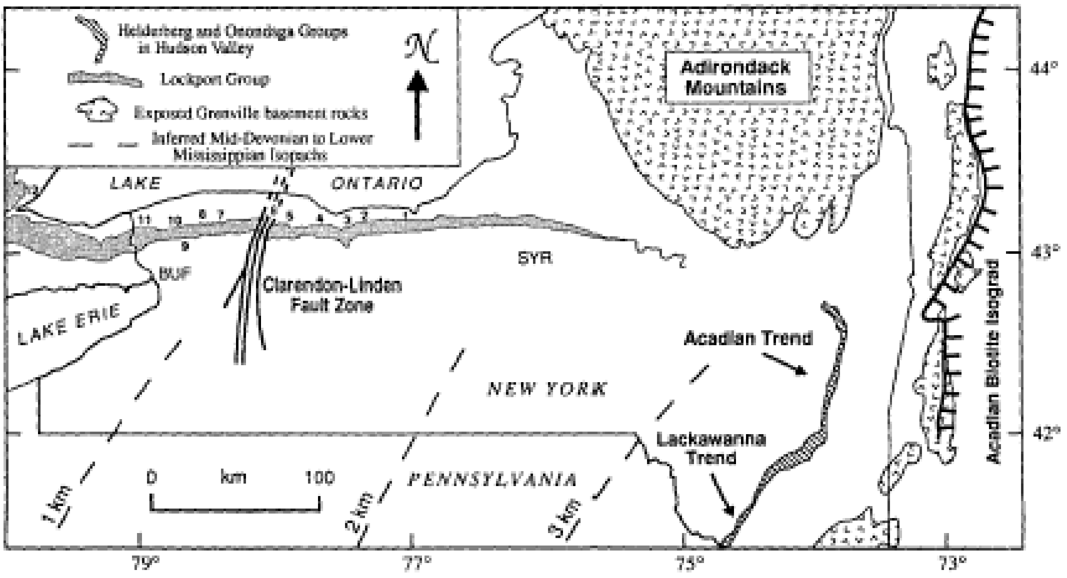


Figure 17: Sampling locations of a systematic calcite vein set in the Lockport dolostone. North-northeast-trending, calcite-filled veins are the dominant fracture set at sites 1 through 5. The veins are also present at sites 11 and 12, although their orientation is almost due-east. The vein set is absent at sites 6 through 10. From Gross et al., 1992.

Gross et al. (1992) proposed a regional model in which an isotopically heavy fluid (tectonic, metamorphic or highly evolved meteoric) from the east was recharged down into the Lockport Group, and was trapped beneath the overlying Salina salt units. High hydraulic heads to the east in the orogen caused high fluid pressures to develop in the Lockport Group. Because fluids could not circulate upward through the overlying salt, veins propagated through the upper section of the Lockport Group, consistent with the observation that calcite veins are not present in the basal formations. The veins in the Lockport Group are considered to be extension fractures, because there is no evidence of shear movement. Extension fractures propagate parallel to the maximum horizontal principle stress. Based on the compatibility of east-west trend in the maximum horizontal stress with the observed trend in the systematic vein set, Gross et al. (1992) constrained the timing of fluid circulation and precipitation of the vein calcites to an Acadian tectonic event in western New England and the Hudson Valley.

Secondary (authigenic) illite in the Lower Silurian Cataract Group sandstones in southern Ontario (Appalachian Basin) was examined by O'Shea and Frape (1988). The Grimsby Formation was sampled most extensively, with fewer samples examined from the Cabot Head shale and the Whirlpool sandstone (see also Figure 4). The primary cement in the sandstones is silica, with less than 5% secondary illite infilling pores. A minor amount of illite from within was observed to be associated with intergrown chlorite and quartz, formed by the reaction of smectite with K-feldspar. The temperatures required for the formation of illite from smectite of between 60 and 100 °C are consistent with the maximum burial temperatures of 80 °C reached in the Silurian sequence, as reported by Legall et al. (1981). However, over 90% of the illite within the sandstones was found to be associated with partially dissolved (or corroded) K-feldspar and measurable quantities of gas. This type of illite is thought to have formed by direct precipitation from concentrated pore fluids by reaction of K-feldspar with brine. Formation waters which are associated with gas reservoirs and sampled from within the Cataract sandstones have sufficient salinity (180,000 to 267,000 mg/L total dissolved solids), and potassium and silica concentrations for direct precipitation of illite from solution. O'Shea and Frape (1988) suggest that the leaching of K-feldspars and transport of dissolved aluminium may have been facilitated by organic acids, perhaps released during the early stages of hydrocarbon maturation. This indirectly suggests an association between the brines from which illite was precipitated and hydrocarbons, consistent with the coexistence of brines and hydrocarbon gases observed today in reservoirs within the Thorhold/Grimbsy formations in the Appalachian Basin, southwestern Ontario.

4.2 Dolomitization

Dolomitization is the most extensive of the diagenetic processes which influenced the sedimentary sequence underlying southern Ontario. Hydrocarbon reservoirs were created in low porosity Ordovician limestones through either fracturing or faulting and subsequent dolomitization of the adjacent limestone, which results in increased porosity and permeability (e.g., Carter et al., 1996; Coniglio et al., 1994; Middleton et al., 1993; Carter, 1991; Sanford et al., 1985). As a result, research has focused on Ordovician formations (e.g., Coniglio et al., 1994; Middleton et al., 1993; Coniglio and William-Jones, 1992) which are known to host hydrocarbon reservoirs. The available information on the nature of the dolomitizing fluids (temperatures, salinities), any constraints on the timing of the dolomitization events, and relationships to other diagenetic fluids based on observations in the Ordovician and Silurian formations are summarized in the following sections. A comprehensive review of dolomitization in the Michigan Basin is given by Gartner Lee Limited (2008b).

4.2.1 Ordovician Formations

Coniglio et al. (1994) synthesized the available information on the diagenesis of Middle and Late Ordovician strata in Ontario, including Trenton and Black River Groups, and the Blue Mountain Formation in subsurface core samples from southwestern Ontario (Middleton et al., 1993), and samples from outcrops in the Manitoulin Island area, where the Georgian Bay Formation was also sampled (Coniglio and William-Jones, 1992). These studies involved petrographic analyses, mineral and whole rock analysis for stable isotopes (C, O and S) and geochemistry, and fluid inclusion analyses. The mineral phases examined included early-stage calcite cement, which predates dolomitization, dolomites, and late-stage calcite cement which postdates dolomitization.

Information on the nature of the fluids present during mineral precipitation can be obtained from trapped fluid inclusions, particularly when the inclusions can be demonstrated to be primary (precipitated during crystallization). For primary fluid inclusions in fracture-related dolomite cements from southwestern Ontario, Middleton et al. (1993) measured homogenization temperatures ranging between 100 and 220 °C. Based on melting temperatures, the compositions of the fluid inclusions were $NaCl\text{-}MgCl_2 \pm CaCl_2$ brines, with salinities between 22 and 41 wt. % NaCl. In late-stage calcite cements, fluid inclusion analyses suggest that the fluids were lower temperature (70 to 170 °C) and less saline (16 to 28 wt % NaCl). Fluid inclusions analyzed in carbonates from the Manitoulin area suggest that early calcites and dolomite were precipitated from fluids with temperatures of approximately 100 °C, salinities between 18 and 31 wt. % NaCl, and $NaCl\text{-}CaCl_2 \pm MgCl_2$ compositions (Coniglio and William-Jones, 1992). Late calcites (post-dolomitization) were likely precipitated from less saline (<19 wt. % NaCl) solutions. The homogenization temperatures for these fluid inclusions show a bimodal temperature distribution; the lower temperature mode occurs at 107 °C, and the higher between 150 and 210°C. However, because the majority of these fluid inclusions were either secondary or indeterminate, any diagenetic interpretation based on the fluid inclusion data is less certain.

The temperatures measured in dolomites and calcites from both locations are substantially higher than those likely generated during peak burial of the sedimentary sequence. In the Manitoulin Island area, the maximum burial depth based on reconstruction is estimated at 1500 m, which would yield a peak burial temperature of 55 °C (Coniglio and William-Jones, 1992). In southwestern Ontario, an estimated maximum burial depth of 2,000 m would give maximum peak temperatures of 66 °C (Coniglio et al., 1994). On this basis, the temperatures generated by burial alone cannot account for the temperatures of fluids involved in calcite cementation and dolomitization, as determined from fluid inclusion analyses. Higher paleogeothermal gradients between 35 and 50 °C/km have been suggested for the Michigan Basin (e.g., Cercone, 1984; Vugrinovich, 1988), and would produce higher burial temperatures at the reconstructed depths. A combination of increased sediment thickness and geothermal gradients could produce the temperatures recorded in fluid inclusions. However, Coniglio et al. (1994) point out that this is not well supported by available information on the regional burial history, particularly conodont studies, which suggest maximum burial temperatures of approximately 60°C (Legall et al., 1981). The interpretation favoured by Coniglio et al. (1994) is that these data reflect the involvement of variable hydrothermal burial fluids in the precipitation of the early calcite cement, dolomites and late calcite. The heat source for these hydrothermal fluids is unknown.

It is thought that fracture-related dolomitization and hydrocarbon migration in the Michigan Basin likely occurred during the Late Paleozoic to Early Mesozoic (Prouty, 1989; Hurley and Budros, 1990; Budai and Wilson, 1991). These authors compared fracture-related dolomite in the Michigan Basin with Mississippi Valley-type (MVT) deposits in the central and eastern United States. These emplacement processes in the Ordovician sediments are considered to be contemporaneous, and were likely the result of the Alleghenian deformation and thrusting events taking place in the east. The Ordovician carbonates in southwestern Ontario contain minor (<1%) quantities of late-stage diagenetic minerals, including anhydrite, gypsum, pyrite, authigenic quartz and feldspar, fluorite, barite and celestite, which resemble the various gangue minerals which characterize MVT deposits (Middleton et al., 1993). An association with MVT deposits is further strengthened by the existence of non-economic MVT mineralization in Silurian strata in southern Ontario (Farquhar et al., 1987; see also section 4.3). In southwestern Ontario, the observation of solid hydrocarbons coating saddle dolomite and late-stage calcite cement also supports a close association between hydrocarbon migration into the dolomitized Ordovician reservoir rocks and these late-stage diagenetic phases (Coniglio et al., 1994). This is also consistent with the findings of Budai and Wilson (1991) for samples from the Trenton and Black River Groups in the central Michigan Basin.

4.2.2 Silurian Formations

The distribution, origin and diagenetic evolution of regional-scale dolomite in the Middle Silurian Guelph Formation were interpreted by Coniglio et al. (2003). The study integrated data collected from core observations, cathodluminescence microscopy, analyses of major and trace elements (Ca, Mg, Sr, Na, Fe and Mn) and stable isotopes (O and C) in >50 whole-rock calcite and dolomite samples, two calcite and two dolomite cements, and radiogenic strontium isotopic ratios ($^{87}Sr/^{86}Sr$) from a selection of dolomite and calcite whole-rock samples.

A seawater source for the dolomitizing fluid is supported by both the $\delta^{13}C$ values (+1.1 to 5.0 ‰ PDB) and the $^{87}Sr/^{86}Sr$ ratios, which range from 0.70845 to 0.70910 (Coniglio et al., 2003), although two dolomite samples had $^{87}Sr/^{86}Sr$ ratios which were more radiogenic. The large range in $\delta^{18}O$ signatures (-5.2 to -9.7 ‰ PDB) observed both geographically and stratigraphically in the dolomites is thought to reflect varying degrees of recrystallization due to increasing temperatures during burial. The nature and extent of recrystallization may have been controlled in part by the porosity and permeability of precursor rock textures, which would influence fluid-rock interactions. In pinnicale reefs in northern Michigan, Cercone and Lohmann (1985) suggested that early alteration and cementation occurred in saline fluids, possibly from fluid migration from the overlying Salina A1 Carbonate; Coniglio et al. (2003) argue that this interpretation is also applicable to the reefs in southwestern Ontario. Based on a preliminary examination of primary fluid inclusions, the composition of the diagenetic fluids were Na-Ca-Mg-Cl brines with salinities from 14 to 30 wt. % NaCl, and temperatures between approximately 65 and 130 °C (Coniglio et al., 2003, after Zheng, 1999). This suggests that either some of the carbonates experienced much higher burial temperatures than estimated from reconstructions, or that some of the fluids were hydrothermal in nature, as suggested by Coniglio et al. (1994) for the Ordovician strata in Ontario.

In terms of the timing of dolomitization, Coniglio et al. (2003) postulate that the flow system was active during the Upper Silurian for a geologically brief period, which likely began after the onset of deposition of the A1 Evaporite, and ended as a result of the deposition of impermeable B Evaporite or younger Salina evaporites. Late-stage post-dolomitization phases observed in the Guelph Formation include anhydrite and halite, with halite precipitation post-dating anhydrite (Coniglio et al., 2003). Although both anhydrite and halite are minor (<1%) constituents in the dolomites of the Silurian succession which post-date dolomitization, Coniglio et al. (2003) note that plugging by halite is the “single most important porosity-destroying process in many basinward pinnacle reefs”. Hydrocarbon emplacement post-dates dolomitization in the Silurian reservoirs of southwestern Ontario, and was essentially the last process to occur after halite and anhydrite deposition, with the exception of some localized pressure-dissolution and re-precipitation of evaporites that post-dates hydrocarbon emplacement in some areas (Coniglio et al., 2003).

4.3 Mississippi Valley-Type Sulphide Deposits

Mississippi Valley-type (MVT) ore deposits are low-temperature (80 to 150 °C) hydrothermal deposits that occur in carbonate rocks near basin margins or basement highs in tectonically stable continental interiors. Evidence from fluid inclusions indicates that the mineralizing fluids associated with these deposits were highly saline Na-Ca-Cl brines with 10% wt. NaCl (approximately 3 times the salinity of seawater) or greater (Ingebritsen et al., 2006).

MVT lead-zinc sulphide mineralization occurs in the Middle Silurian dolomites in southern Ontario. On the basis of geographic and mineralogical differences, Tworo (1985; after Farquhar et al., 1987) grouped the occurrence of sulphides into two groups; the Bruce District to the north of the Algonquin Arch on the eastern margin of the Michigan Basin, and those of the Niagara District southeast of the Algonquin Arch on the northwestern margin of the Appalachian Basin.

Farquhar et al. (1987) compared lead isotope analyses for K-feldspars in granite, massive sulphide ores and sedimentary rocks within the Appalachian Basin. This comparison suggests a common source for Pb within the sediments of the Appalachian Basin and those in galenas of the Niagara District, consistent with a conceptual model in which lead from Late Precambrian to Early Paleozoic sediments (~400 Ma) was extracted by brine fluids and mobilized northward from the centre of the basin and into New York State and Pennsylvania during the late Paleozoic – early Mesozoic tectonic thrusting in New York and Pennsylvania.

McKenna et al. (1992) examined lead and strontium isotopic ratios of brines sampled from producing oil and gas wells and dry wells (i.e., containing no hydrocarbons) by Dollar (1988,1991). Based on linear relationships observed between $^{207}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ versus $^{206}Pb/^{204}Pb$ diagrams for the brines, two groups of model ages were identified. The first group has model ages ranging between 2.0 and 2.3 Ga, and includes brines from Ordovician carbonates, Silurian carbonates and Mississippian sandstones in Michigan, and from Silurian sandstone in Ontario. Model ages determined for brines from Ordovician and Silurian carbonates in Ontario are younger (0.52 to 0.76 Ga). McKenna et al. (1992) caution that if the model ages are meaningful, the dates likely reflect the age of the source for the lead, rather than the age of the brines. Lead may have been directly leached from the underlying crystalline rocks of the Grenville and Southern Provinces which range in age from 2.7 to 1 Ga, or by interaction of the brines with clastic, reworked Grenville rock within the Paleozoic sedimentary formations. Consistent with the findings of Farquhar et al. (1987) for galenas, brines from Ordovician formations within the Michigan Basin were found to have more radiogenic Pb ratios than those from within the Appalachian Basin in southwestern Ontario. Strontium isotopic ratios showed an opposite trend, with the most radiogenic signatures observed to the east in the Appalachian Basin.

Strontium and lead ratios in late stage diagenetic phases, including calcite, dolomite, pyrite and anhydrite in core from the Hillman field in southwestern Ontario, were also measured by McKenna et al. (1992). The results were compared to those measured for the brines from within the sample producing interval within Ordovician-aged carbonates of the Trenton-Black River Formation. The brines were found to be most similar to the Paleozoic sulphides and carbonates. However, the authors observed that the brines presently sampled from within the formation are not in Pb or Sr equilibrium with either the host rock or the late-stage secondary minerals, suggesting that these fluids were emplaced after the formation of the secondary minerals.

Fluorite is a mineral which is often associated with MVT deposits. Kinsland (1977) examined fluid inclusions in three samples of fluorite within the Lockport Formation from the same location. The results of this initial study suggested that the mineralizing fluids within the formation had a temperature within the range of 132 to 142 °C. This conclusion was later questioned by Haynes and Mostaghel (1979), in part because these authors argue that fluorite is a poor choice for fluid inclusion studies, due to its tendency to fracture along perfect cleavages. Haynes and Mostaghel (1979) also suggested that analysis of fluid inclusions from quartz, sphalerite, and calcite crystals from within the Lockport Formation at different localities would be required to verify the findings of Kinsland (1977). However, it should be noted that the fluid inclusion temperatures measured in fluorite by Kinsland (1977) are fairly consistent with the higher end of temperatures reported for fluids associated with dolomitization (approximately 65 to 130 °C) based on preliminary examination of fluid inclusions in Silurian-aged formations (section 4.2.2).

4.4 Hydrocarbons

The majority of waters included in this synthesis are brines collected from producing hydrocarbon (oil and or gas) reservoirs (section 2.2.1). An improved understanding of the origin and evolution of these groundwaters and their residence times within the sedimentary formations is facilitated by understanding the association between the generation and migration of hydrocarbons and their associations with other diagenetic fluids. A detailed summary of the petroleum geology of southwestern Ontario is included in the Regional Geology Report (Gartner Lee Limited, 2008b). The current understanding of hydrocarbon generation and migration in reservoirs in southwestern Ontario is summarized in the following sections.

4.4.1 Generation of Hydrocarbons

In sedimentary basins, the generation of hydrocarbons involves the thermal decomposition of organic matter, which is best preserved in rocks formed in low energy environments, such as shales. The formation of productive hydrocarbon reservoirs requires primary migration of hydrocarbons generated within the low-permeability source rocks into a carrier bed (or aquifer) and secondary migration within the aquifer to a structural, stratigraphic or diagenetic “trap” which constitutes the reservoir. When there is a close association between the reservoir rocks in which the hydrocarbons have accumulated and the source rocks, the hydrocarbons are said to have formed in-situ, with only short secondary migration distances (e.g. several kilometres). In other cases, the distance between probable source rocks and the hydrocarbon reservoirs may be considerable. For example, in the Western Canadian Basin, oil and or gas generated in source rocks travelled as much as several hundred kilometres before accumulating in reservoirs (Ingebritsen et al., 2006). Distinguishing between in-situ hydrocarbon generation and migration from elsewhere requires information on the thermal maturity of the formations, and geochemical characterization of the hydrocarbons, including oils within the reservoir and within the formations, and gases from within the reservoir. The available information from the open literature for hydrocarbon generation in southern Ontario is summarized below and in the Regional Geology Report (Gartner Lee Limited, 2008b).

Legall et al. (1981) examined the thermal maturity of the formations within the sedimentary sequence underlying southwestern Ontario using colour alteration indices (CAI). Maximum burial temperatures of less than 60 °C were determined for Devonian- to Middle Ordovician-age strata (Trenton Formation) based on a CAI of 1.5, indicating that these formations are immature to barely mature in terms of oil generation. In the lower part of the Ordovician sequence, maximum burial temperatures of 60 to 90 °C were determined, with CAI between 2 and 2.5 which is within the mature “Liquid window” for hydrocarbon generation.

Geochemical characterization of oils from reservoirs within the sedimentary sequence was conducted by Powell et al. (1984). These authors examined 36 oil samples from Devonian, Silurian, Ordovician and Cambrian reservoirs, and examined 105 rock samples from 24 stratigraphic units underlying southwestern Ontario. Three families of oil were identified, each with a distinctive organic geochemical composition, enabling distinction of the different types:

i) Cambro-Ordovician oils, which are typical of oils derived from marine organic matter;
ii) Silurian oils, which show the greatest diversity in geochemical characteristics, and are typical of oils occurring in carbonate-evaporite type environments; and
iii) Devonian oils, which are also typical of oils derived from marine organic matter.

On the basis of this geochemical characterization, Powell et al. (1984) identified potential source rocks for the Cambrian-Ordovician and Silurian oils. The Ordovician-aged Collingwood member of the Lindsay (Cobourg) Formation was identified as a potential source rock for Cambro-Ordovician oils, and the Middle Silurian Eramosa member (Guelph Formation) was identified as a possible source for Middle Silurian reef-hosted oils (Powell et al., 1984). Based on subsequent biomarker research, Obermajer et al. (1999) suggested that the organic-rich laminated dolomite of the younger Salina A-1 Carbonate is likely the primary source of oil in the Guelph Formation. Powell et al. (1984) were not able to identify a source formation for Devonian oils, because the Devonian rocks in southwestern Ontario are immature to marginally mature, and therefore below the thermal maturity required for oil generation. The authors suggested potential source rocks down-dip in the Michigan Basin including the Kettle Point, Dundee and Marcellus formations.

The geochemical compositions of natural gases from reservoirs in Silurian-aged formations, including the chemical and carbon and hydrogen isotopic compositions were examined by Barker and Pollock (1984). Several samples from reservoirs within the Middle Ordovician and Cambrian formations were also examined. Geochemical indicators of hydrocarbon source maturity derived from the analysis of the isotopic composition of methane, which is the major component of the natural gases (mean concentration 85% CH_4), consistently indicated a very mature or overmature source rock. Other indicators, in particular the dominance of nitrogen gas over CO_2 and H_2S in the non-hydrocarbon gas, suggested an immature source. On this basis, Barker and Pollack (1984) suggested that although some of the methane may have been generated in-situ from local, immature sources, the majority of methane was generated from overmature source rocks. Thermally overmature methane could not have been generated in-situ, because the thermal maturity of the formations within the sequence is insufficient. This overmature methane may have originated by lateral migration into southwestern Ontario from more mature source rocks in the Michigan and Appalachian Basins, or from upward migration from a Precambrian basement source (Barker and Pollock, 1984).

Sherwood Lollar et al. (1994) examined natural gases from within Ordovician and Cambrian reservoirs in southwestern Ontario, and characterized the gases using isotopic and compositional indicators. Consistent with the findings of Barker and Pollock (1984), gases from the Cambrian and Ordovician reservoirs are composed predominantly of CH_4, and N_2 is the dominant non-hydrocarbon gas. The Cambrian and Ordovician gases were found to be thermogenic in origin, with no evidence of bacterial CH_4 contributions. Where the sedimentary rocks were in direct contact with the Precambrian basement, the gases sampled had He values of approximately 1.2% by volume, which is substantially elevated with respect to the average concentration in gas samples from all other producing zones in the region of <0.15% (Sherwood Lollar et al., 1994). These elevated He concentrations and $^3He/^4He$ ratios may reflect mixing between gas produced in-situ in the Cambrian and Ordovician strata, and an end-member enriched in helium. Possible sources for the He-rich end-member include methane from within deep within the Precambrian basement rock, or an external He-enriched fluid that migrated from deeper within the sedimentary system along structurally controlled pathways (Sherwood Lollar et al., 1994).

Based on the structural interpretation of the Chatham Sag, identified pinch-out structures in oil and gas reservoirs (e.g., Sanford et al., 1985; Carter et al., 1996), and data on the temperature of emplacement and maturity levels of the hydrocarbons from their study, Sherwood Lollar et al. (1994) concluded that natural gases from reservoirs to the southeast of the Algonquin Arch/Cambrian pinch-out boundary display elevated thermal maturities, which would support migration from the Appalachian Basin. Hydrocarbon reservoirs to the northwest, which would coincide with migration from the Michigan Basin, do not display such elevated maturities. The authors concluded that the dominant migration pathways for oil and gas (and hydrothermal fluids) within the Chatham Sag were structurally and/or lithologically controlled by the nature of the Cambrian strata, or by the nature of the contact between the Cambrian and Precambrian basement geology in the southeastern portion of the Algonquin Arch, or a combination of both these factors.

In summary, based on the thermal maturity of organic matter within the formations underlying southern Ontario, strata from the Middle Ordovician Trenton formation up through the sequence to the Devonian are immature to barely mature (Legall et al., 1981). Geochemical characterization of the oils (Powell et al., 1984; Obermajer et al., 1999) determined possible source rocks within the sequence for in-situ generation of both the Cambrian-Ordovician and Silurian oils. However, the Devonian oils could not have been generated in-situ from Devonian source rocks underlying southwestern Ontario, which are not sufficiently mature to have produced oil. Based on the characterization of natural gases by Barker and Pollack (1984) and Sherwood Lollar et al. (1994), the dominance of N_2 in the non-hydrocarbon component of these gases suggests an immature source, which could have been generated in-situ. However, the majority of methane, which is the dominant hydrocarbon component, is thermogenic and thermally overmature, was likely generated deeper in the Michigan or Applachian Basin. Hydrocarbon gases from reservoirs in both Silurian- and Ordovician-Cambrian-aged formations contain a large component which was generated outside of the sedimentary sequence underlying southwestern Ontario, and was either transported in laterally from more mature source rocks deeper in either the Michigan or Applachian Basin, or was transported upwards from a basement source in the underlying Precambrian rocks.

4.5 Synthesis

In the following sections, the evidence for flow of diagenetic fluids across formations is summarized. The associations between the diagenetic fluids which provide constraints on their relative timing of emplacement are then presented and discussed within the context of the current scientific understanding of the processes involved in migration of these fluids and the existence of the driving forces required for their emplacement.

4.5.1 Evidence of Cross-Formational Flow

In general, the evidence for the interaction of diagenetic fluids within the sedimentary sequence as described in the preceding sections provides evidence of cross-formational flow during diagenesis. In this section, the evidence for more localized occurrences of cross-formational flow are described.

On the basis of the distinct compositions identified for oils from reservoirs within the Cambrian-Ordovician, Silurian and Devonian-aged formations, two anomalies were identified for reservoirs within the Silurian-aged A1-Carbonate, in the Chatham-Kent area in Ontario (Powell et al., 1984). Oil in the Fletcher Reservoir was identified as belonging to the Cambro-Ordovician family, and oil in the Mosa Reservoir was found to be a mixture of Cambro-Ordovician and Silurian oils. The presence of Cambrian-Ordovician oils in Silurian reservoirs suggests that, at least locally, some cross-formational flow of hydrocarbons occurred between reservoirs.

There is some evidence of interaction, and a relationship between the Ordovician and Silurian diagenetic fluids, as discussed by Obermajer et al. (1999). These authors indicate that there is evidence of cross-formational flow between the Ordovician and Silurian units (e.g. Mosa reservoir) and possibly some relationship between the overlying Devonian oils and the Ordovician source rocks, but emphasize that no clear evidence exists that links those cross-formational fluids to the Silurian dolomitization events.

Historical evidence of episodes of fluid movement during or after the last glaciation retreat (c.a. 10 ka.) include the observation in the mid-1800's of petroleum products and saline waters in the glacial till overlying Devonian-aged bedrock (Weaver et al., 1992). The most probable source of these fluids is the underlying Devonian carbonate oil-bearing Dundee formation, present at depths of 50-100 m below the base of the glacial tills. Indirect evidence for localized mixing with glacial waters was presented by Weaver et al. (1995). These authors proposed that previously mixed, saline waters with depleted δ^2H isotopic signatures derived from the underlying Silurian salt formations migrated vertically along fracture networks from depths of several hundred meters into the oil-bearing Devonian formations during or after the last deglaciation. Mixing between waters similar (but more dilute) than those from the Silurian A2 Evaporite Formation with a glacial recharge water was postulated to explain the observed chemical and isotopic signature of ground waters from the Oil Springs field sampled within the Devonian-aged Dundee carbonate (Weaver et al., 1995).

4.5.2 Associations Between Diagenetic Fluids and Timing of Emplacement

In southwestern Ontario, the strongest associations observed between diagenetic fluids are between those fluids involved in dolomitization, mineralization of MVT-type sulphide deposits and hydrocarbons. Associations are observed between dolomitization and late-stage calcite cements as well as late-stage anhydrite and gypsum (Coniglio et al., 1994). The Ordovician carbonates in southwestern Ontario contain minor (<1%) quantities of late-stage diagenetic minerals, including anhydrite, gypsum, pyrite, authigenic quartz and feldspar, fluorite, barite and celestite, which resemble the various gangue minerals which characterize MVT deposits (Middleton et al., 1993). This association with MVT deposits is further strengthened by the existence of non-economic MVT mineralization in Silurian strata in southern Ontario (Farquhar et al., 1987; see also section 4.3). Faquhar et al. (1987) suggest that regional differences in the isotopic composition of lead observed in galenas are related to separate sources of lead originating in the Appalachian Basin to the east (Niagara Peninsula) and the Michigan Basin to the west (Bruce Peninsula). This is consistent with the proposal that lead was extracted from rocks of Late Precambrian to early Paleozoic age by brines migrating northward from the depo-centre of the Appalachian Basin during the late Paleozoic – early Mesozoic thrusting in New York and Pennsylvania (Farquhar et al., 1987). Similarly, evidence for differing compositions of brines involved in the formation of MVT deposits in the Appalachian Basin versus those in the mid-continent region of the U.S.A. were reported by Kesler et al. (1996) based on an examination of Na-Cl-Br relations in fluid inclusions.

Middleton (1991) reported a possible link between brines responsible for hydrothermal dolomitization (HTD) in southwestern Ontario and the mineralizing fluids associated with MVT deposits in the eastern United States. Several other studies have compared fracture-related dolomite elsewhere in the Michigan Basin with Mississippi Valley-type (MVT) deposits in both the central and eastern United States (Prouty, 1989; Hurley and Budros 1990; Budai and Wilson 1991). The formation of fracture-related dolomitization and hydrocarbon migration in the

Michigan Basin in the Ordovician formations are considered to be contemporaneous, and were likely the result of the Alleghenian deformation and thrusting events taking place in the east during the Late Paleozoic to Early Mesozoic (350 to 250 Ma BP). Coniglio et al. (1994) observed solid hydrocarbons coating saddle dolomite and late-stage calcite cement, supporting a close association between hydrocarbon migration into the Ordovician reservoir rocks and these late-stage diagenetic phases. This is also consistent with the findings of Budai and Wilson (1991) for samples from the Trenton and Black River Groups in the central Michigan Basin.

4.5.3 Conceptual Model for Migration of Diagenetic Fluids

The migration of diagenetic fluids including those involved in dolomitization, the mineralizing fluids from which MVT-type sulphide minerals precipitated and the migration of hydrocarbons requires i) pathways with sufficient permeability to facilitate the transport of these fluids and associated brines over tens to hundreds of kilometres from deep in the center of a sedimentary basin to its margins; and ii) a driving force for flow of hydrothermal brines.

Regional aquifers such as permeable sandstones are thought to be the main pathways for lateral transport of hydrothermal brines from basin centers towards the margins, with vertical fractures or faults as conduits into overlying sedimentary formations. In southern Ontario, hydrocarbon traps within the Middle Ordovician limestones of the Trenton and Black River formation occur adjacent to faults where localized dolomitization caused by hydrothermal fluids has created porous and permeable zones (e.g. Carter et al., 1996; Conglio et al., 1994; Middleton et al., 1993; Carter, 1991; Sanford et al., 1985). Away from these fractures or faults, the unaltered, impermeable limestone forms the seals for the reservoirs (Horvath et al., 2004 after Smith, 2006). This type of hydrocarbon trap is referred to as a “diagenetic” (e.g. Hickman and Kent, 2005) or hydrothermal dolomite trap (HTD) (Gartner Lee Limited, 2008b). Similar HTD hydrocarbon reservoirs occur in the Ordovician Black River Group in south-central New York, and in the Trenton-Black River groups in Ohio and Michigan (e.g. Smith, 2006; Hickman and Kent, 2005). The Cambrian sandstones underlying the Ordovician limestones of the Trenton and Black Rivier formations are thought to have facilitated transport and migration of the dolomitizing fluid to the fault and fracture systems in southern Ontario (Bailey, 2005). The Cambrian-aged Mount Simon sandstone was similarly proposed as a deep aquifer and source of dolomitizing fluid in the Trenton-Black River formations in Ohio (Hickman and Kent, 2005).

HTD traps develop where hydrothermal flow is focused and vertically directed and on a regional scale, most likely on arches at regional aquifer or seal terminations (Hickman and Kent, 2005). MVT deposits and hydrocarbon accumulations hosted in HTD reservoirs are both characterized by dolomitization, silicification and carbonate solution produced by low-temperature, hydrothermal fluids.

Figure 18 illustrates the conceptual model for these processes in which diagenetic fluids are transported from down-dip in a sedimentary basin to its margins. Hickman and Kent (2005) suggest that MVT deposits or alteration is part of a continuum with diagenetic (HTD) hydrocarbon traps; MVT deposits contain metal sulphides and minor amounts of hydrocarbons, whereas HTD reservoirs contain hydrocarbons and minor MVT type sulphide minerals.

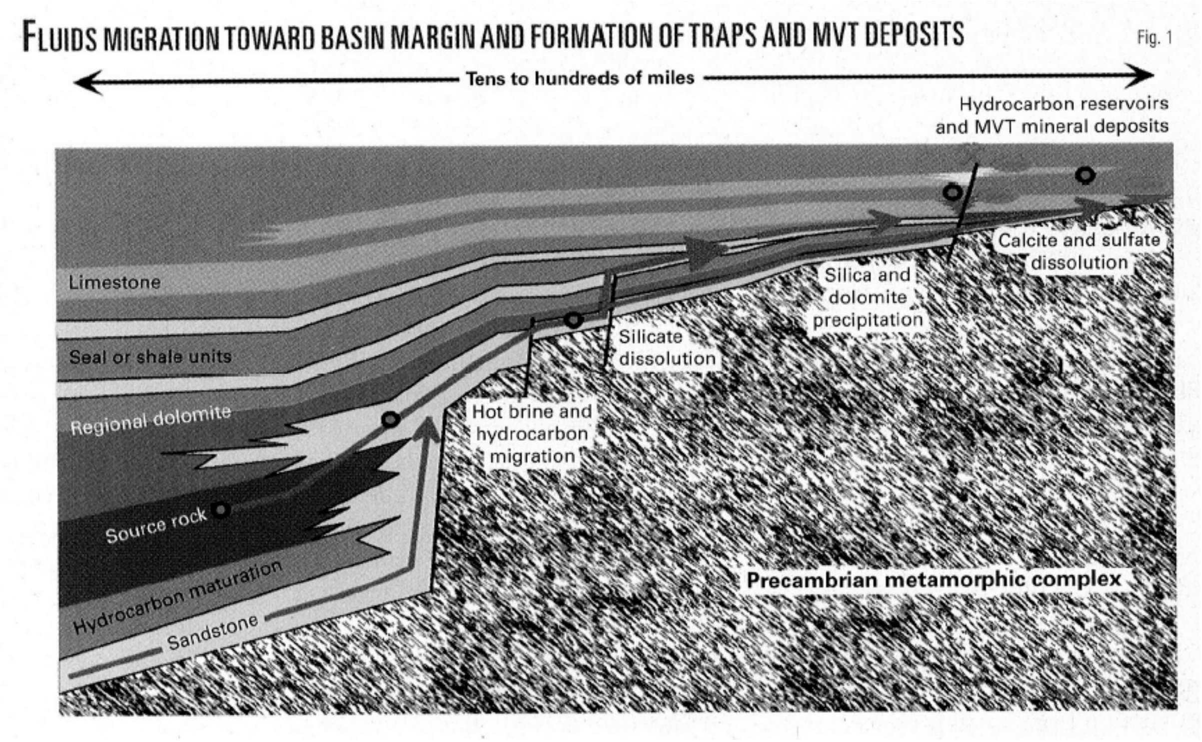


Figure 18: Schematic illustrating the lateral migration of hydrothermal brines associated with MVT ore deposits and HTD reservoirs through deep, regional aquifers towards the basin margins. From Hickman and Kent (2005).

In terms of mechanisms to drive the migration of hydrothermal brines associated with dolomitization/MVT ore deposits /hydrocarbons over tens to hundreds of kilometres within the basin, there are four main flow models which have been proposed (after Ingebritsen et al., 2006):

1. In topographically-driven flow models, regional-scale groundwater flow is initiated by major orogenic events. Groundwater recharged in uplifted orogenic belts and drives saline fluids evolved at depth in basin into shallower strata.

2. Compaction-driven flow models assume that brines are driven upward and toward margin basins by vertical loading and/or tectonic compression.

3. In thermal convection models, orogenic events enhance permeability in the crystalline basement rock underlying the sedimentary strata allowing convection cells to develop. Heat and metals are transported via these convection cells into an overlying topographically-driven flow system (e.g. Deming, 1992).

4. The newest and untested gas generation models assume that pressures developed as a result of gas generation expelled brines from deep within sedimentary basins.

Both compaction-driven flow and thermal convection have been proposed as possible mechanisms for flow of dolomitizing fluids in the Ordovician-aged rocks underlying southern Ontario. Coniglio and Williams-Jones (1992) suggested that dolomitization of the Ordovician limestones in southern Ontario may be the result of brines generated during compaction which travelled up-dip from deeper in the Michigan basin. For hydrothermal dolomitization (HTD) observed in Ontario, Congilio et al. (1994) proposed thermal convection cells were responsible for fluid flow, driven by a heat source in the Precambrian basement.

In terms of understanding the timing of fluid migration associated with these diagenetic processes, the important observation is that the main driving forces proposed for fluid flow were present during diagenesis (e.g. compaction-driven flow, gas generation) or were associated with major orogenic events (e.g. topographically-driven flow, thermal convection). In the Michigan and Applachaian basins, the most recent orogenic event was the Alleghanian Orogeny between approximately 350 and 250 Ma BP. Since approximately 250 Ma ago, passive margin conditions have been dominant in eastern North America.

5. GEOCHEMICAL DATA SETS FOR SOUTHWESTERN ONTARIO

In this study, research conducted at the University of Waterloo over a period of 25 years on the geochemical nature of waters within the sedimentary formations underlying southwestern Ontario and eastern Michigan have been combined in a single regional geochemical database. In Table 2, the formations from which waters were sampled and references to the associated research studies are given.

Table 2: Age and names of formations sampled for fluids in the studies included within this synthesis.

Age	Formations Sampled	Study
Devonian	Berea	Dollar (1988), Walter (Pers. Comm.)
	Kettle Point	Cloutier (1994); Walter (Pers. Comm.); Husain (1996)
	Antrim Shale	Martini et al. (1998)
	Hamilton	Cloutier (1994);
	Dundee	Weaver (1994); Cloutier (1994); Dollar (1988)
	Detroit River	Weaver (1994)
	Richfield	Dollar (1988)
Silurian	Salina F-salt	Dollar (1988)
	Salina A2-salt	“
	Salina A1-carbonate	“
	Guelph	“
	Niagaran	Dollar (1988); Walter (Pers. Comm.)
	Thorold-Grimsby	Dollar (1988)
	Whirlpool	Dollar (1988)
	Guelph/Lockport	Hanratty (1996)
	Goat Island, Gasport	“
	Thorhold	“
Ordovician	Blue Mountain	Sherwood Lollar and Frape (1989)
	Lindsay	“
	Veralum	“
	Bobcaygeon	“
	Gull River	“
	Shadow Lake	“
	Trenton Group	Dollar (1988)
	Prairie du Chien	Dollar (1988) ; Walter (Pers. Comm.)
Cambrian	Undifferentiated	Dollar (1988)
Precambrian	Undifferentiated	Sherwood Lollar and Frape (1989)

5.1 Classification of Waters

Numerous classification schemes have been devised to describe the characteristics of formation fluids. In Table 3, the classification scheme first proposed by Davis (1964) and then revised by Carpenter (1978) is shown. Saline waters have total dissolved solids (TDS) loads between 10,000 and 100,000 mg/L. For example, seawater which has a TDS value of approximately 35,000 mg/L, is classified as saline. Fluids with TDS values of greater than 100,000 mg/L are classified as brines.

Table 3: Classification scheme for formation fluids based the total dissolved solid load (Based on Carpenter, 1978).

Water Type	Total Dissolved Solids mg/L
Fresh	<1000
Brackish	1000 to 10,000
Saline	10,000 to 100,000
Brine	>100,000

5.2 Collection of Waters

Over 90 percent of the waters in the database were sampled from producing oil and gas wells. The remaining waters were collected from multilevel wells, or from isolated intervals using a packer system.

5.2.1 Oil and Gas Wells

Most producing oil and gas wells yield a mixture of oil, gas and brine in variable proportions. The histories of the wells obtained from the producers are used to determine the production practices applied in the past, in order to avoid wells where chemical treatments have been used (e.g., acid-wash, surfactants).

Samples from production wells normally flow under high pressure or are extracted by pumping from considerable depths. This can result in changes in temperature (cooling), depressurization, volatilization, degassing, corrosion reactions, and exchange reactions with well casing or surface storage tanks. These processes can affect both the inorganic geochemical and stable isotopic properties of the fluid. Samples taken directly from the production drill stem, which is a closed system, are higher quality than samples from storage tanks – storage tank fluid samples run the risk of having been effected by evaporation, oxidation, and degassing processes.

Ideally, formation water samples are collected down hole at the in-situ temperatures and pressures of the formation; the sampler effectively preserves these parameters when the samples are brought to the surface. However, logistical problems such as pump-jacks installed in wells, the depth of the wells, the upward flow of fluids, high formation pressures, and economic constraints, normally make it impossible to collect samples using this method. Instead, a method for sampling directly from the well head is used wherever possible; otherwise waters were collected from individual lines upon entry to collection and separation tanks. A sampling method modified from Lico et al. (1982) and Kharaka et al. (1987) is used, as illustrated in Figure 19. A sampling container (usually a nalgene bottle with a plastic bag) is connected to the well head and rapidly filled (Figure 19). The bag is filled with nitrogen, to reduce potential for sample oxidation during separation. The brine-oil mixture is allowed to separate over a period of minutes to hours by natural separation – the density difference between brine fluid/water and oil yields a two-phase sample, with the lower density oil floating on the surface of the higher density brine water. The brine water is then drained from the base of the carboy by a bottom spigot, allowing for complete separation of the brine fluid from the oil phase. The sample, which consists of the water phase, is filtered through glass wool to remove coarse oil globules, and then through a 0.45 μm filter (or small pore-size filter) to remove fine oil globules and particulate matter. The filtered water sample is split into three aliquots. One aliquot is acidified to pH <2 for cation-metal analyses using HCl or HNO_3, while the second, non-acidified aliquot is retained for anion analysis. The third aliquot is used to measure the master variables including pH, temperature, bicarbonate alkalinity and electrical conductivity in the field (e.g., Weaver 1994).

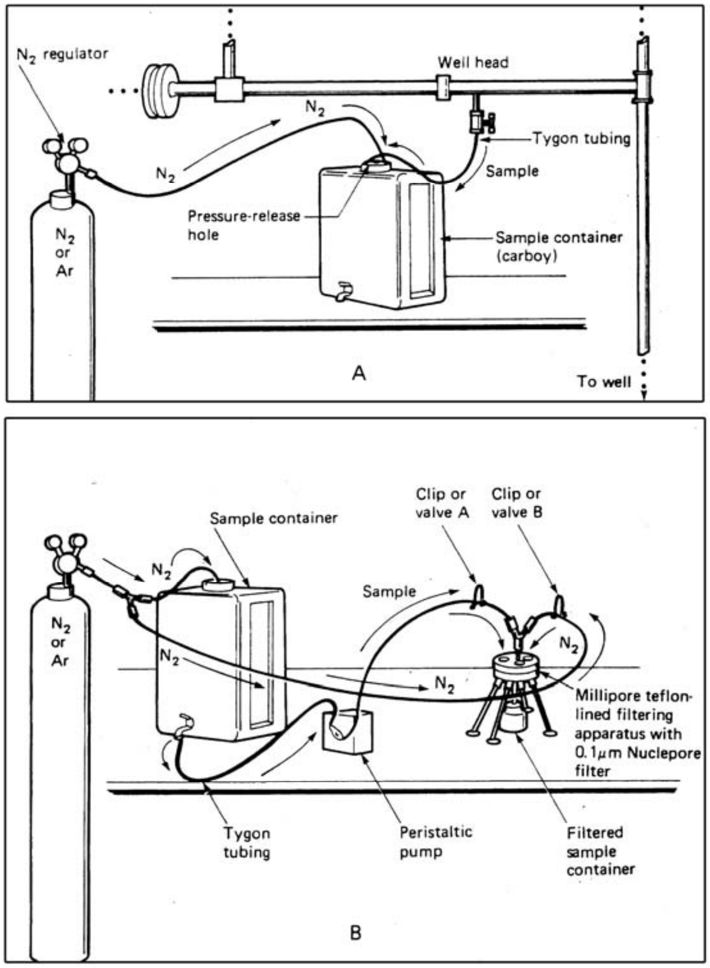


Figure 19: Sampling Procedure for Oil and Gas Wells (from Kharaka et al., 1987).

5.2.2 Groundwater Monitoring Wells

Piezometer nests were used to obtain water samples from the Devonian Kettle Point and the overlying Quanternary till (Husain et al., 2004; Husain, 1996). In two boreholes (OHD-1 and UN-2), water sampling was conducted using multi-level groundwater and pressure monitoring systems (Westbay® MP System) installed in each borehole (Jensen et al., 1987; Sherwood Lollar and Frape, 1989). Selected formation intervals are separated via packers, allowing detailed sampling of formation fluids without mixing between intervals. Samples are collected from a central closed tube via valved ports that provide access to the various packed-off monitoring zones, thus protecting sample integrity.

5.3 Analytical Methods

Water samples were analyzed for master variables including temperature and electrical conductivity in the field at surface. In situ borehole temperature (BHT) can be estimated by the equation BHT = 14.5 + 0.0192*depth (m) (Vugrinovich 1989). In addition to temperature and electrical conductivity, Weaver (1994) also reported pH values measured in the field. Alkalinity was measured in the laboratory using endpoint titration and reported as total alkalinity in mg/L HCO_3, except for Hanratty (1996) where alkalinity is reported in mg/L $CaCO_3$. The methods used to measure the major ions for waters sampled from each study are given in Table 4. The only study which provided error estimations was Sherwood Lollar and Frape (1989), where the uncertainty in the values of major ions was reported to be ± 5%. On the basis that the analyses of major ions were performed at the Water Quality Laboratory at University of Waterloo for all studies (with the exception of waters sampled from the study by Hanratty (1996), which were determined by Barringer Laboratories for Golder Associates Ltd. (Golder Associates Ltd., 1990; 1988, after Hanratty, 1996), a standard deviation of ± 5% is also estimated for analytical results from the other studies.

Table 4: Methods used to measure major ion concentrations in the various studies included in the current synthesis (AAS = Atomic Adsorption Spectrometry; IC = Ion Chromatography; ICP-AES = inductively coupled plasma-atomic emission spectrometry; NA = Not Available).

Study	Method	
	Cations	Anions
Cloutier (1994).	AAS	IC
Dollar (1988)	AAS	IC
Hanratty (1996)	NA	NA
Husain (1996)	AAS	IC
Sherwood Lollar & Frape (1989)	AAS	IC
Weaver (1994)	AAS	IC, Si by AAS
Walter (Pers. Comm.)	NA	NA

The methods used to measure the isotopic signatures of fluids sampled in each study are listed in Table 5. The analytical uncertainties in the measured isotopic values reported in the database are reported in Table 6. Stable chlorine, oxygen, hydrogen isotopes and tritium were analyzed at the University of Waterloo; Details on the analytical procedures are provided in Appendix A. Strontium isotopic analyses ($^{87}Sr/^{86}Sr$) were measured on a VG-354 mass spectrometer, following separation by standard ion-exchange techniques at McMaster University, Hamilton, Ontario.

Table 5: Analytical methods applied for isotopic analyses of waters from each study (NA = not available; NM = not measured).

Study	$\delta^{18}O$	$\delta^{2}H$	^{3}H	$^{87/86}Sr$	$\delta^{37}Cl$
Cloutier (1994)	T.P. 13	T.P. 4	Distilled	NM	T.P.27
Dollar (1988)	CO_2Eq	Distilled	Distilled	MS + Ion exchange	E1
Hanratty (1996)	T.P. 13	T.P. 4	T.P. 1	NM	T.P.27
Husain (1996)	T.P. 13	T.P. 4	Distilled	NM	T.P.27
Martini et al. (1998)	CO_2Eq	Zn-Red	NM	MS + Ion exchange	T.P.27
Sherwood Lollar & Frape (1989)	CO_2Eq	Distilled	Distilled	NM	E1
Weaver (1994)	W1	W1	W2	NM	T.P.27
Walter (Pers. Comm.)	NA	NA	NA		T.P.27

Codes: AAS = Atomic Adsorption Spectroscopy; IC = Ion Chromatography; T.P. = Technical Procedure, as described in Appendix A; Zn-Red = Zinc reduction method of Venneman and O'Neil, 1993). E1 = Eggenkamp (1994); W1 = Fritz et al. (1986); W2 = Taylor (1977); W3 = Yanagisawa and Sakai (1983); W4 = Sakai and Krouse (1971).

Table 6: Analytical uncertainty in major ion and stable isotopic analyses for formation waters included in the database (NM = Not measured; UN = Unknown)

Study	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	^{3}H (TU)	$^{87/86}Sr$ (%)	$\delta^{37}Cl$ (‰)
Cloutier (1994)	± 0.2 ‰	± 2.0 ‰	± 0.8	NM	± 0.2
Dollar (1988)	± 0.15	± 2.5	NM	± 0.003	± 0.2
Hanratty (1996)	0.0005%	0.0005%	± 0.8	NM	NM
Husain (1996)	± 0.2 ‰	± 2.0 ‰	± 0.8	NM	NM
Sherwood Lollar & Frape (1989)	± 0.15	± 2.5	± 0.8	NM	± 0.2
Weaver (1994)	± 0.20	± 2.0	± 0.8	± 0.003	± 0.2
Walter (Pers. Comm., 1990)	UN	UN	UN	UN	± 0.2

In several cases, the analyses of major ions (Cloutier, 1994), oxygen and hydrogen (Cloutier, 1994), chlorine stable isotopes (e.g., Dollar, 1988; Weaver, 1994) or strontium isotopes (e.g., Weaver 1994) were analyzed on archived samples after the original study was completed, and are therefore not reported in the original references.

5.4 QA/QC of the Database

5.4.1 Traceability of Data

Data as reported in the original studies (Cloutier, 1994; Dollar, 1988; Hanratty, 1996; Husain, 1996; Sherwood Lollar & Frape, 1989; Weaver, 1994 and Walter (Pers. Comm.)) were compiled in Microsoft Excel, and then checked to confirm that all values included were consistent with the original references. The sampling methods and sample quality are also included in the database (Appendix B). For samples where additional analyses were conducted on archived samples after completion of the original study, the results were checked against the analytical results reported by the laboratory, when available.

The sample number in the database refers to that reported in the original data source, such that the data are directly traceable to the original reference. The only exceptions are the data from Walter (Pers. Comm., 1990) and from Hanratty (1996). In Hanratty (1996), chemical compositions were reported for 3 to 4 water samples taken from a given sampling interval on different dates (Table 2 in Hanratty, 1996). For these samples, an average chemical composition for that interval was calculated by averaging the ion concentrations measured for the water samples taken on different dates. These average ion concentrations are reported in the database (Appendix B). For the stable water isotopes ($\delta^{18}O$, $\delta^{2}H$) and for tritium, only one value was reported for each interval by Hanratty (1996). These values are reported directly in the database (Appendix B), as they appeared in the original reference.

In the original references, variability in the number of significant figures was observed. In the database (Appendix B), the number of significant figures reported for each parameter was corrected to be consistent with the reported analytical uncertainty in the measurement (Mazor, 1991).

5.4.2 Data Selection

The scope of the current study was limited to a synthesis of the available data on the geochemistry of groundwaters where they occur in bedrock formations in southwestern Ontario, Canada, eastern Michigan and central Michigan, U.S.A as determined by researchers at the University of Waterloo. Several of the theses also include chemical and isotopic information on waters sampled in Quaternary aquifers and aquitards (Cloutier, 1994; Husain, 1996); these waters are outside the scope of the current study and have not been included in the geochemical database.

Tritium data included in Dollar (1988) and also reported in Sherwood Lollar and Frape (1989) were excluded in the Ontario Geological Survey Open File Report published by Dollar et al. (1991). The tritium analyses reported by Dollar (1988) were measured at the Environmental Isotope Laboratory, University of Waterloo. At the time the sample measurements were made, a high temperature distillation method was used to separate the water phase from the solutes. The technique required temperatures of up to 300 °C to remove residual water and hydrated waters from minerals remaining in the boiling chamber. It was later discovered that in brines, the high temperatures used in distillation resulted in the transfer of salts to the distilled water chamber, causing interferences in the measured tritium values (Drimmie, Pers. Comm., 2008). The tritium numbers originally reported by Dollar (1988) are therefore not representative of tritium concentrations in groundwater and consequently, were not included in Dollar et al. (1991) or in the geochemical database.

Isotopic analyses for dissolved sulphate ($\delta^{18}O$, $\delta^{34}S$), and $\delta^{34}S$ for H_2S from Weaver (1994) and later published in Weaver et al. (1995) are not included in the current database, because this was the only study in which these parameters were measured. The well names reported in Weaver et al. (1995) are the same as those originally reported in Weaver (1994) and have been retained as sample identification codes in the regional geochemical database (Appendix B), to ensure that data is traceable between these references.

Trace element concentrations reported in Hanratty (1996) are not included in the database because this was the only thesis referenced which included information on trace elements. Only data on isotopic compositions (oxygen, deuterium and tritium) and major ion compositions reported in Table 2 of Hanratty (1996) have been included in the database, as described in section 5.4.1.

5.4.3 Culling Criteria for Data

In studies which involved the sampling of oil and gas wells, including Dollar (1988) and Weaver (1994), selected culling criteria as described by Hitchon and Brulotte (1994) were considered to determine whether or not the sampled formation waters should be included in the database. For example, both Dollar (1988) and Weaver (1994) reported the quality of the formation waters assessed based on the production or sampling method. Samples identified as suspect in the two studies have not been included in the current geochemical database.

The chemical composition (cation and anion concentrations) of each sample in the database was used to determine the charge balance of the samples:

$$\text{Charge balance} = (\text{cations} - \text{anions}) / (\text{cations} + \text{anions})$$

In this calculation, cation and anion concentrations are expressed in millequivalents (meq = concentration in mg/L x charge of the ion). The majority of the 202 samples included in the database had charge imbalances of <5%; 20 had charge imbalances >5%, and 3 had charge balances of >10%. The highest calculated charge imbalance was 12.4%. Therefore, all samples included in the database had charge imbalances which were lower than the 15% recommended by Hitchon and Brulotte (1994) as a rejection criteria for formation water analyses.

5.4.4 Other Considerations

The investigations summarized as part of this study were originally undertaken to explore the geochemical nature of fluids within the Michigan Basin and Appalachian Basins in southwestern Ontario. As a result of precautions taken during the selection of wells for sampling and during sample collection (section 5.2.1), the samples included in the geochemical database provide representative groundwater compositions for the formations or reservoirs sampled. However, given the original intent of the research, there are several limitations of the current database in terms of the spatial distribution of the information available and its use in geochemical modelling or three-dimensional visualizations of the data:

- Waters sampled are primarily brines associated with producing oil and gas wells. Careful selection of wells for sampling based on production history has resulted in a high quality database. However, the distribution of data regionally is limited to those areas where sampling of producing hydrocarbon wells could be arranged. The majority of the waters in the database were collected in the most southwestern areas of Ontario, where oil and gas wells are most abundant. A more comprehensive regional hydrogeochemical assessment would require access to sampling locations (piezometers, deep boreholes, or producing oil and gas wells) to the north and east in Ontario.
- At the time that many of the waters were sampled, measurement of the master variables including pH, Eh, temperature etc. were not routinely measured on brines, in part because accurate pH measurements were difficult to obtain in brines given the technology available at the time. In addition, geochemical modelling of groundwaters was just beginning. Although geochemical modelling of brines is still evolving and many challenges remain, more recent tools such as PHREEQC (Parkhurst and Appelo, 1999) are now more readily available for modelling these highly concentrated fluids. In this light, any future sampling campaigns should include measurement of all these master variables.
- No information on hydraulic pressures is available at the depths from which the samples were taken. Ideally, a comprehensive regional hydrogeochemical assessment for the Michigan and Appalachian Basins, such as that conducted by Rostron et al. (1997) in the Alberta Basin would include measurement of the hydraulic parameters, as well as geochemical parameters.
- In order for these data to be incorporated into three-dimensional scientific visualization software, the locations of the wells (latitudes and longitudes), the sampling depths, as well as the elevation of the top collar of the boreholes are required for accurate representation.

6. RESULTS

The geochemical database including chemical and isotopic compositions for 202 waters sampled from the eastern margin of the Michigan Basin (southwestern Ontario), the central Michigan Basin (Michigan), and the western margin of the Appalachian Basin (Lake Erie) is presented in Appendix B.

Water samples were collected at various depths ranging from near surface to almost 4 km. A large variation in TDS is observed for the waters, with TDS values ranging from less than 1,000 mg/L to more than 400,000 mg/L. Applying the classification scheme developed by Carpenter (1978; section 5.1), 67% of the waters are brines, 20% are saline and 10% are brackish. Only 3% of the waters in the database are classified as fresh waters.

The TDS values of waters are plotted as a function of sampling depth in Figure 20 for those waters where the depth of sampling was known. Most formation waters have high TDS values of between 140,000 and 400,000 mg/L. The highest salinity formation water reported from the Michigan Basin is a Ca-Na-Cl-type brine sampled from the Salina Formation of the Michigan Basin with TDS values of 643 000 mg/L (Case, 1945). In the current database, the most saline formation waters (TDS ≈ 400,000 mg/L) are also Ca-Na-Cl-type waters, sampled in central Michigan from the Silurian carbonates of the Niagaran Formation at depths between 1200 and 1400 m and from Ordovician sandstones of the Prairie du Chien formation at depths of greater than 3200 m. Three formation waters from Ordovician-aged carbonates sampled at depths of 200 m or less have TDS values ranging from 44,000 to 100,000 mg/L. Waters from Devonian carbonate formations and some Silurian carbonate formations sampled at depths of 300 m or less have TDS values below 20,000 mg/L.

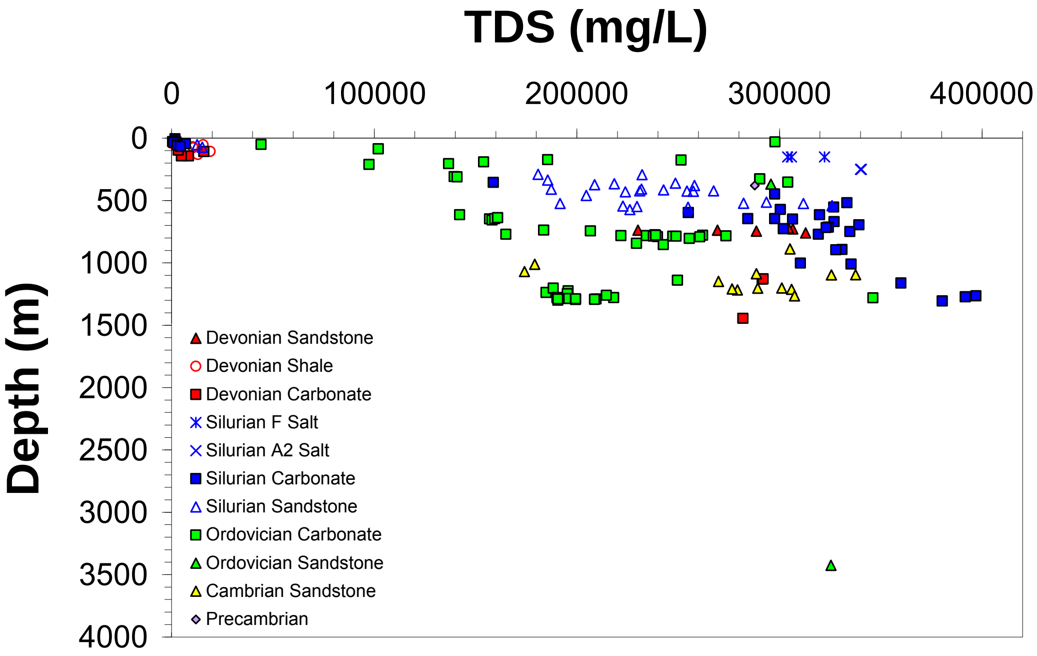


Figure 20: Total Dissolved Solids measured in formation waters from southwestern Ontario plotted as a function of sampling depth (only samples with depth information are included. See also Appendix B). The majority of waters are brines having TDS values of between 150,000 and 400,000 mg/L.

6.1 Chemical Composition

The chemical compositions of the waters (Appendix B) from different formations have been classified into water-types based on the concentrations of major cations and anions, expressed in meq/L (Table 7). For example, in a Na-Ca-Cl type water, sodium and calcium are the principal cations, with Na occurring at the highest concentration and chloride is the dominant anion. However, in several waters containing both Na and Ca as major ions, the difference in the concentrations of these two cations (meq/L) was less than 10%, and therefore, the order of the cations is likely not significant. This includes several waters sampled from the Berea Formation (sample numbers MB-1, Brennan, Campbell #7, Campbell #9, and James 122), the Guelph (SG-13), the Grimsby-Thorhold (STGr-9, -14), the Trenton-Black River (OT-7, -11 and -12), from the Veralum, Bobcaygeon and Gull River formations in the UN-2 borehole (UN-2 #11, #5, #4, and #2), and from the Cambrian sandstone (C-11).

Waters sampled from Devonian and Silurian-aged formations at depths of up to 150 m below ground surface are generally Na-Cl-type waters with TDS values between 640 and 25,200 mg/L. However, there are several exceptions:

- Ca-SO_4-type waters reported by Hanratty (1996) in the Silurian-aged Guelph, Lockport or Goat Island formations sampled at depths of between 5 and 65 m in the Hamilton region of southwestern Ontario and have TDS values ranging from 480 to 15,100 mg/L.

- Na-Ca-Mg-Cl-type waters sampled from the Detroit River Group at depths of between 100 and 120 m in Lambton County, Ontario (Weaver 1994) have TDS values ranging from 13,150 to 48,700 mg/L. In these waters, the concentrations (expressed in meq/L) of calcium and magnesium are similar.

- Ca-Na-Cl type waters from Ordovician-aged formations sampled at depths between 30 and 370 m at Lakeview and Darlington, Ontario (Sherwood Lollar and Frape, 1989) have TDS values between 44,100 and 305,000 mg/L. These are distinct from the Na-Ca-Cl type waters sampled from producing hydrocarbon wells within the same formations (Trenton-Black River Group) at locations across southwestern Ontario and in eastern Michigan (Dollar, 1988; Dollar et al., 1991).

At greater depths in the bedrock formations (>150 m), waters sampled from the Devonian-aged Berea Formation and the Devonian-aged Dundee Formation in Central Michigan, from the Silurian-aged Grimsby-Thorhold formations and from the Ordovician-aged Trenton-Black River formations are predominantly Na-Ca-Cl type waters, with TDS values between 141,000 and 380,000 mg/L. The exceptions are several samples from the Silurian-aged Grimsby Sandstone (SGr-18, -19, -20 and -21) sampled at the eastern-end of Lake Erie, which are Ca-Na-Cl-type waters (TDS ranges from 181,000 to 219,000 mg/L). Waters sampled in close proximity from the Whirlpool Formation (SW-1 through SW-4) are also Ca-Na-Cl type waters. In the Silurian-aged Guelph and Whirlpool formations and in the Cambrian-aged sandstone formations, the waters sampled are Ca-Na-Cl-type waters, with the exception of five (5) samples (SG-1, -2, -3, -5 and -12) sampled from the Guelph Formation and one sample (C-6) from the Cambrian-aged formations, which are Na-Ca-Cl-type waters.

Table 7: Types of Waters Sampled from Different Formations Within the Database, Based on Dominant Ion Concentrations Expressed in meq/L.

Age	Formation	Rock Type	Depth/ Range (m)	Water Type	Exceptions	TDS (mg/L)
Devonian	Berea	Sandstone	720-760 m**	Na-Ca-Cl	Campbell #7 & 9 (Ca-Na-Cl)	176,000 to 380,000
	Kettle Point	Shale	40-50	Na-Cl-HCO$_3$	LD-90-3-5 (Na-Cl)	640 to 15,500
	Hamilton	Shale	65-130	Na-Cl	-	7,500 to 19,100
	Antrim	Shale	Not Known	Na-Cl	-	123,000 to 241,000
	Dundee	Carbonate	100-140	Na-Mg-Ca-Cl	LD-90-3-1 (Na-SO$_4$-Cl); DD-2 (Ca-Na-Cl) DD-1, DOW-90-3-1 (Na-Cl) PD-COCH (Na-Ca-Mg-Cl) RA-NE, RA-SE, RA-SW (Na-Ca-Cl)	3,300 to 25,200
		Carbonate	1130	Na-Ca-Cl		292,000
	Detroit River	Carbonate	100-120	Na-Ca-Mg-Cl	CFN-C, CFS-D, LBO-2 (Na-Mg-Ca-Cl)	13,150 to 48,700
	Richfield	Carbonate	1445	Ca-Na-Cl	-	282,000
Silurian	Salina F	Salt	150	Na-Cl	-	305,000 to 322,000
	Salina A2	Salt	250	Ca-Na-Mg-Cl	-	340,000
	Salina A1	Carbonate	650	Ca-Na-Cl	-	284,000 to 306,000
	Guelph	Carbonate	355-770	Ca-Na-Cl	SG-1, -2, -3, -5 & -12 (Na-Ca-Cl)	159,000 to 335,000
	Guelph/Lockport/ Goat Island	Carbonate	5-65	Ca-Mg-SO$_4$	87-2-2 (Na-Ca-Cl); 87-1-2, 87-2-3 (Ca-Na-Mg-SO$_4$-Cl); 88-1-5 (Ca-Mg-HCO$_3$)	480 to 15,100
	Niagaran	Carbonate	715-1305	Ca-Na-Cl	Cold Springs WH1-29; SN-6 (Ca-Cl); SN-3, SN-4 (Ca-Mg-Cl)	310,000 to 397,000
	Grimsby/Thorhold	Sandstone	290-570	Na-Ca-Cl	SGr-18,-19, -20 & -21 (Ca-Na-Cl)	181,000 to 326,000
	Thorhold	Sandstone	55-75	Na-Ca-Cl	-	12,600 to 15,200
	Whirlpool	Sandstone	360-460	Ca-Na-Cl	-	205,000 to 268,000
Ordovician	Blue Mountain	Carbonate	173	Ca-Na-Cl	-	186,000
	Trenton: Lindsay	Carbonate	50 200	Na-Ca-Cl Ca-Na-Cl	-	44,100 to 137,000
	Trenton: Veralum	Carbonate	85	Na-Ca-Cl	-	102,000
	Trenton: Bobcaygeon	Carbonate	30-325	Ca-Na-Cl	UN-2 #5 (Ca-Na-Mg-Cl)	251,000 to 298,000
	Black River: Gull River	Carbonate	190-350	Ca-Na-Cl	-	97,000 to 304,000
	Black-River: Shadow Lake	Sandstone	370	Ca-Na-Cl	-	154,000
	Trenton-Black River (undifferentiated)	Carbonate	310 to 1300	Na-Ca-Cl	OT-30 (Ca-Na-Cl)	141,000 to 346,000
	Prairie du Chien	Sandstone	3234 or 3425	Ca-Cl	Depth unknown for 3 samples Foster 1-21, OP-1 (Ca-Na-Cl)	325,000 to 392,000
Cambrian	(undifferentiated)	Sandstone	890-1265	Ca-Na-Cl	C-6 (Na-Ca-Cl)	174,000 to 338,000

*Note: **Depth unknown for 7 samples*

6.1.1 pH and Redox Conditions

Weaver et al. (1994) reported pH values measured in the field for formation waters sampled in both the Dundee and Detroit River formations at the eastern rim of the Michigan Basin in southwestern Ontario. The pH values of waters from the Dundee Formation ranged from 6.35 to 7.05 (based on 31 samples), and ranged from 5.95 to 7.05 for waters sampled from the Detroit River Formation (based on 12 samples). Wilson and Long (1993a) report pH values between 3.5 and 6.2 for waters sampled from the Dundee Formation in the central part of the Michigan Basin (based on 26 samples), and pH values of 3.9 and 4.9 for two samples from the Detroit River Formation.

Redox conditions in groundwaters are generally defined in terms of the principal redox couples that control the oxidation state at a given depth (e.g., Fe^{2+}/Fe^{3+}; S^{2-}/SO_4^{2-}; CO_2/CH_4). Constraining the dominant redox couple requires measurement of reduction-oxidation potential (Eh) or measured concentrations of the dominant redox species in solution. Information on dissolved gases, stable carbon or sulphur isotope ratios and/or information the distribution of redox-sensitive minerals can also be used to constrain the redox conditions. Although this type of information is not available for most the waters within the geochemical database, the presence of methane gas in oil and gas wells from southwestern Ontario as reported by Barker and Pollak (1984) and Sherwood Lollar et al. (1994) may provide indirect evidence that the redox conditions in waters from the producing formations are reducing. However, an understanding of the redox conditions in these waters would also need to encompass the observation that many of the brines in the geochemical database contain dissolved SO_4^{2-}, which is an oxidized species. A potential source of sulphate in groundwater is the dissolution of soluble salts such as anhydrite and gypsum (e.g. Chapelle, 1992; Apello and Postma, 1994). Under reducing conditions, sulphate concentrations in groundwaters are normally reduced by bacterially-catalyzed reduction of sulphate by organic matter to form hydrogen sulphide (e.g. Apello and Postma, 1994). If the redox conditions within the reservoirs are reducing, it may be that sulphate persists because waters with high salinities (> 200,000 mg/L) such as those sampled in southwestern Ontario cannot sustain populations of sulphate-reducing bacteria.

6.1.2 Major Ions and Stable Water Isotopes (δ^{18}O and δ^{2}H)

6.1.2.1 Regional Geochemical Database

Figure 21 illustrates the Cl and Br concentrations (mg/L) measured for all waters in the database. The Cl and Br concentrations expected for present-day seawater during evaporation are also shown (McCaffery et al., 1987). The similarity in the trend in Cl and Br concentrations for the highest salinity waters (with Br concentrations of over 1,000 mg/L and Cl concentrations in excess of 10,000 mg/L) suggests that these waters may have evolved from seawater by evaporation. As evaporation of seawater proceeds beyond halite saturation, Cl is removed from solution as halite (NaCl) precipitates. Because the Br is not incorporated proportionally into the halite crystal structure, a larger amount of Br remains in the residual solution, resulting in an increase in Br relative to Cl (see also section 3.1.1). Other processes which can alter the Cl/Br ratios include i) incongruent dissolution of Na-K-Ng-Cl mineral assemblages during burial, which may result in Br/Cl ratios in excess of those expected for evaporated seawater (e.g. Hanor, 1987; Land et al., 1995); and ii) introduction of Br from organic compounds (Land and Prezbindowski, 1981).

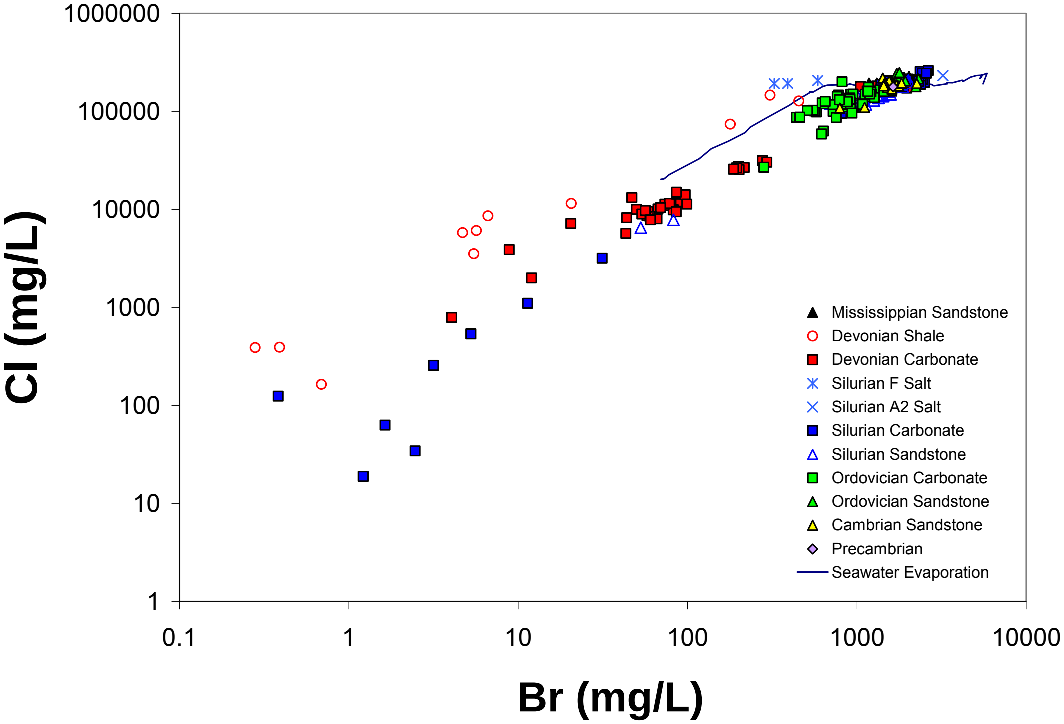


Figure 21: Chloride versus bromide concentrations measured for all water samples in the regional geochemical database. Increases during the evaporation of present-day seawater are also shown (data from McCaffrey et al., 1987).

The trends in sodium concentrations relative to bromide (Figure 22) are similar to those observed for chloride. The concentrations of calcium, magnesium, potassium and strontium are plotted versus bromide in Figure 23. The expected concentrations of these ions during the evaporation of present-day seawater are also shown (McCaffery et al., 1987). The concentrations of calcium are much higher than those expected as a result of the evaporation of present-day seawater. In sedimentary basins, the enrichment of calcium relative to Na in formation waters is most often attributed to geologically long intervals of water-rock interaction in the subsurface (section 3.1.1.1). Specific reactions which can lead to increased Ca include dissolution of evaporite minerals such as anhydrite or gypsum, dolomitization and albitization. The potential influence of water-rock interactions on the chemical compositions of the waters in the geochemical database are discussed further in section 6.1.3.

In Figure 24, the stable isotopic compositions (δ^{18}O versus δ^{2}H) for all waters are shown. The isotopic signatures of the majority of waters are typical of sedimentary basin brines in that they are enriched in ^{18}O relative to modern day meteoric water, plotting to the right of the Global Meteoric Water Line (GMWL). This enrichment could be the result of extensive water-rock interaction or evaporation of seawater, as discussed in section 3.1.1.2. However, many waters sampled from within the Devonian-aged shale and carbonate formations and several sampled from Silurian-aged carbonate and sandstone formations have isotopic signatures which are similar to modern day meteoric waters, falling on or close to the GMWL in Figure 24.

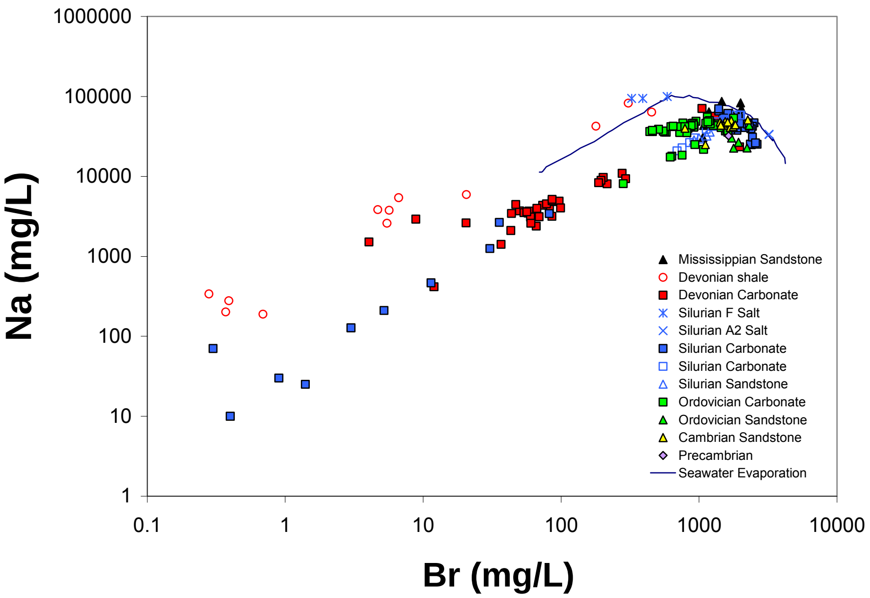


Figure 22: Sodium versus bromide concentrations of the formation waters in (mg/L). Increases during the evaporation of present-day seawater are also shown (data from McCaffrey et al., 1987).

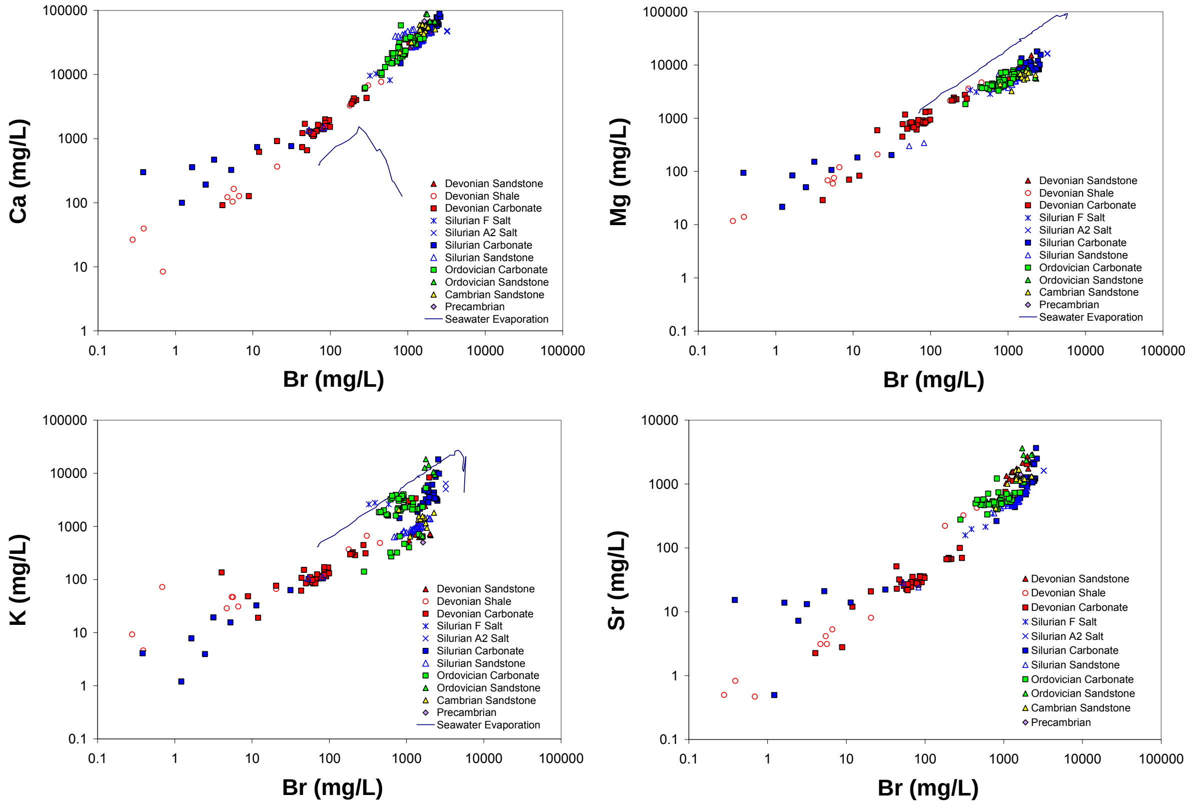


Figure 23: Concentrations of calcium, magnesium, potassium and strontium in waters plotted as a function of bromide concentrations. The expected concentrations of the cations (with the exception of Sr) during the evaporation of present-day seawater are also shown (data from McCaffery et al., 1987).

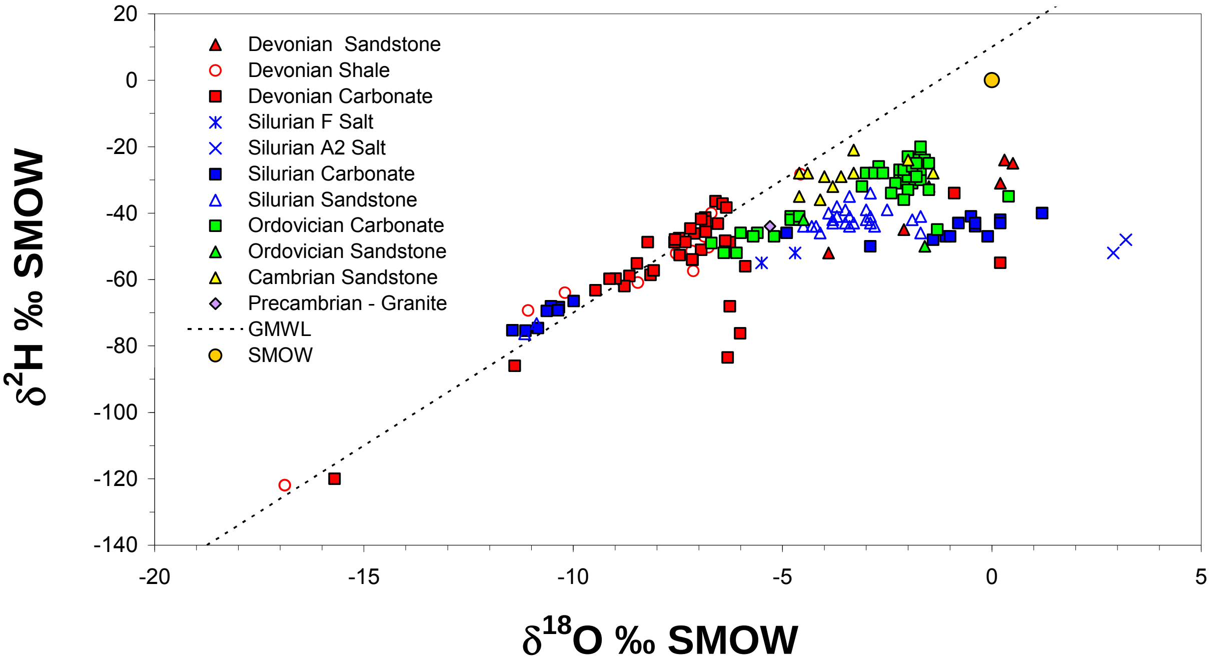


Figure 24: Hydrogen versus oxygen isotopic signatures for all waters within the geochemical database. The Global Meteoric Water Line (dashed line) and modern day seawater (SMOW) are also shown.

In Figure 25, only the most concentrated waters classified as brines (>100,000 mg/L) are shown, including those from Devonian, Ordovician, and Cambrian formations and most waters from Silurian formations. A curve showing the evolution of the δ^{18}O and δ^2H signatures during seawater evaporation (after Holser, 1979) is also shown in Figure 25. The dashed line extrapolated from 10x to 45x evaporation is from Knauth and Beenaus (1986), and is based on an incomplete dataset.

Grouping or "clustering" of the isotopic signatures is observed for waters from within the same producing interval (e.g., from within Ordovician-aged carbonates, Silurian-aged sandstones versus Silurian-aged carbonates) in Figure 25. Some overlap is observed between the isotopic signatures of waters from the Cambrian sandstones and Ordovician carbonates. Detailed discussion of the stable water isotopic signatures observed for each of these groups is presented in the following sections.

6.1.2.2 Devonian

The majority of waters from Devonian-aged shales and carbonates were sampled on the eastern margin of the Michigan Basin, in southwestern Ontario (Figure 5). The exceptions are waters from the Antrim shale and waters from the Berea Formation sandstone, which are from central Michigan (Martini et al., 1998; Walter, Pers Comm. 1990).

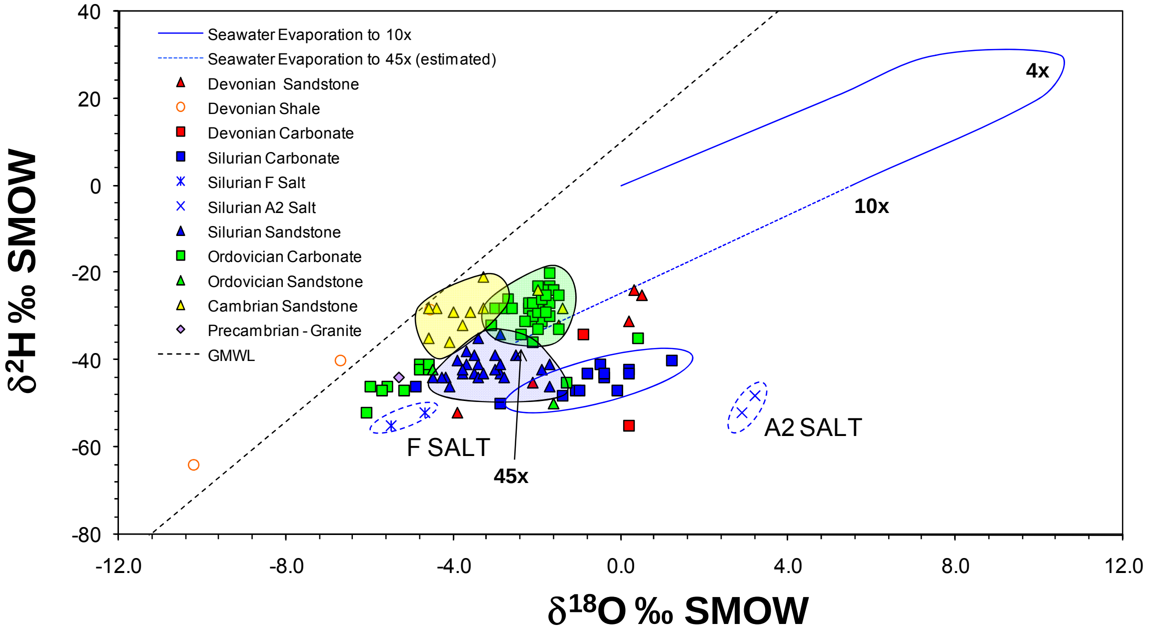


Figure 25: Isotopic signatures of hydrogen and oxygen for brines (>100,000 mg/L TDS) from southwestern Ontario. A clustering of the isotopic signatures is observed for the brines; particularly for brines from Cambrian sandstones, Ordovician carbonates and Silurian-aged sandstones. The evolution of $\delta^{18}O$ and $\delta^{2}H$ during seawater evaporation are also shown (to 10x after Holser, 1979; extrapolation to 45x from Knauth and Beeunas, 1986).

The relationship between Cl and Br for waters sampled from Devonian-aged formations is shown in Figure 26. Waters sampled from the Berea sandstone formation at a depth of approximately 750 m (MB-1 to -6) and from the Dundee and Richfield carbonate formations at depths between 1,130 and 1,145 m in central Michigan (samples DD-3, DD-4 and DR-1) plot on or close to the seawater evaporation curve, suggesting that these waters evolved from seawater by evaporation past halite saturation. Waters from these same formations sampled on the eastern margin of the Michigan Basin in Ontario at depths between 40 and 140 m below ground surface contain lower concentrations of both Cl and Br (e.g. DD-2, LD-90-3-1, WB-2, DOW-90-3-1). Waters sampled from the Detroit River Formation (including CFS-A,-B,-C, -D, CFN-E and CFN-161) are more concentrated than present day seawater (circled in Figure 26), whereas the remaining waters sampled from the Detroit River and Dundee formations have Cl and Br concentrations lower than modern seawater.

Mass balance calculations were used to predict the Cl and Br concentrations expected when varying proportions of concentrated brine from the Dundee Formation (DD-4) is mixed with meteoric water or seawater. The composition of water from a shallow aquifer (R-AQ1 from Weaver et al., 1995) was used as the meteoric end-member water. The resulting mixing trends are also shown in Figure 26, and demonstrate that the majority of waters sampled from Devonian-aged carbonates could be derived from a brine with a composition similar to that of DD-4 by mixing with meteoric water. The exceptions are three samples from the Devonian carbonates (WB-2, DOW-90-3-1, and LD-90-3-1), which have Cl concentrations which are higher relative to Br than predicted by dilution. All water samples from the Devonian-aged shales also show this trend, with high Cl concentrations relative to Br.

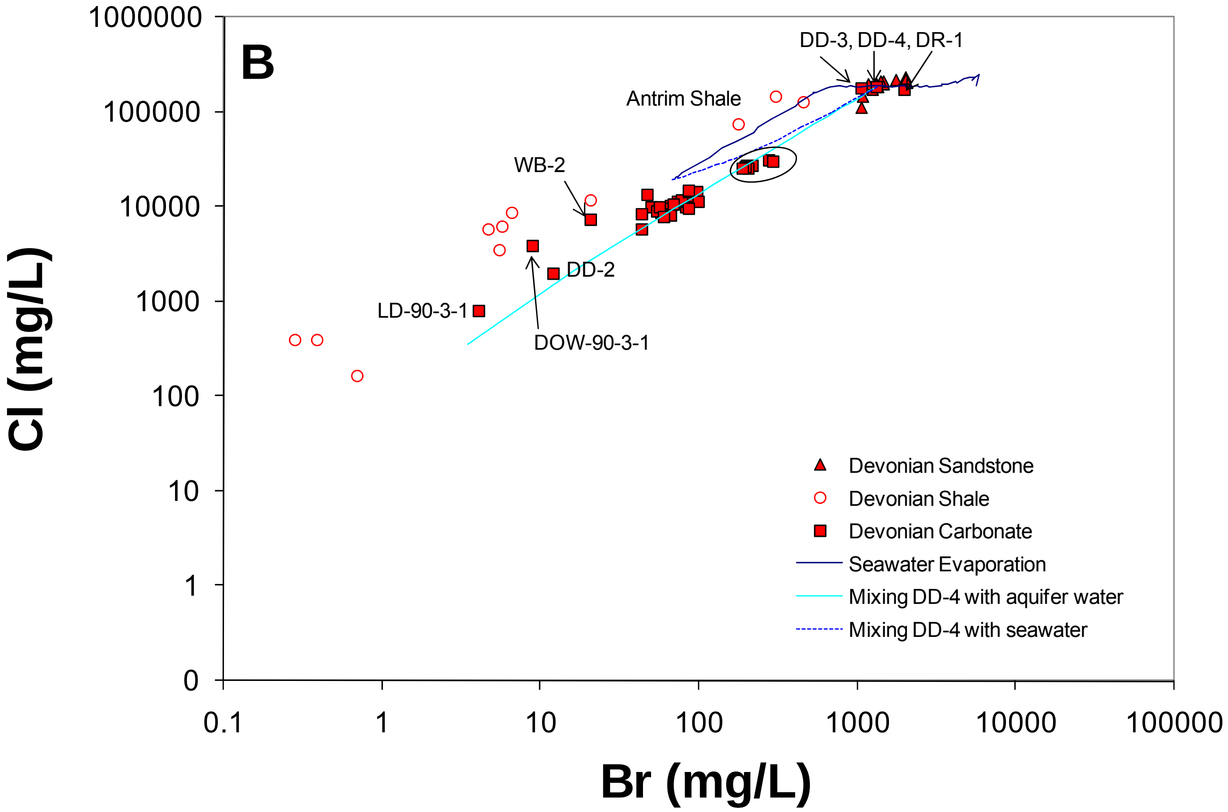
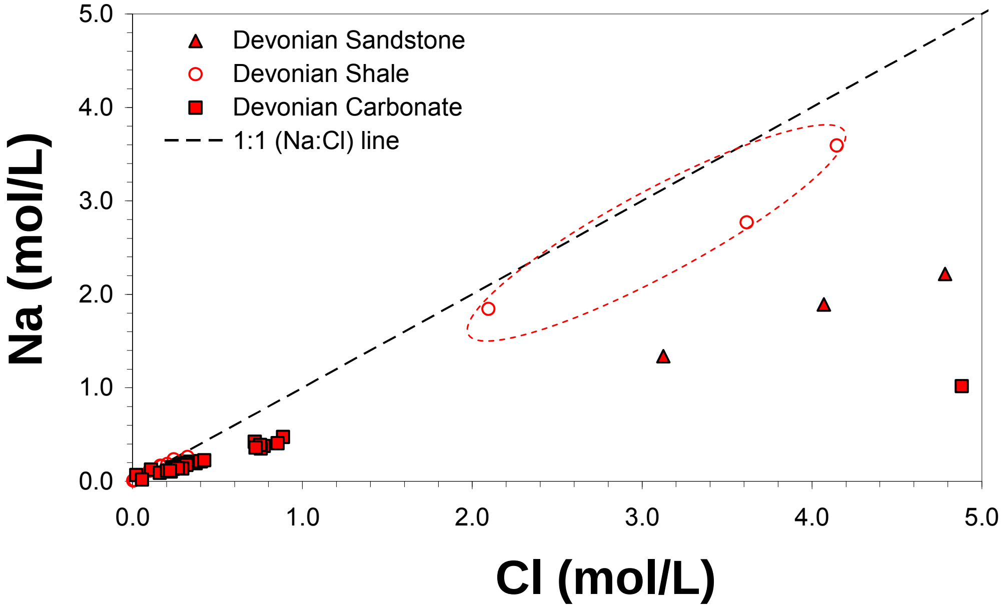


Figure 26: Relationship between chloride and bromide concentrations for waters sampled from Devonian-aged shale and carbonate formations. The light blue mixing line was calculated using DD-4 and meteoric water (aquifer water R-AQ1 from Weaver et al., 1995) as end members. Circled samples are CFS-A,-B,-C, -D, CFN-E and CFN-161 from the Detroit River Formation that are more concentrated than seawater.

In order to evaluate the extent of interaction of waters from Devonian-aged formations with halite, Na concentrations in the waters are plotted versus Cl concentrations, expressed in moles/L in Figure 27. When halite (NaCl) dissolves, Na and Cl are released in a 1:1 molar ratio (dashed line in Figure 27). In Figure 27A, the circled samples are from the Antrim Shale in central Michigan (HGR D4-6, SP A2-32 and WSMC2-10), and have Na and Cl concentrations which are just below the 1:1 ratio expected for halite dissolution. In Figure 27B, waters with Na and Cl concentrations lower than 0.5 mol/L are shown. Samples with a molar ratio of close to Na:Cl of 1:1 are from the Devonian-aged Kettle Point and Hamilton shales. Two samples from the Devonian-aged carbonates (DOW-90-3-1 and LD-90-3-1) sampled at depths of 140 m below ground surface in Lambton county (Cloutier, 1994), also have Na:Cl ratios close to 1:1 suggesting that Na and Cl in these waters can be attributed to the dissolution of halite.

A)



B)

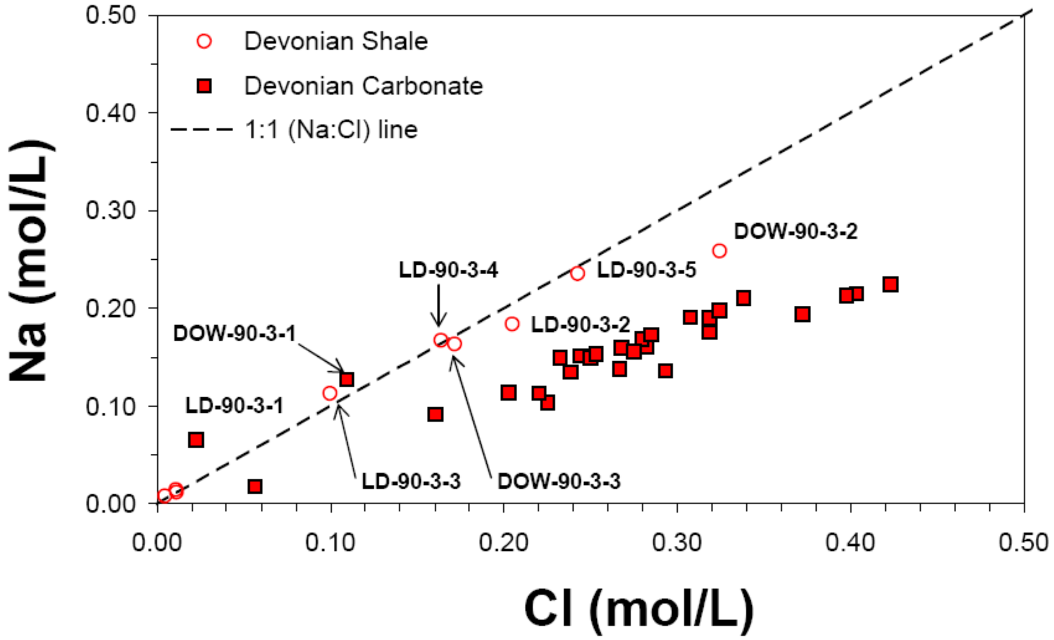


Figure 27: A) Sodium versus chloride concentrations in moles/L for waters from Devonian-aged formations. The 1:1 Na:Cl line shows the predicted Na concentrations in mol/L expected for a given chloride concentration assuming congruent dissolution of halite. A) Three shale samples with Na and Cl closest to the 1:1 line are from the Antrim Shale, central Michigan. B) Samples with lower concentrations of Na and Cl (lower TDS samples).

The isotopic signatures of waters from the Devonian sandstone, carbonate and shale formations are shown in Figure 28a. The waters from Devonian formations which have the most enriched $\delta^{18}O$ values are from the Berea Formation (sandstone), the Dundee Formation (DD-4) and the Richfield Formation (DR-1). These waters were sampled from the central Michigan Basin at depths of 750, 1,128 and 1,445 m, respectively. Both the $\delta^{18}O$ and $\delta^{2}H$ signatures for these waters fall within the range of isotopic signatures for waters from the majority of Silurian, Ordovician and Cambrian formations (Figure 24).

The majority of waters from Devonian-aged formations have isotopic signatures which are typical of present-day meteoric water, plotting along the GMWL. These waters were sampled from the Kettle Point, Hamilton and Antrim (Michigan) shales and from the Dundee carbonates at depths between approximately 40 and 130 m below ground surface. Weaver et al. (1995) observed that there was a spread in the isotopic signatures of the Devonian-aged waters between $\delta^{18}O$ values of -6 and -9‰ for waters from the Dundee and Detroit River formations. This range increases from -4 to -10‰ when the Devonian-aged shales are included (Figure 28A). Weaver et al. (1995) attributed this variation along the GMWL to mixing of waters from these formations with varying amounts of meteoric waters. In regions where significant petroleum production has occurred, dilution by recently recharged meteoric water may occur as the result of forced input of shallow water to enhance petroleum production, as a result of regional draw-down due to long-term pumping over the past 100 years, or due to leakage from the surface or shallower formations through improperly sealed abandoned wells. Measurable tritium in waters indicates that some leakage of meteoric water to oil-bearing formations has occurred in the past (Weaver et al., 1995).

Several of the waters have isotopic signatures which are indicative of a cold climate at the time of recharge, including the waters labelled DD-1 and -2, BRP-143 and -151, and LD-90-3-5 (Husain et al., 2004; Cloutier, 1994; Dollar et al., 1998). These samples have $\delta^{18}O$ values between -17 and -11‰, which is within the range of $\delta^{18}O$ values estimated for glacial meltwaters within the Great Lakes regions (-25 to -11‰) (e.g., Husain et al., 2004). Samples DD-1 and DD-2 were taken at depths of approximately 100 m at the western margin of the Appalachian Basin near Lake Erie. The remaining three samples (BRP-143 and -151, and LD90-3-5) are from the Kettle Point Shale and were sampled in Lambton County, Ontario (north-east of Lake St. Clair and south of Lake Huron) on the eastern margin of the Michigan Basin. The BRP-samples were taken at a depth of 45 m, and LD-90-3-5 was taken at a depth of 60 m (Husain et al., 2004; Cloutier, 1994).

Weaver et al. (1995) identified seven water samples from the same oil field (Southern Oil Springs, Lambton County) which displayed distinct solute and stable-isotopic compositions. Although the $\delta^{18}O$ values are similar for the series of waters in Figure 28a which includes CFS-161, CFS-A, CFS-D and CFN-E, the $\delta^{2}H$ values increase from the most depleted sample (CFS-161) to values more similar of meteoric waters. Weaver et al. (1995) proposed a staged-mixing model to explain this trend in the $\delta^{2}H$ values, as illustrated in Figure 28b. In the first stage of mixing, low-salinity waters with a cold-climate signature from an overlying aquifer (sample R-AQ1 in Weaver et al., 1995) were mixed with a high salinity water such as that represented by waters sampled from the Silurian-aged A-2 salt to produce a water similar to the most saline, $\delta^{2}H$ depleted water from the Southern Oil Springs (CFN-161). Based on the stable isotope values, a mixture of 45% of a brine similar to that sampled from the Salina A2 salt, and 55% glacial water was required to reproduce the $\delta^{2}H$ and $\delta^{18}O$ value of sample CFS-161. Using a hypothetical fluid with a similar isotopic composition and similar but less saline major ion

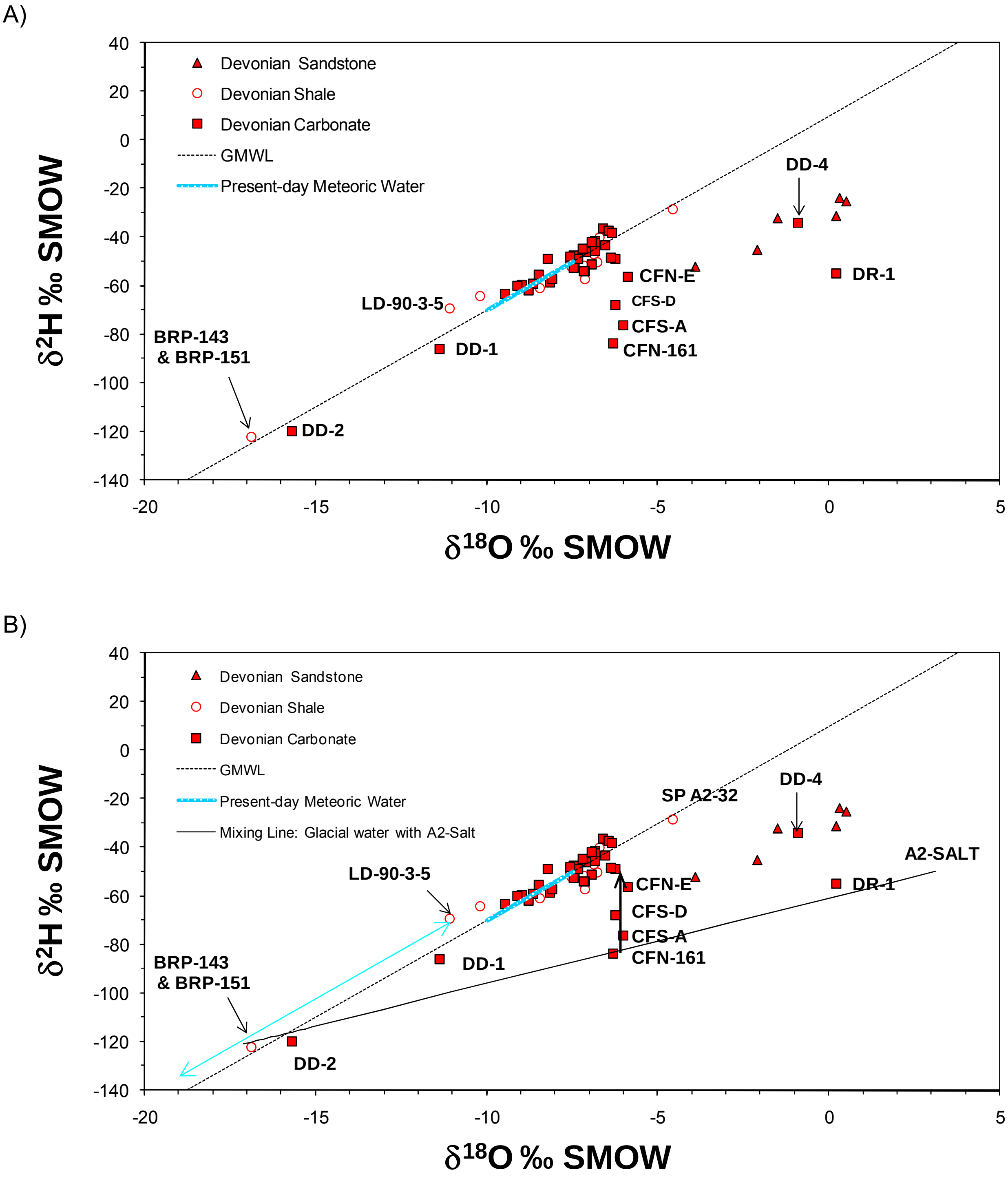


Figure 28: **Stable hydrogen and oxygen isotopic signatures for waters from Devonian formations. Mixing between glacial water and waters similar to those within the A2-Salt was proposed by Weaver et al. (1995) to generate the composition of water sample CFN-161.**

composition to waters sampled from the Silurian A2 salt, Weaver et al. (1995) were able to produce a fluid with concentrations of Cl, Mg and Ca within 15% of those measured in CFS-161. In the second stage, water with a composition similar to CFS-161 migrated into the Devonian-aged Dundee Formation and Detroit River Group, and mixed with water already present in these formations. Fluids within these formations have oxygen isotopic signatures which are essentially the same as those in CFS-161 but differing δ^2H signatures, with a trend of decreasing δ^2H observed for samples CFS-A through CFN-E (Figure 28b).

6.1.2.3 Silurian

Waters sampled from Silurian-aged carbonates, sandstones and salts are shown in Figure 29. The majority of waters have concentrations of both Cl and Br which are consistent with evolution from seawater by evaporation past halite saturation. However, eight water samples from carbonates and two from sandstones sampled at depths between 5 and 75 m below ground surface in the Hamilton region of southwestern Ontario which have concentrations of both Cl and Br that are well below present-day seawater (Hanratty, 1996). Within this group of samples (circled in Figure 29), the deepest waters sampled at this location (55 to 75 m) from the Thorhold Formation are the most concentrated. The concentrations of both Cl and Br decrease upwards through the stratigraphic section, with samples from the Guelph/Lockport Formations sampled at depths between 5 and 35 m having the lowest concentrations.

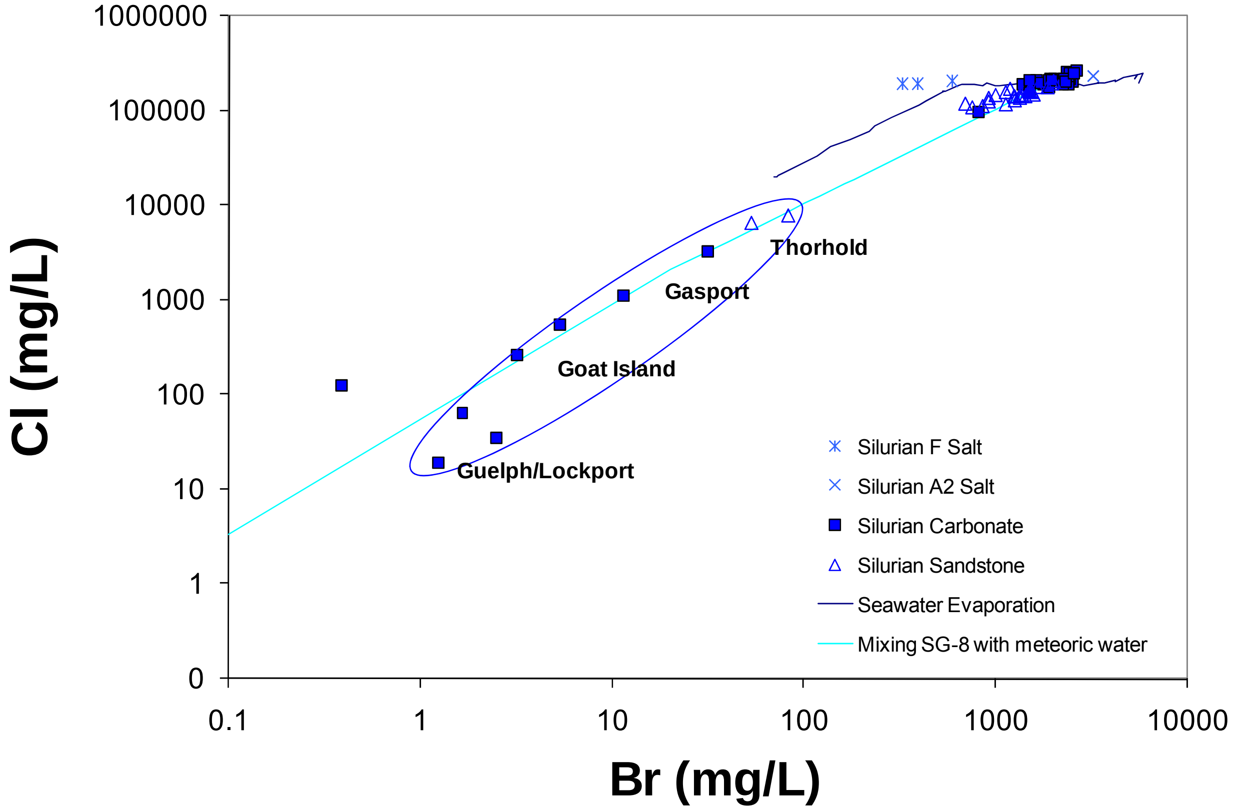


Figure 29: Relationship between Cl and Br concentrations in waters sampled from Silurian-aged carbonates, sandstones and salts. The light blue line is a calculated mixing line between a concentrated brine from the Guelph Formation carbonate (sample SG-8) and meteoric water.

Mass balance calculations were used to predict the Cl and Br concentrations expected when varying proportions of concentrated brine from the Guelph Formation (SG-8) is mixed with meteoric water. The chemical composition of water from Lake Ontario reported by Sherwood Lollar et al. (1989) was used as the meteoric end-member water. The resulting trend line is plotted on Figure 29, and demonstrates that the majority of waters sampled from the shallow Silurian-aged carbonates and sandstones could be derived from brine similar to SG-8 by mixing with meteoric water. The exceptions are three samples from the Guelph/Lockport Formations, which have Cl concentrations which are either slightly higher or lower relative to Br than predicted by dilution.

Figure 30 highlights the relationships observed between Cl and Br concentrations in the higher TDS samples from Silurian-aged formations sampled at depths of 150 m or greater. Waters from Silurian-aged F-salt formation are Na-Cl type waters and are enriched in Cl relative to the Br concentration in evaporated seawater, likely as a result of halite dissolution (section 3.1.1.1). The waters associated with the Silurian-A2 salt are Ca-Na-Mg-Cl type and have the highest Br concentrations of all samples in the database (Figure 21). Waters from the A2-salt are also enriched in Cl relative to evaporated seawater. The majority of waters from Silurian-aged carbonates are also enriched in Cl. The elevated Cl relative to Br observed in the samples suggests that the waters have been either enriched in Cl (e.g. due to redissolution of halite) or depleted in Br relative to evaporated seawater (Wilson and Long, 1993b). More than 60% of the waters from Silurian-aged carbonates are Ca-Na-Cl type (15 out of 24 samples), the remainder are Na-Ca-Cl (5 samples) or Ca-Cl (4 samples). In contrast, approximately 70% of waters from Silurian-aged sandstones are Na-Ca-Cl type (17 samples); the remainder are Ca-Na-Cl type. Two waters from the sandstone formations have concentrations which are at or above the Cl concentrations expected for evaporated seawater (STGr-14 and STGr-10). The remainder have Cl and Br concentrations below those expected for seawater evaporated to halite precipitation.

To investigate the impact of dilution, mass balance calculations were conducted to predict the Cl and Br concentrations expected in mixtures containing different proportions of water STGr-14 (the brine end-member) and using meteoric water or unevaporated seawater as the dilute end-member (Figure 30). The results of these calculations demonstrate that dilution could account for the observed Cl and Br concentrations for a portion of the waters from the Silurian-aged sandstones (Na-Ca-Cl type) and three samples from carbonate formations; one water sample from the Salina A1 Formation (sample SA1-1) and two water samples from the Guelph Formation (samples SG-12 and SG-1). Based on the Cl and Br concentrations, the maximum degree of dilution observed in the sandstone and carbonate samples is approximately 60%.

In the eight Ca-Na-Cl type waters from sandstone formations (circled in Figure 30), the observed Cl and Br concentrations cannot be explained by dilution alone, because the samples have higher Cl concentrations relative to Br than the remainder of the waters from the same formations. One possible explanation is that these waters evolved from an evaporated seawater end-member which was not as evolved as water STGr-14, which was subsequently diluted. However, the observed trend for these samples can also be modelled by considering dilution of water with a chemical composition similar to STGr-14 by a maximum of 50% meteoric water, with the addition of chloride by dissolution of halite (Kharaka et al., 1987). As seen in Figure 30, the observed trend in Cl and Br concentrations can be simulated by considering that the approximately 70% of the Cl is from the original brine, and 30% from the dissolution of halite.

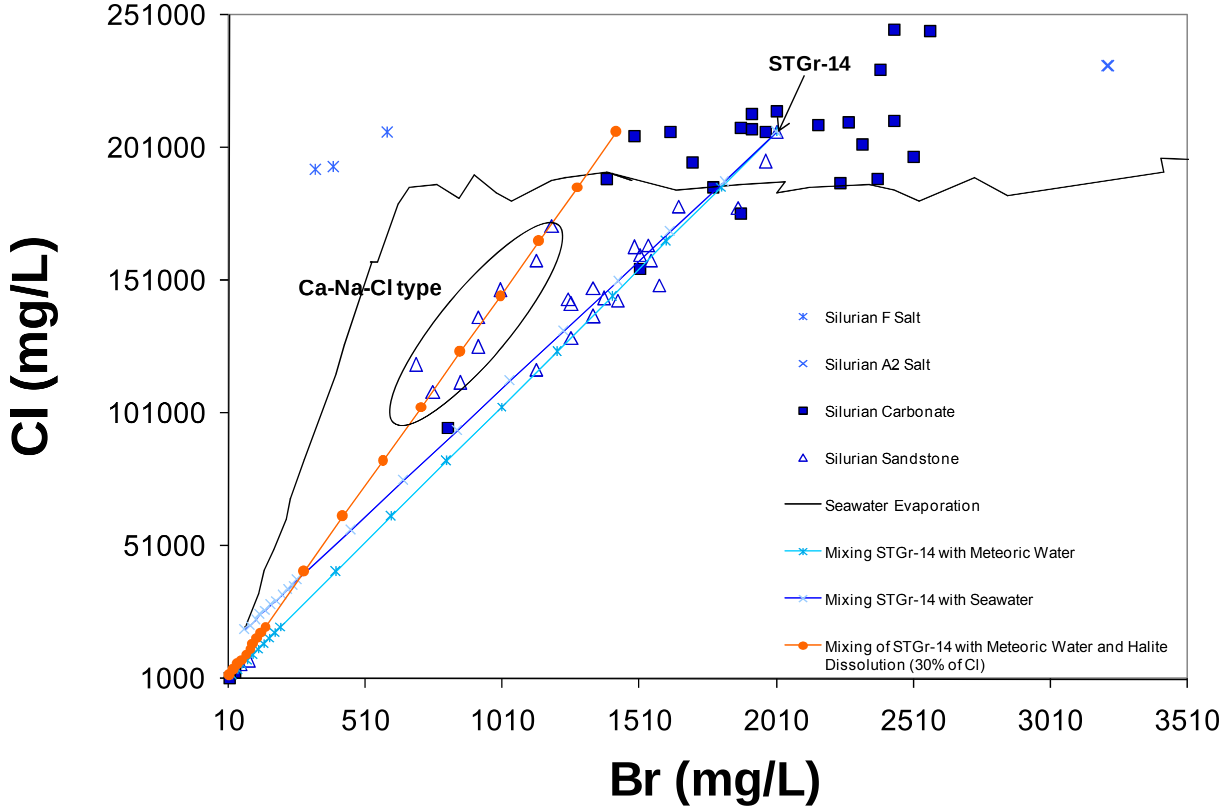


Figure 30: Concentrations of Cl versus Br in mg/L measured in waters from Silurian-aged formations (only most concentrated waters are shown). Mixing of brine STGr-14 with different proportions of meteoric or seawater were simulated using mass balance calculations (light and dark blue lines); and considering that 30% of the Cl in the brine is from halite dissolution (orange line).

The stable isotopic compositions of waters from Silurian-aged formations are plotted in Figure 31. The majority of waters in Figure 31 sampled from Silurian-aged sandstones and carbonates, and all waters from salt formations have δ^{18}O values which are enriched in ^{18}O relative to the GMWL. The exception is the group of waters from carbonate (Guelph, Lockport, Goat Island and Gasport formations) and a sandstone (Thorold Formation) unit sampled in two shallow multilevel sampling wells in the Hamilton region of southern Ontario, at depths of between 5 and 73 m, as described above (Hanratty, 1996). These waters fall along the GMWL, with δ^{18}O values ranging from -9.0 to approximately -11.5 ‰, which is at the light-end of the range of isotopic signatures for present-day meteoric water, and at the heavy-end of the range for waters recharged under cooler-climate conditions (-25.0 to -11.0 ‰). This may suggest that at least a portion of the waters in these formations was recharged under cold-climate conditions. These waters contain measurable tritium, with the highest value of 25 TU measured at a depth of 27 m, decreasing to approximately 1 TU at a depth of 73 m in the same borehole, indicating a component of recent meteoric water. For comparison, the weighted mean annual isotopic composition of present day meteoric waters in southwestern Ontario and Michigan (Fritz et al., 1987) is also plotted in Figure 31.

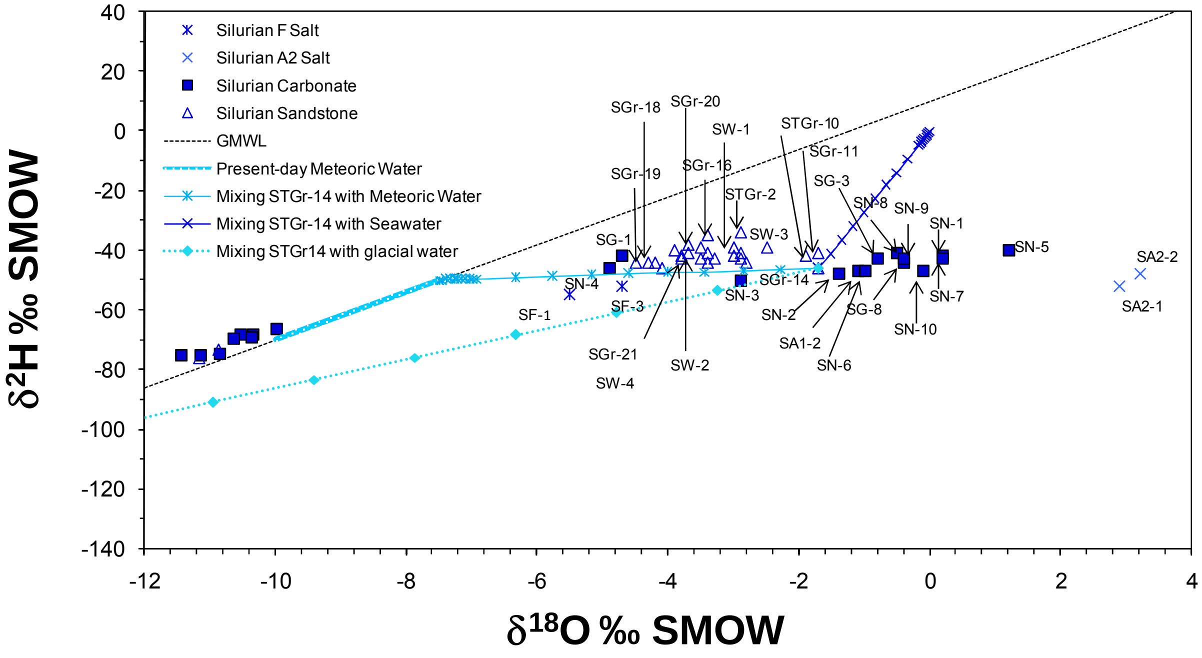


Figure 31: Stable hydrogen and oxygen isotopic signatures for waters from Silurian formations only. Circled samples are from depths of less than 85 m (Hanratty, 1996).

Of the samples which are enriched in ^{18}O relative to the GMWL, waters sampled within the Silurian A2-salt having the most enriched δ^{18}O signatures (δ^{18}O = +3‰; δ^{2}H = -50‰). Waters from the F-salt have approximately the same hydrogen isotopic values, but are depleted in ^{18}O by 8‰ relative to the A2 salt (Dollar, 1988; Dollar et al., 1991). Waters from the Silurian-aged sandstones have δ^{2}H values which range between -34 and -46‰ and δ^{18}O values between -4.7 and -1.7‰. The majority of waters from Silurian-aged carbonates have δ^{2}H values which range between -50 and -60‰, and δ^{18}O values between -1.4 and +1.2‰. The exceptions are samples SN-3 and SN-5 from the Niagaran Formation, which have more depleted δ^{18}O signatures of -2.9 ‰ and -4.9‰, respectively, and sample SG-1 from the Guelph Formation, which has a δ^{18}O signature of -4.7‰.

Using stable water isotopic compositions, mass balance calculations were conducted by mixing the brine end-member (STGr-14) with unevaporated seawater, with meteoric water similar to the most enriched signatures observed in present-day waters and with a glacial meltwater signature (Figure 32). For the glacial meltwater end-member, the isotopic signature of water R-AQ1 was used, as reported by Weaver et al. (1995). Based on the resulting trend lines, mixing with unevaporated, modern seawater can be eliminated as a mechanism to generate the isotopic signatures for waters from Silurian-aged formations. The observed trends in δ^{18}O and δ^{2}H for these waters cannot be explained by mixing with a glacial meltwater end-member. Although the range of δ^{18}O values observed in waters from the sandstone formations could be consistent with mixing of up to 60% meteoric waters, the δ^{2}H values in the measured waters are enriched in ^{2}H relative to those expected for mixing with even the most enriched present-day waters (δ^{2}H = -50‰). One possibility is that the brine end-member had a δ^{2}H signature more similar that of water STGr-2. Although it was possible using Cl and Br concentrations to simulate measured concentrations observed in the waters from sandstone formations by the dilution of a single brine end-member (STGr-14) with meteoric water, it appears that this is not the case for their stable isotopic compositions. The shift in the $\delta^{18}O$ values to the right of the meteoric line may reflect oxygen isotopic equilibrium with quartz in the sandstones at present-day formation temperatures or at higher paleo-temperatures. Although fractionation factors are available for $\delta^{18}O$ exchange between quartz or secondary phases such as illite and water as a function of temperature (e.g. Kharaka and Thordsen, 1992), representative $\delta^{18}O$ values for quartz or secondary illite in the formations from southern Ontario or alternatively, ranges for these minerals within Paleozoic formations will be required in order to evaluate this process quantitatively.

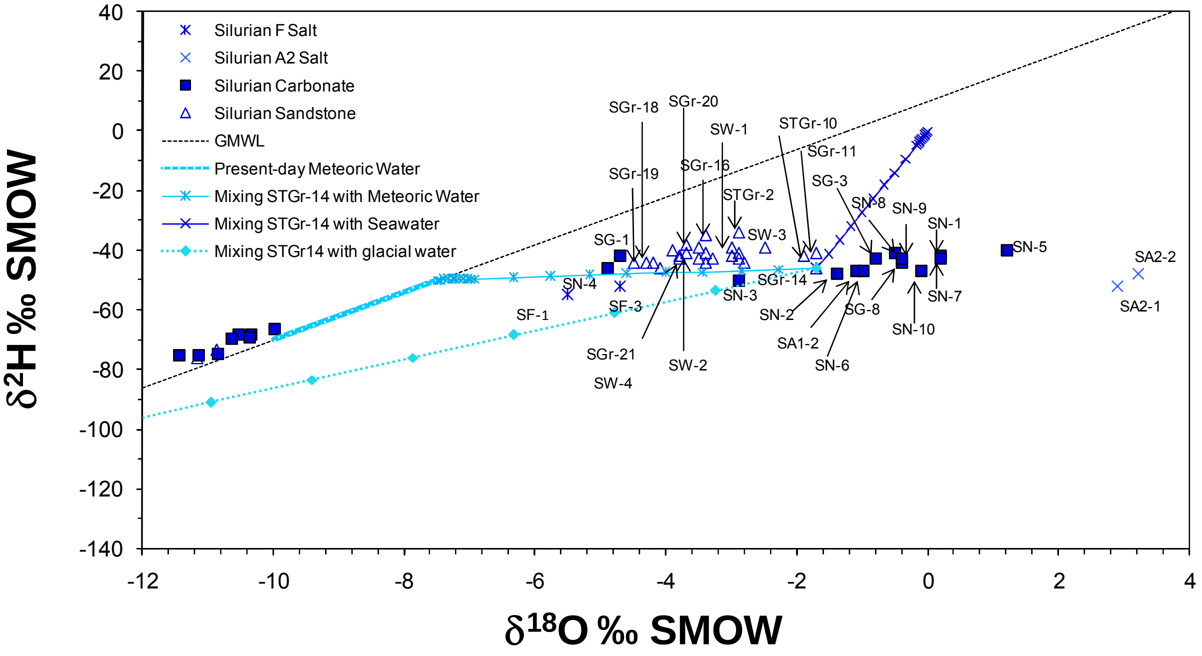


Figure 32: Stable hydrogen and oxygen isotopic signatures for waters from Silurian formations. Calculated trends for mixtures of water STGr-14 with seawater, present-day meteoric water, and a potential glacial end-member are also shown.

In Figure 33, the $\delta^{18}O$ value of water in equilibrium with calcite is calculated as a function of temperature and compared to the measured $\delta^{18}O$ values of the waters sampled from Silurian carbonate reservoirs. Temperatures were not reported for these waters by Dollar et al. (1991), therefore, formation temperatures at the depths from which the waters were collected were estimated using the following equation (Vugrinovich, 1989):

$$\text{BHT } (^\circ\text{C}) = 14.5 + 0.0192 \times \text{depth (m)}$$

Where BHT is the bottom hole temperature.

Clayton et al. (1966) compared measured $\delta^{18}O$ for brines in the Michigan basin to those predicted for water in equilibrium with calcite of +25.3‰ based on a best fit to their data. Wilson and Long (1993a) used a similar, average $\delta^{18}O$ value for calcites from the Devonian Detroit River Group of 24.93‰, and bracketed these calculations by also considering typical values for Paleozoic calcites with values of -1 and -8‰ PDB. This same approach has been taken in Figure 33, where the δ^{18}O of equilibrated water was calculated using a fractionation factor 10^3ln = 2.78 x 10^6T^{-2} – 2.89 (as reported by Kharaka and Thordsen, 1992). Similar to the results of Wilson and Long (1993a) for waters from Devonian formations within the Michigan Basin, the measured δ^{18}O values for brines from Silurian-aged carbonates do not follow the equilibrium lines but do plot between the limits of waters equilibrated with calcites with δ^{18}O values within the range measured for Paleozoic carbonates, with the exception of one sample (sample SN-4, from the Niagara Group). The observed scatter in the δ^{18}O values for waters from Silurian carbonates may indicate that the brines equilibrated with calcites of differing isotopic compositions.

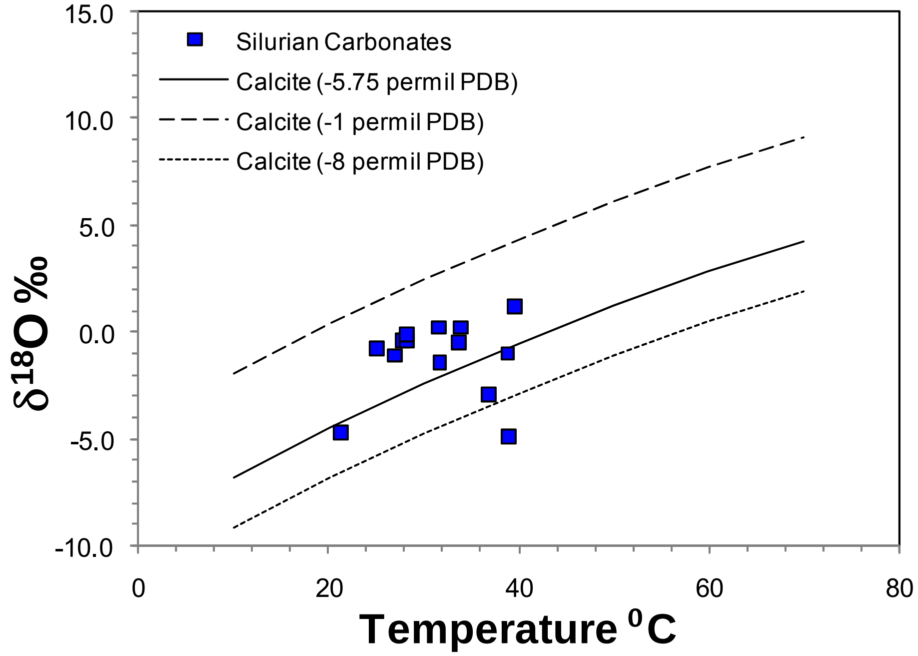


Figure 33: Plot of δ^{18}O of water (‰ SMOW) versus estimated formation temperature (°C) for water samples from the Silurian Carbonates in the regional geochemical database. The calculated δ^{18}O values of water in equilibrium with calcite having a δ^{18}O composition of -1, -5.75 and -8 ‰ PDB are also shown (solid and dashed lines).

An alternative approach is to assume that the calcite in these reservoirs has a δ^{18}O of approximately +25.3‰ SMOW (from Clayton et al., 1966) and then to estimate the temperatures at which the waters from Silurian carbonates reservoirs reported in this study would be in equilibrium with this calcite. The majority of the carbonates have δ^{18}O values between-1.4 and +1.2‰. Using the calcite equilibrium curve as a function of temperature for the Michigan Basin from Clayton et al. (1966), this would correspond to a range of temperatures between approximately 35 and 47 °C. In this case, waters within the Silurian carbonates are not at equilibrium with respect to calcite at present-day formation temperatures, which are estimated to range from 16 to 30 °C for the depths from which samples were collected. This temperature range is lower than the range of temperatures estimated for hydrothermal dolomite in the Silurian carbonates of between 65 and 130 °C, based on fluid inclusion temperatures (section 4.2.2), and is also below the maximum burial temperatures for the Michigan Basin of between 55 and 66 °C based on reconstructions of the sedimentary sequence.

Similar calculations were conducted to compare the $\delta^{18}O$ measured for waters from the Silurian carbonates with the values for dolomite reported for Silurian dolomites in southern Ontario of between -5.2 and -9.7‰ PDB by Conglio et al. (2003). In this case, the $\delta^{18}O$ of the equilibrated water was calculated using a fractionation factor for dolomite of $10^3\ln = 3.34 \times 10^6T^{-2} – 3.34$ (as reported by Kharaka and Thordsen, 1992). The results of this comparison (Figure 34) show that the waters from Silurian carbonate formations are not within the range of $\delta^{18}O$ values calculated in equilibrium with dolomites at the estimated present-day formation temperatures. Similar results were found when the fractionation factor for protodolomite reported in Kharaka and Thordsen (1992) was used (not shown). However, these waters may reflect equilibration between dolomite and the brines at temperatures higher temperatures of between approximately 60 and 100 ºC, which is close to the temperature range of 65 to 130 ºC indicated for dolomitizing fluids based on analyses of primary fluid inclusions in Silurian dolomites from southern Ontario (Coniglio et al., 2003).

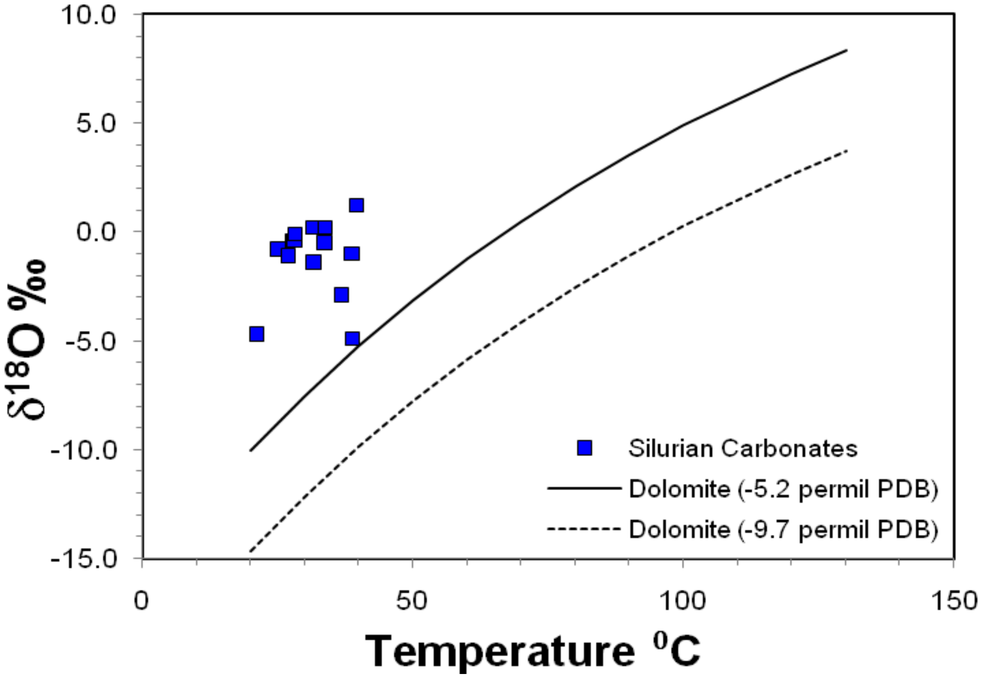


Figure 34: Plot of $\delta^{18}O$ of water (‰ SMOW) versus estimated formation temperature (ºC) for water samples from the Silurian Carbonates in the regional geochemical database. The calculated $\delta^{18}O$ values of water in equilibrium with dolomite having a $\delta^{18}O$ composition of -5.2 and -9.7‰ PDB reported by Coniglio et al. (2003) for Silurian dolomites are also shown (solid and dashed lines).

6.1.2.4 Ordovician and Cambrian

Waters from the Ordovician-aged formations are characterized by high TDS values of between 44,000 to 300,000 mg/L. The least concentrated waters were sampled using a multi-level water sampling system (Westbay® MP system) in two boreholes (OHD-1 at Lakeview and UN-2 at Darlington), on the shore of Lake Ontario at depths between 70 and 370 m (Sherwood Lollar and Frape, 1989). The least concentrated of these samples (UN-2 #13) has a TDS of 44,000 mg/L, which is slightly more concentrated than seawater (TDS of 35,000 mg/L). Waters from the Ordovician Trenton-Black River carbonate formations are predominately Na-Ca-Cl type (44 samples). The exceptions are OT-30 from west-central Michigan (Figure 5) and samples from boreholes OHD-1 and UN-2 the eastern edge of the study, which are predominantly Ca-Na-Cl type waters (8 of 11 remaining samples; see also Table 7). Waters from Cambrian-aged formations were sampled at depths between 890 and 1270 m bgs and have TDS values between 170,000 and 340,000 mg/L. Water sample C-6 is the only Na-Ca-Cl type water sampled; the remaining 12 samples were Ca-Na-Cl-type (Table 7). Similar to waters from Devonian and Silurian-aged formations sampled at depths below 150 m, the relationship between Cl and Br concentrations for waters sampled from Ordovician and Cambrian aged formations (Figure 35) suggests that these waters evolved from seawater by evaporation past halite saturation, with three groups of waters showing evidence of subsequent dilution.

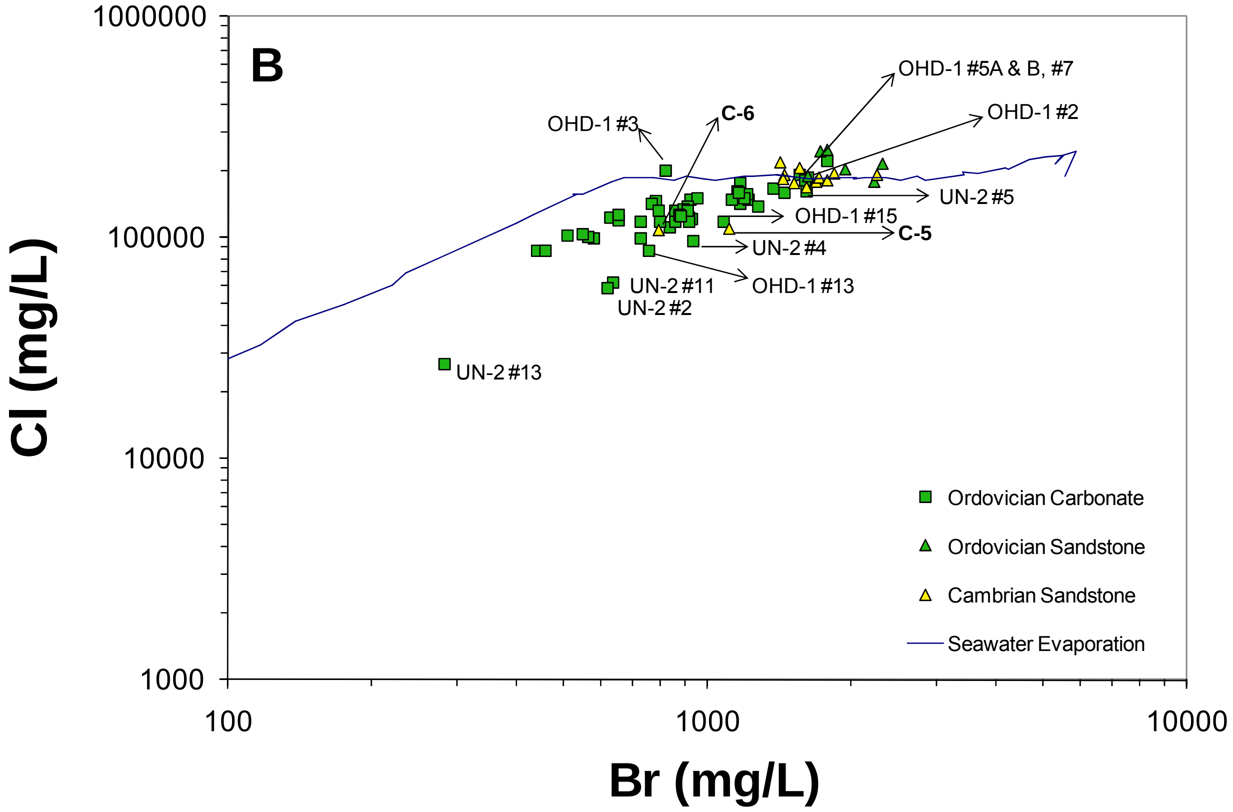


Figure 35: Relationship between Cl and Br concentrations for waters sampled from Ordovician aged carbonate and sandstone formations, and from Cambrian aged sandstones. The least concentrated water samples are from boreholes OHD-1 and UN-2 sampled at depths between 30 and 370 m at the eastern margin of the study area.

In Figure 36, potential mixing relationships between brine and meteoric water, as represented by the composition of Lake Ontario water (as reported by Sherwood Lollar and Frape, 1989) are explored. The Cl and Br concentrations of samples from the UN-2 and OHD-1 boreholes can be simulated using water OT-11 as the brine end-member with dilution by meteoric water. A second group of waters from the Ordovician carbonates is observed to fall along the trend line representing a mixture of brine OT-10 with a maximum of 40% meteoric water (or seawater; not shown), while a third group of Na-Ca-Cl type waters may reflect dilution of a brine end-member similar to OT-10 by up to approximately 50% meteoric or seawater (not shown), with a contribution of approximately 20% of the total Cl in these waters from the dissolution of halite (orange line in Figure 36).

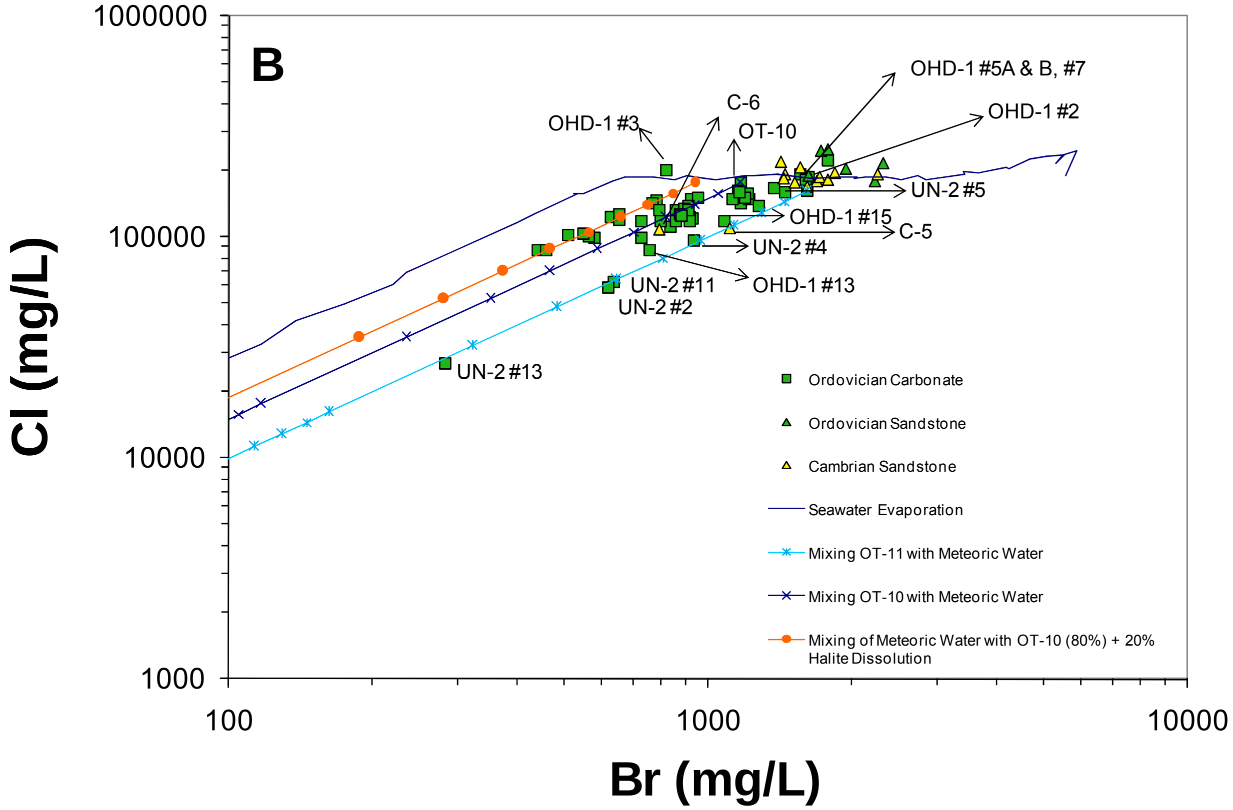


Figure 36: Relationship between Cl and Br concentrations for waters sampled from Ordovician aged carbonate and sandstone formations, and from Cambrian aged sandstones. Trend lines for mixing between a brine end-member (OT-10 or OT-11) and meteoric water are also shown. Mixing with seawater as the dilute end-member produced similar trends (not shown).

When plotted with respect to their stable water isotopic signatures (Figure 37) waters sampled from Ordovician carbonates are observed to fall into three different groups. The majority of the samples fall into a cluster to the right of the meteoric water line. These waters were sampled from producing hydrocarbon wells in the Trenton and Black River Group formations in the most southwestern part of Ontario and from the centre of the Michigan Basin (Figure 5) from depths between 650 and 1,300 m. Waters from Cambrian-aged sandstone formations cluster with a range of δ^{18}O and δ^{2}H signatures which is distinct from waters sampled with the Ordovician carbonates; the exceptions are waters C-6 and C-11 (Figure 37). Figure 38 provides a more detailed examination of the variation of the isotopic signatures of waters within this first group. In this figure, there are five waters sampled from the Ordovician carbonates (OT-21, OT-39, OT-

40, OT-41 and OT-42) which are shifted slightly towards the meteoric water line compared to the remainder of the samples. The mass balance calculations indicated that this observed shift could result from mixing with less than 10% meteoric water. Referring again to the Cl versus Br plot in Figure 36, these samples occur within the trend of Na-Ca-Cl waters which may reflect dilution of the end-member brine (OT-10 in this case) by a maximum of 40% meteoric water, with approximately 20% of the total Cl from halite dissolution. The only exception is water OT-21, which has Cl and Br composition very similar to OT-10 in Figure 36.

The second group of waters from Ordovician-aged formations observed in Figure 37 contains two waters sampled from carbonate formations and one from Ordovician sandstone (Prairie du Chein group) sampled from a depth of 3,400 m near the centre of the Michigan Basin. These waters are the most enriched in ^{18}O and have isotopic signatures which are more similar to those of brines from the Silurian carbonates. This is most clearly illustrated in Figure 25, in which only waters that are classified as brines are included.

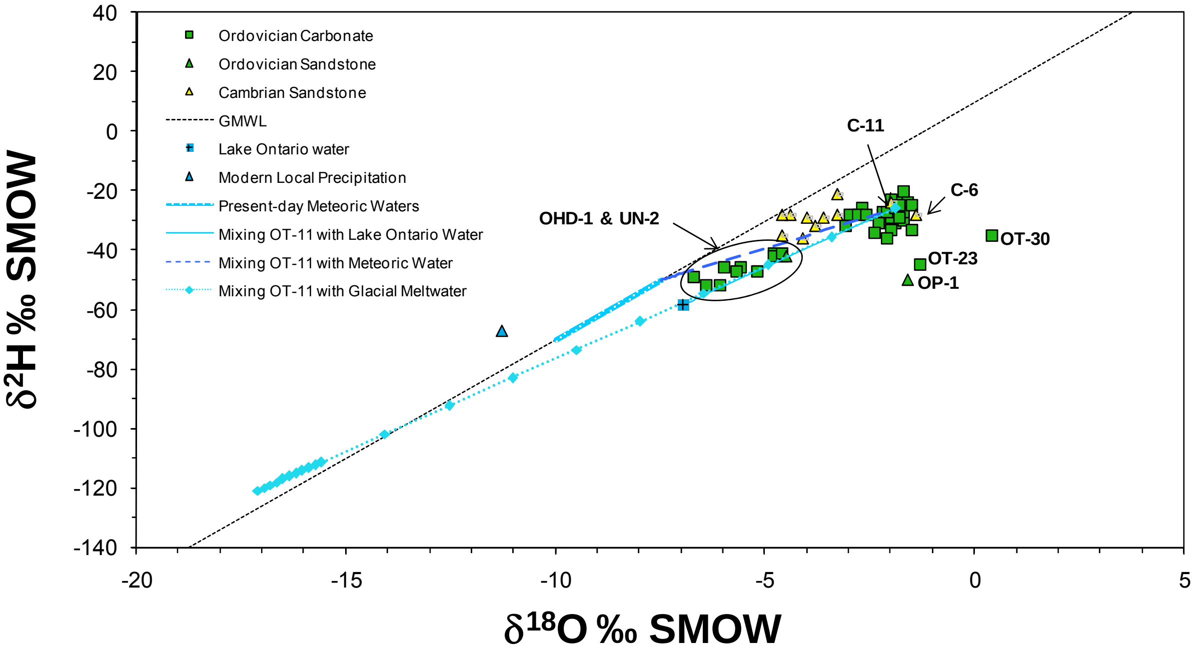


Figure 37: Stable hydrogen and oxygen isotopic signatures for waters from Ordovician aged formations. Circled waters are from boreholes OHD-1 and UN-2 sampled at the eastern edge of the study area. Mixing trends between brine (OT-11) and dilute end-members (Lake Ontario water, meteoric water and glacial meltwater) calculated using mass balance are also shown.

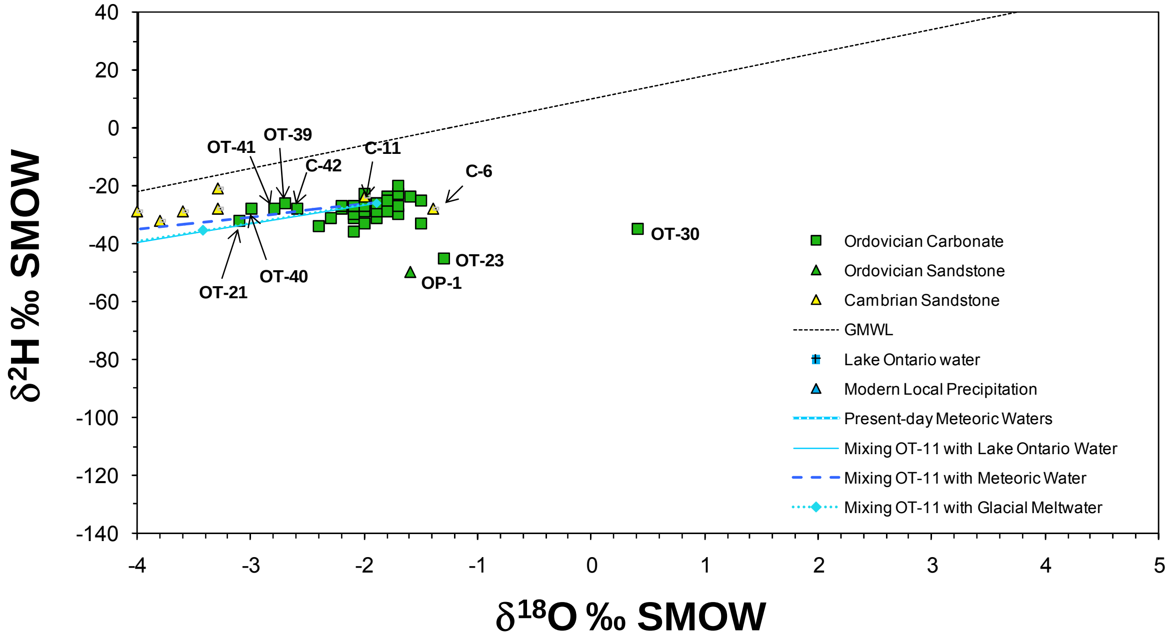


Figure 38: Plot illustrating the hydrogen and oxygen isotopic signatures for the largest group of waters sampled from Ordovician-aged formations. Mixing trends between brine (OT-11) and dilute end-members (Lake Ontario Water, meteoric water and glacial meltwater) calculated using mass balance are also shown.

The third group (circled in in Figure 37) contains 11 waters sampled from isolated intervals using a multi-level water sampling system (Westbay® MP system) in two boreholes (OHD-1 at Lakeview and UN-2 at Darlington). Both the OHD-1 and the UN-2 boreholes were drilled using water from Lake Ontario. The stable isotopic composition of Lake Ontario water reported by Sherwood Lollar and Frape is also plotted in Figure 37 ($\delta^{18}O$ = -6.97‰; $\delta^{2}H$= -58.5‰). Mixing lines were also calculated between:

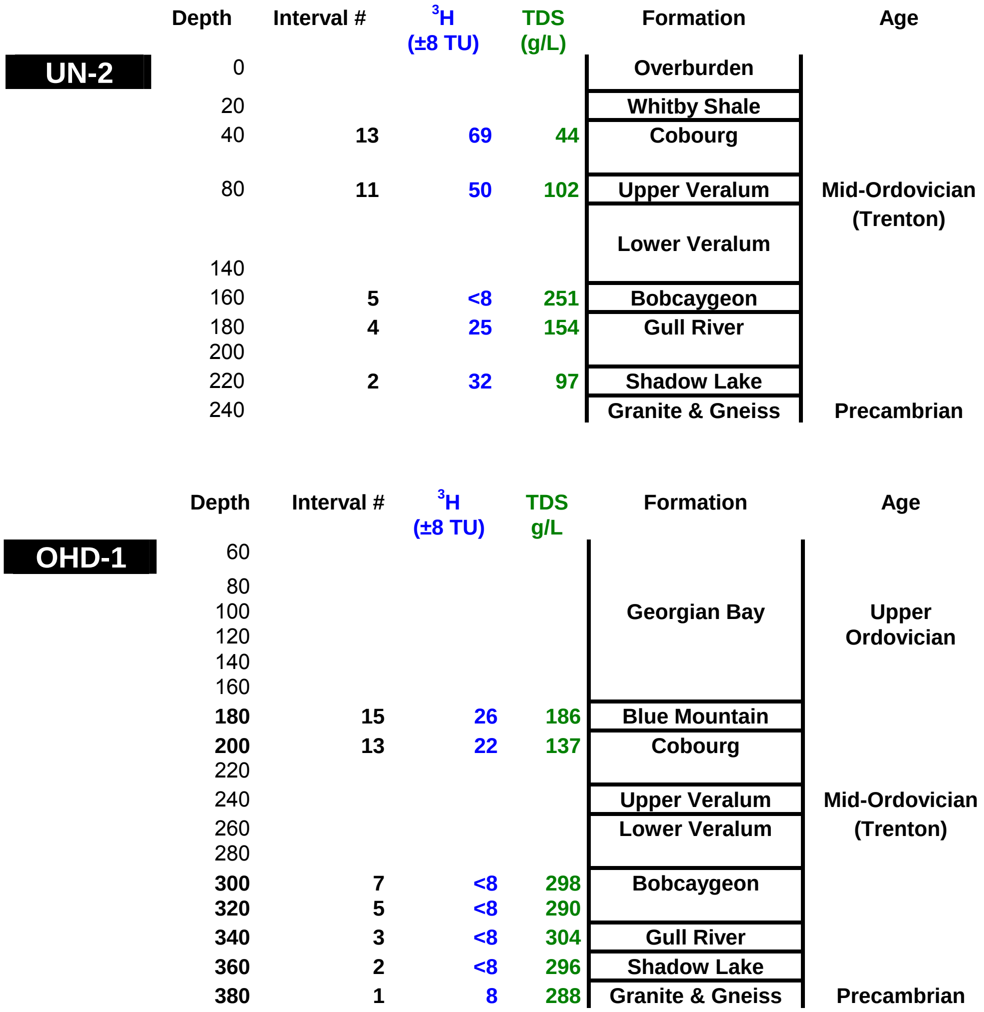
i) Water sample OT-11, which has an enriched isotopic signature to represent the isotopic composition of waters sampled from producing hydrocarbon wells within the Ordovician carbonates, is mixed with water from Lake Ontario;

ii) Water sample OT-11 mixed with modern precipitation. In this case, the most isotopically enriched end-member of modern precipitation was used as the dilute end-member in these mixing calculations; and

iii) Water sample OT-11 mixed with water having an isotopic signature representative of glacial meltwater. The composition of sample R-AQ1 from Weaver et al. (1995) was used as the glacial meltwater end-member.

These mixing calculations show that the isotopic compositions of the waters from both OHD-1 and UN-2 can be bracketed by considering mixing of water with an isotopic composition similar to that from OT-11 with either drill fluid (Lake Ontario water), modern precipitation or with a water with a glacial meltwater isotopic signature. Based on the isotopic signature alone, mixing with glacial meltwater versus Lake Ontario water cannot be distinguished (Figure 37). However, as discussed below, the presence of ^{3}H in the water samples provides strong evidence that mixing with the Lake Ontario water used in drilling has occurred.

Simplified stratigraphic profiles for both the OHD-1 and UN-2 boreholes are given in Figure 39, showing the measured TDS values and tritium concentrations in each sampling interval. The measured tritium concentration in water from Lake Ontario was 112 TU. Assuming that all of the tritium in the samples could be used as a tracer for the drilling water (Lake Ontario water) and that the TDS value of the lake water is negligible, the percentage of drill water in each sample from OHD-1 and UN-2 was calculated. The TDS expected for water from each interval was then calculated by assuming that the remainder of the volume was brine; the most concentrated waters from each borehole were used as the brine end-members (waters OHD-1 # 3 and UN-2 #5). The calculated and measured TDS values for waters from each interval are compared in Table 8.



UN-2

Depth	Interval #	^3H (±8 TU)	TDS (g/L)	Formation	Age
0				Overburden	
20				Whitby Shale	
40	13	69	44	Cobourg	
80	11	50	102	Upper Veralum	Mid-Ordovician (Trenton)
				Lower Veralum	
140					
160	5	<8	251	Bobcaygeon	
180	4	25	154	Gull River	
200					
220	2	32	97	Shadow Lake	
240				Granite & Gneiss	Precambrian

OHD-1

Depth	Interval #	^3H (±8 TU)	TDS g/L	Formation	Age
60					
80					
100				Georgian Bay	Upper Ordovician
120					
140					
160					
180	15	26	186	Blue Mountain	
200	13	22	137	Cobourg	
220					
240				Upper Veralum	Mid-Ordovician
260				Lower Veralum	(Trenton)
280					
300	7	<8	298	Bobcaygeon	
320	5	<8	290		
340	3	<8	304	Gull River	
360	2	<8	296	Shadow Lake	
380	1	8	288	Granite & Gneiss	Precambrian

Figure 39: Simplified stratigraphic profiles for boreholes UN-2 (Darlington) and OHD-1 (Lakeview) showing isolated sampling intervals, measured TDS in g/L and tritium values (Sherwood Lollar and Frape, 1989; after Ontario Hydro 1987).

Table 8. Calculated degree of mixing between brine and drill water (Lake Ontario water), using the simplifying assumptions that i) all tritium measured in the samples is from drill water, and ii) the brine end-member can be represented by the most concentrated water observed in each borehole.

Sample	^3H (±8 TU)	Lake Water % by vol.	Brine % vol.	Calculated TDS (mg/L)	Measured TDS (mg/L)	Difference (%)
OHD-1 #1	8	7.1	92.9	282366	287807	1.9
OHD-1 #2	<8	<5.4	>94.6	>287796	295752	2.7
OHD-1 #3	<8	<5.4	>94.6	>287796	304086	5.4
OHD-1 #5A	<8	<5.4	>94.6	>287796	290235	0.8
OHD-1 #5B	<8	<5.4	>94.6	>287796	290351	0.9
OHD-1 #7	<8	<5.4	>94.6	>287796	297766	3.3
OHD-1 #13	22	20	80	244355	136737	-79
OHD-1 #15	26	23	77	233495	185570	-26
UN-2 #2	32	29	71	179554	97385	-84
UN-2 #4	25	22	78	195265	153987	-27
UN-2 #5	<8	<5.4	>94.6	>237908	251375	5.4
UN-2 #11	50	45	55	139154	101983	-36
UN-2 #13	69	62	38	96510	44133	-119

For sampling intervals within OHD-1, the measured tritium values were close to or below detection. The predicated TDS values for these intervals were within 5% of the measured values for intervals between depths of between 300 and 380 m. However, for the two shallowest intervals (OHD-1 #13 at 200 m and OHD-1 #15 at 180 m), the measured TDS values are much lower than those predicted considering only mixing with drill fluid. This may suggest that at these shallower depths, mixing with another component, such as meteoric water, has occurred.

In borehole UN-2, only sample UN-2 #5 was below detection for tritium (<8 TU), indicating little or no mixing with the lake water used as drilling fluid. However, in all other intervals, the predicted TDS values were more than 30% higher than those actually measured for the waters. This again suggests an additional component is involved; given the shallow sampling depths (between 20 and 200 m), this component is likely meteoric water. These results are consistent with the findings based on stable isotopic compositions, which suggest that the compositions of the waters from both UN-2 and OHD-2 may be mixed with either meteoric water or water from Lake Ontario.

6.1.3 Stable Strontium Isotopes ($^{87}Sr/^{86}Sr$)

Approximately 60% of the strontium values (80 measurements) included in the regional geochemical database were previously reported by McNutt et al. (1987). Fifty additional stable strontium isotopic ratios ($^{87}Sr/^{86}Sr$) for waters from Cambrian- to Devonian-aged formations were measured on archived water samples as part of this study and are included in the regional geochemical database (Figure 9).

Table 9: Total number of water samples included in McNutt et al. (1987) and in the regional geochemical database (Appendix B).

Formation Ages	McNutt et al. (1987)	Regional Database
Devonian carbonates, shales	11	23
Silurian - Salina Salts	3	3
Silurian carbonates & sandstones	16	29
Ordovician	29	48
Cambrian	7	10

Measured $^{87}Sr/^{86}Sr$ values for the waters within the geochemical database are plotted versus the inverse of the Sr concentration in Figure 40. The $^{87}Sr/^{86}Sr$ ratios range from 0.70807 to 0.71112. Most of the waters are more enriched in ^{87}Sr relative to seawater in comparison to the curve of Burke et al. (1982) for their respective periods of sediment deposition. The exceptions are the Silurian salts of the Salina Formation, which lie on the seawater curve for the Middle Silurian period.

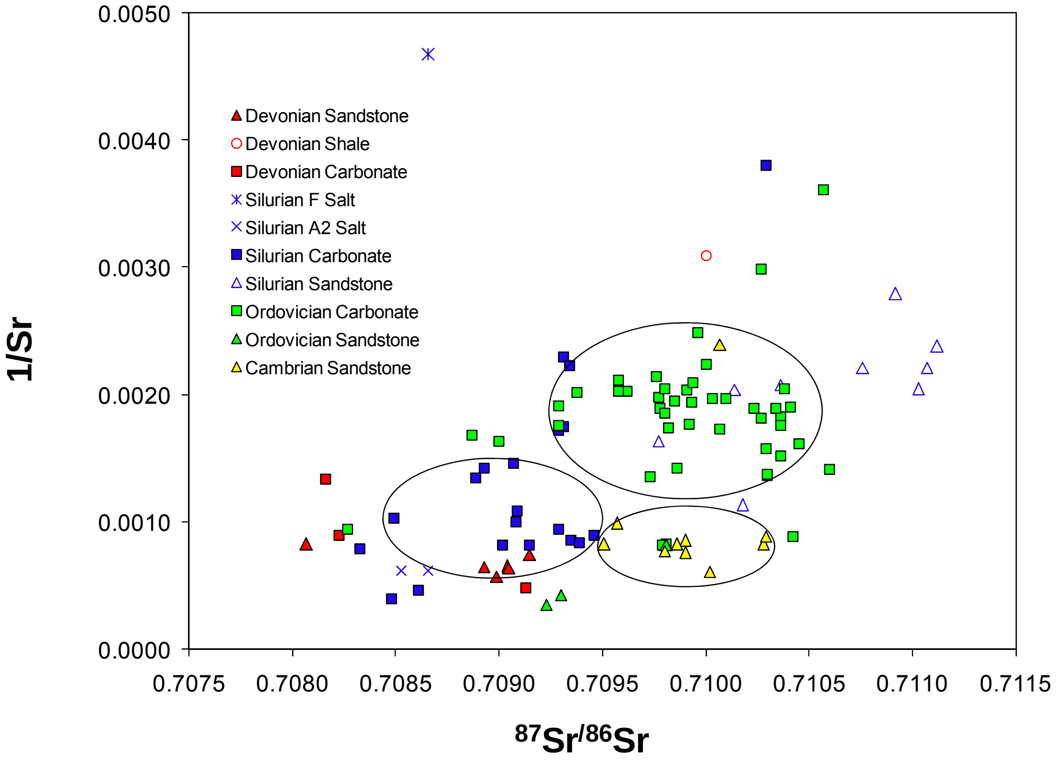


Figure 40: 1/Sr (in mg/L) versus $^{87}Sr/^{86}Sr$ for waters within the geochemical database. Circles indicate the overall clustering observed in both Sr concentration and isotopic ratio in carbonate-hosted and clastic-hosted waters with respect to age. Note that many waters from Devonian-aged formations are off-scale, as a result of their very low Sr concentrations.

McNutt et al. (1987) identified groups of waters with measured $^{87}Sr/^{86}Sr$ values and Sr concentrations which were correlated to the age of the formation and rock type (clastic or carbonate). These groups are also identifiable in the geochemical database, as shown in Figure 40; each group contains some outliers. The $^{87}Sr/^{86}Sr$ ratios and Sr concentrations for waters sampled from Devonian-, Silurian-, Ordovician- and Cambrian-aged formations are discussed in the following sections.

6.1.3.1 Devonian

The majority of waters sampled from Devonian-aged carbonate formations have $^{87}Sr/^{86}Sr$ values between 0.70813 and 0.709852 (Figure 41), within the range of Devonian Seawater ratios (0.70780 to 0.70870). The exceptions are i) DR-1, sampled from the Richfield formation at a depth of 1445 m; ii) DD-2 sampled from within the Dundee Formation at a depth of 97 m; and iii) SP A2-32 sampled from within the Antrim shale in central Michigan, all of which have more enriched $^{87}Sr/^{86}Sr$ ratios (0.70913 to 0.71000). Waters from the Devonian-aged Berea sandstones sampled at depths of >700 m have high strontium concentrations (~ 1200 to 1700 mg/L) and also have enriched $^{87}Sr/^{86}Sr$ ratios relative to Devonian seawater. The exception is water MB-6 which has a ratio within the range of Devonian seawater.

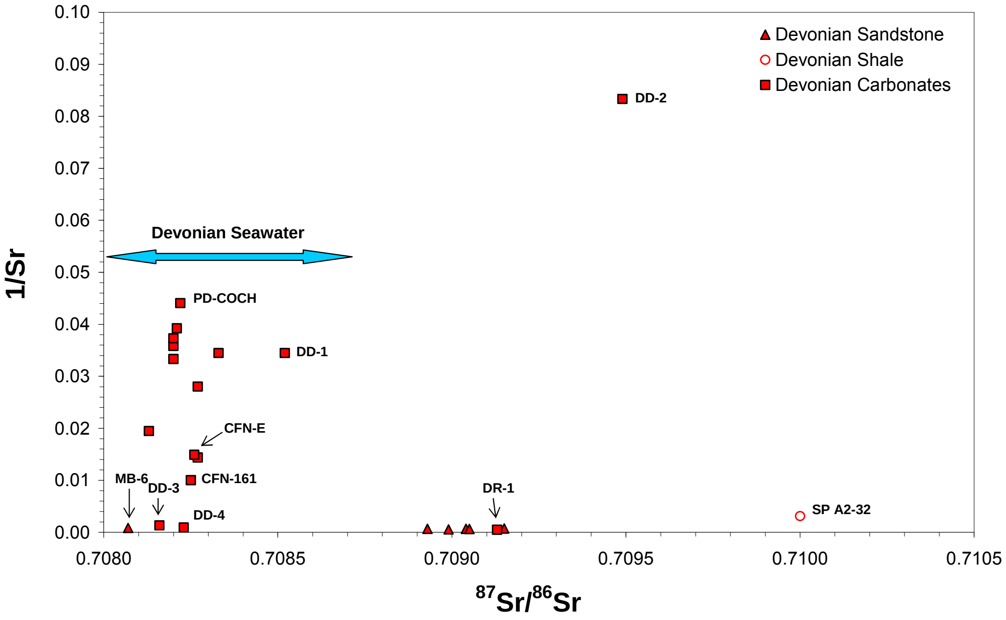


Figure 41: 1/Sr versus $^{87}Sr/^{86}Sr$ measured for waters sampled from Devonian-aged formations. Blue arrow shows range of $^{87}Sr/^{86}Sr$ ratios in Devonian seawater.

In Figure 41, a trend is observed for a group of waters from within the Devonian-aged carbonates which have similar $^{87}Sr/^{86}Sr$ ratios within the range of Devonian seawater, but a wide range of strontium concentrations from 22 mg/L (PD-COCH) to 100 mg/L (CFN-161). This is consistent with observations based on the Cl and Br concentrations and $\delta^{18}O$ and $\delta^{2}H$ signatures measured for waters which suggest dilution by either meteoric or cold-climate waters (section 6.1.2.2). In particular, waters DD-2 and DD-1 sampled from the Dundee Formation at depths of 108 and 97 m were identified to have $\delta^{18}O$ and $\delta^{2}H$ signatures consistent with dilution by cold-climate waters. This dilution is also apparent in Figure 42 where the measured $\delta^{18}O$ (a) or $\delta^{2}H$ (b) signature is plotted versus $^{87}Sr/^{86}Sr$ ratio for waters in geochemical database.

However, the $^{87}Sr/^{86}Sr$ value of DD-2 is much more enriched in ^{87}Sr than DD-1 and both waters have more enriched $^{87}Sr/^{86}Sr$ ratios than waters DD-3 and DD-4 which were sampled at depths of >1000 m in the central Michigan Basin. This suggests that waters sampled from DD-1 and from DD-2 are mixtures that contain a component which is enriched in $^{87}Sr/^{86}Sr$.

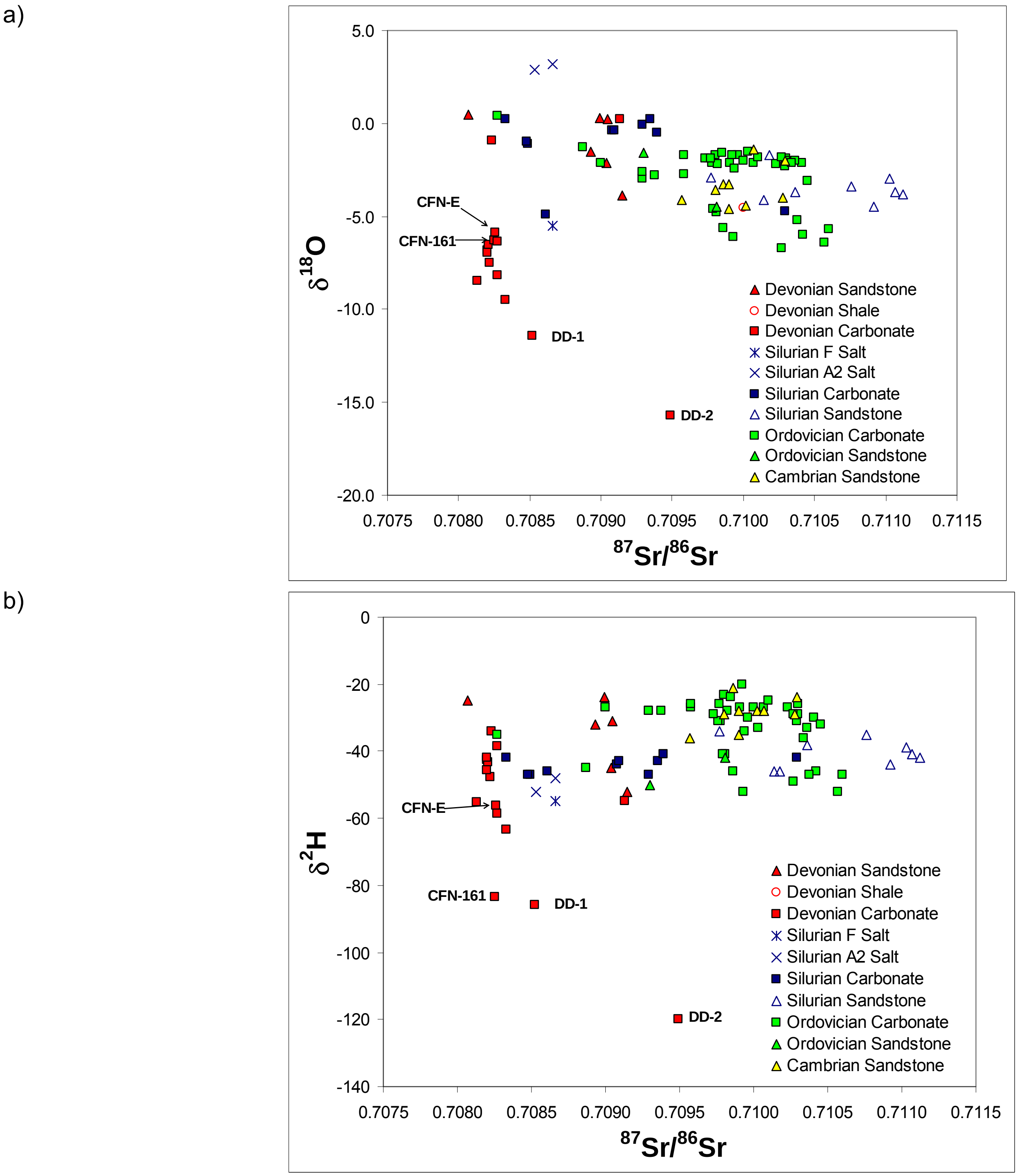


Figure 42: a) $\delta^{18}O$ versus $^{87}Sr/^{86}Sr$ and b) $\delta^{2}H$ versus $^{87}Sr/^{86}Sr$ for waters within the geochemical database.

6.1.3.2 Silurian

Figure 43 is a plot of $^{87}Sr/^{86}Sr$ versus 1/Sr for all waters from Silurian-aged formations, in which three distinct groups are observed. The waters with the highest Sr concentrations, but which are the least radiogenic, are labelled as Group 1 in Figure 43. The $^{87}Sr/^{86}Sr$ ratios of the Group 1 waters range between 0.70833 and 0.70861, within the range of Silurian seawater (0.7080 to 0.70875; Burke et al., 1982). Strontium concentrations range from 969 mg/L to 2500 mg/L. This group contains waters sampled from producing hydrocarbon wells within the Niagaran Formation carbonates of south-central Michigan (Figure 5), from the A1 carbonate unit (SA1-2), and waters sampled from within the Salina A2 unit with $^{87}Sr/^{86}Sr$ ratios between 0.70853 and 0.70866. Although water from the Silurian F Salt has a measured $^{87}Sr/^{86}Sr$ ratio within the range of Group 1, waters from this salt have much lower Sr concentration (158 to 214 mg/L) than waters from the A2 unit (1620 mg/L). Although all waters are labelled for water type in Figure 43, no correlation is observed between water type and $^{87}Sr/^{86}Sr$ ratio or Sr concentration.

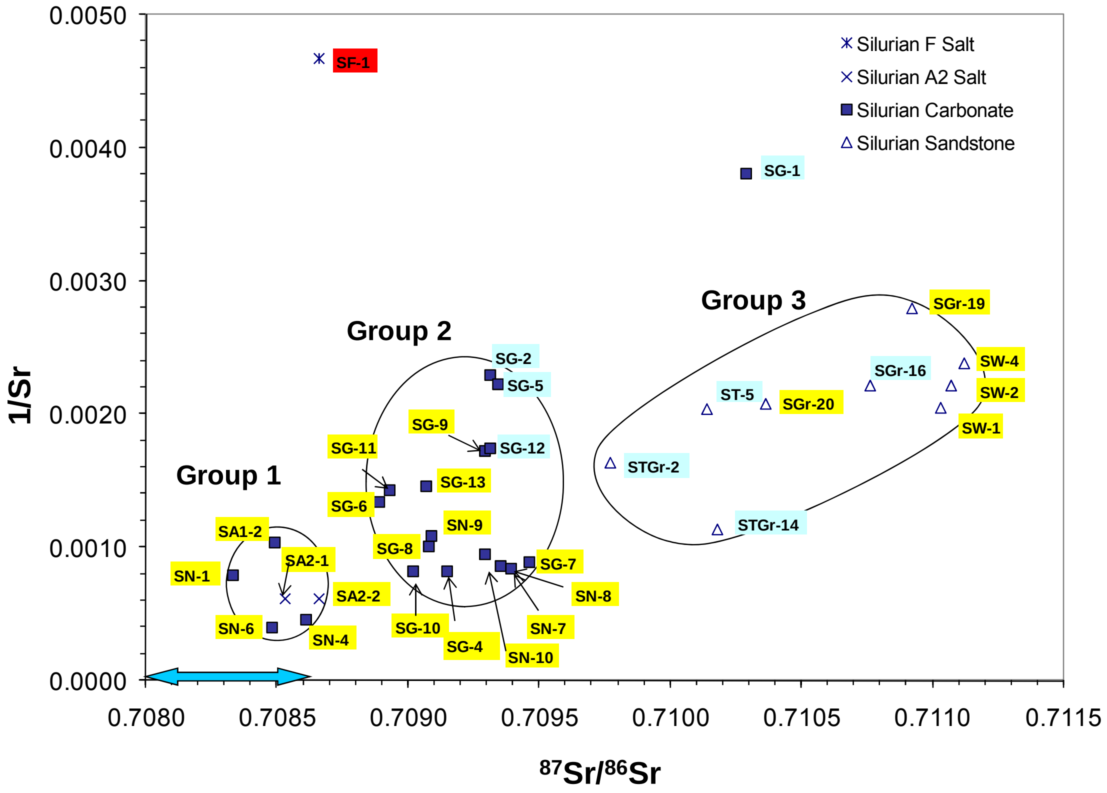


Figure 43: 1/Sr versus $^{87}Sr/^{86}Sr$ for waters from Silurian-aged formations. Sample numbers are also coded for dominant water type: Red = Na-Cl type; Yellow = Ca-Cl or Ca-Na-Cl type; Blue = Na-Ca-Cl type waters. Blue arrow indicates range of $^{87}Sr/^{86}Sr$ ratios for Silurian seawater.

Group 2 in Figure 43 contains waters from the Silurian-aged Niagaran and Guelph carbonate formations. The waters in this group are moderately concentrated with respect to Sr (436 mg/L to 1220 mg/L) and show minor enrichment in ^{87}Sr with respect to Silurian seawater, with $^{87}Sr/^{86}Sr$ ratios ranging between 0.70889 and 0.70946. One water sample (SG-1) from within the Guelph Formation plots in a distinct zone away from Group 2. Water SG-1 has a low Sr concentration (263 mg/L) and an enriched $^{87}Sr/^{86}Sr$ ratio with respect to the other SG- and SN-wells, falling within the range of ratios observed for waters from the Silurian-aged sandstones (Group 3). The waters in Group 3 were collected from producing hydrocarbon wells in sandstones from the Grimsby, Thorold and Whirlpool formations. The $^{87}Sr/^{86}Sr$ ratios of the waters range between 0.70977 and 0.71112 and the Sr concentrations range between 358 mg/L and 883 mg/L.

6.1.3.3 Ordovician and Cambrian

Most waters from Ordovician formations have Sr isotopic ratios which are more enriched than the $^{87}Sr/^{86}Sr$ seawater range (0.70780 to 0.70900), with only three (OT-30, OT-23 and OT-9) plotting within the Ordovician seawater range. The range observed for the Trenton-Black-River Group data summarized in the expanded database is 0.70929 to 0.71045, consistent with the range observed by McNutt et al. (1987) for waters from the Ordovician-aged Trenton-Black River formations (0.70901 and 0.71041). When all waters from Ordovician-aged in the database are considered, this range expands to include $^{87}Sr/^{86}Sr$ ratios from 0.70827 to 0.71060. OP-1 and OP-2 are waters from the Prairie du Chien sandstone in the center of the Michigan Basin at a depth of approximately 3400 m. This unit is not represented in southwestern Ontario. The Sr concentrations in these fluids are greater than 2000 mg/L and they plot in a distinct zone away from the other Ordovician waters in Figure 44.

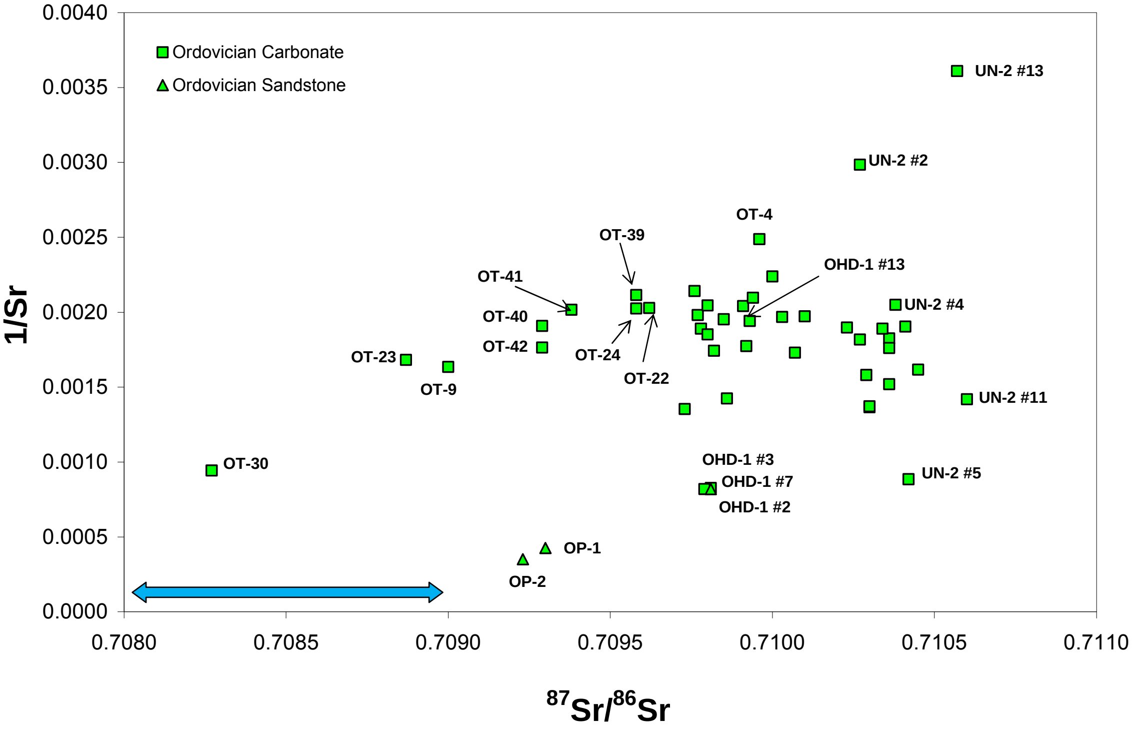


Figure 44: 1/Sr versus $^{87}Sr/^{86}Sr$ for waters from the Ordovician-aged formations. Blue arrow indicates range of $^{87}Sr/^{86}Sr$ ratios for seawater during the Ordovician.

Beyond the original studies of McNutt et al. (1987) and Dollar et al. (1991), waters analyzed for $^{87}Sr/^{86}Sr$ and included in the geochemical database are primarily from Ordovician-aged formations in southeastern Ontario (boreholes OHD-1 and UN-2). These wells are quite shallow, with the deepest water from a depth of 352 m. Waters sampled from both wells fall within a very narrow range of $^{87}Sr/^{86}Sr$ values, although the Sr concentrations differ. These differences in Sr concentration are consistent with dilution by either meteoric water or drilling fluid (Section 6.1.2.4).

Waters from Cambrian-aged sandstone formations have $^{87}Sr/^{86}Sr$ ratios between 0.70951 and 0.71029, as illustrated in Figure 46. All of these waters are enriched in ^{87}Sr with respect to the Cambrian seawater range (0.70900 to 0.70910), although it must be noted that this range is still poorly defined. The waters are all Ca-Na-Cl type waters with similar Sr concentrations (approx. 1000 to 1700 mg/L), with the exception of C-6 which is a Na-Ca-Cl type water with a Sr concentration less than half that measured in the other brines (418 mg/L).

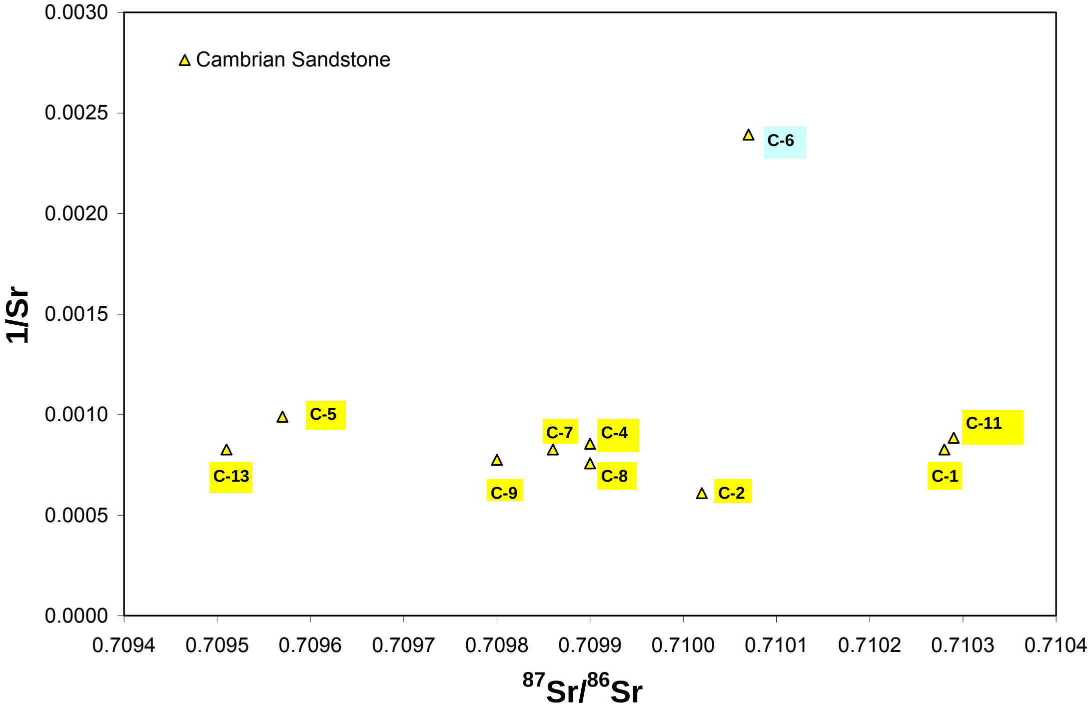


Figure 45: 1/Sr versus $^{87}Sr/^{86}Sr$ for waters from Cambrian-aged formations. Sample numbers are also coded for dominant water type: Yellow=Ca-Na-Cl type; Blue=Na-Ca-Cl type waters.

6.1.3.4 Summary

In Figure 46, the $^{87}Sr/^{86}Sr$ ratios measured for waters within the geochemical database are plotted together with curve from Veizer et al. (1999) showing the variation in the seawater $^{87}Sr/^{86}Sr$ ratio during the Phanerozoic. For waters from the geochemical database, the ages of the formations from which the waters were sampled have been estimated as follows: the Series Epoch (e.g. Lower, Middle or Upper Silurian) for each formation was first identified using Figure 4. The International Stratigraphic Chart (ICS, 2008) was then used to determine the range of ages for each Series Epoch. The median age of each formation was plotted, with error bars encompassing the entire range of ages for each Series Epoch (Figure 45). With the exception of a limited number of waters sampled from the Ordovician-, Silurian- and Devonian-aged carbonates, and one sample from the Devonian-aged sandstone (Berea Formation), the waters are enriched in ^{87}Sr relative to the ^{87}Sr/^{86}Sr ratios for seawater as reported by Veizer et al. (1999).

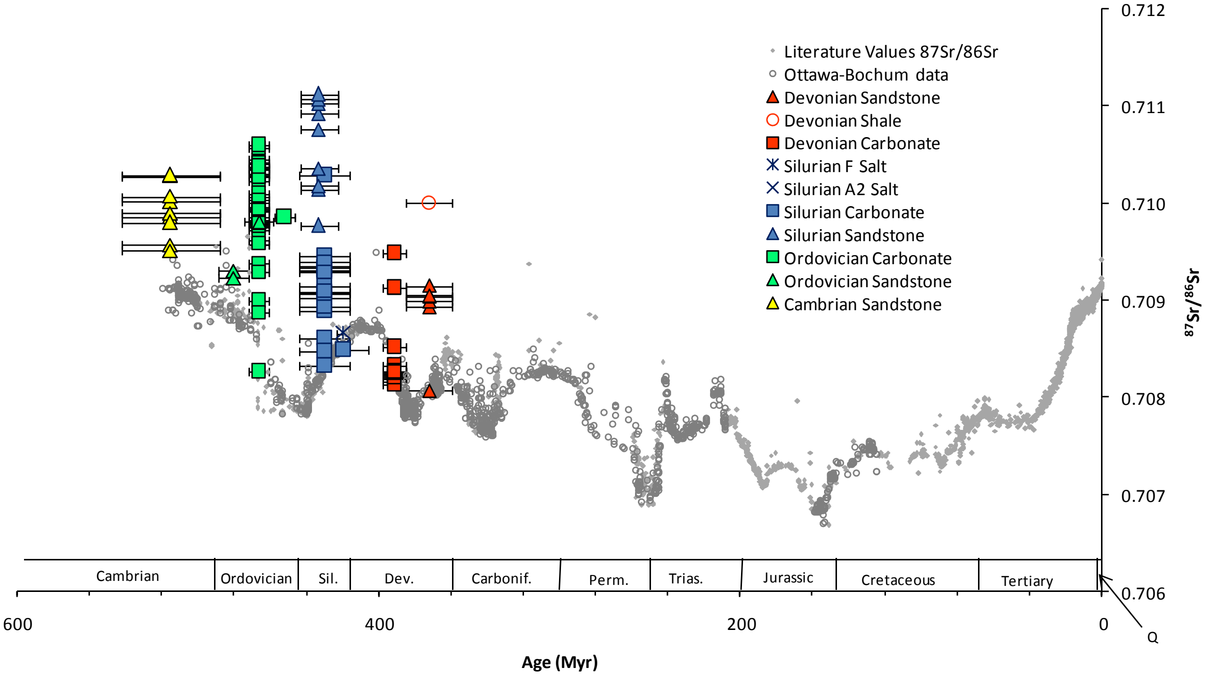


Figure 46: Graph showing the variation in the ^{87}Sr/^{86}Sr ratio of seawater throughout the Phanerozoic using data published by Veizer et al. (1999). The ^{87}Sr/^{86}Sr ratios measured for waters from the regional geochemical database are also shown. Error bars indicate the estimated uncertainty in the age of the formations from which the waters were sampled.

Waters from clastic formations including Cambrian through Devonian-aged sandstone formations and the one water reported in this study from the Devonian-aged Antrim shale generally have the most enriched ^{87}Sr/^{86}Sr ratios. Elevated strontium isotopic ratios are often observed in shale-hosted waters due to the detrital content of the shales (Stueber et al., 1984; Stueber et al., 1987). In sandstones, the elevated ^{87}Sr/^{86}Sr ratios are attributed to interaction between the waters and feldspar minerals which are enriched in ^{87}Sr. The majority of waters hosted in Devonian-aged carbonate formations have ^{87}Sr/^{86}Sr ratios consistent with seawater ratios during the time when the sediments were deposited. This is also true for waters from the Silurian Niagaran Formation sampled in central Michigan (SN-1 through SN-6; group 1 in Figure 43). Waters from this same formation sampled towards the eastern margin of the Michigan Basin (SN-7 to SN-10) are enriched in ^{87}Sr relative to Silurian seawater.

For waters from the Ordovician-aged carbonates of the Trenton-Black-River Group within the geochemical database the range in $^{87}Sr/^{86}Sr$ ratios is 0.70929 to 0.71045, consistent with the range of 0.70901 and 0.71041 reported by McNutt et al. (1987). The range of values for all of the Ordovician fluids compiled in the database ranges from 0.70827 to 0.71060. The consistency observed in the $^{87}Sr/^{86}Sr$ ratios across the study area is consistent with extensive fluid migration (spanning a distance of over 250 km) within the Ordovician-aged formations in association with dolomitization and hydrocarbon emplacement.

6.1.4 Dolomitization

Similar to observations made by Wilson and Long (1993a, b) for brines from Devonian- and Silurian-aged formations from the Michigan Basin, elevated calcium concentrations and depleted magnesium concentrations relative to evaporated seawater are also observed in the majority of waters in the regional geochemical database for southwestern Ontario (Figure 23). Wilson and Long (1993a,b) used a simplified mass balance approach to assess whether the excess Ca observed in the brines could be attributed to the dolomitization of calcite by the reaction:

$$2CaCO_{3\,(s)} + Mg^{2+}_{(aq)} \quad CaMg(CO_3)_{2\,(s)} + Ca^{2+}_{(aq)} \qquad (7)$$

In this approach, the concentration of the bromide ion is assumed to be conservative during the evaporation of seawater and any subsequent water-rock reactions. The Br concentration in each water sample is used to calculate the degree of concentration relative to the concentration of Br in present-day seawater. Based on this calculated degree of concentration, the concentration of Mg ion in the water is calculated. The difference between the measured and the expected Mg concentrations is calculated and where depletion of Mg has occurred, this loss is attributed to dolomitization. The magnesium lost is used to calculate the amount of calcium which would be released into the water as a result of this reaction, assuming a 1:1 molar ratio, as in equation 4. A predicted Ca concentration in the water is then calculated as the expected Ca concentration in seawater at the observed degree of concentration plus the Ca released during dolomitization. This same mass balance approach was applied to waters from Devonian-, Silurian-, Ordovician and Cambrian-aged formations in the geochemical database. The results are shown in Figure 47 through Figure 50, respectively. The actual Ca concentrations measured in the waters are shown as filled symbols, and predicted Ca concentrations are shown as open symbols in these figures.

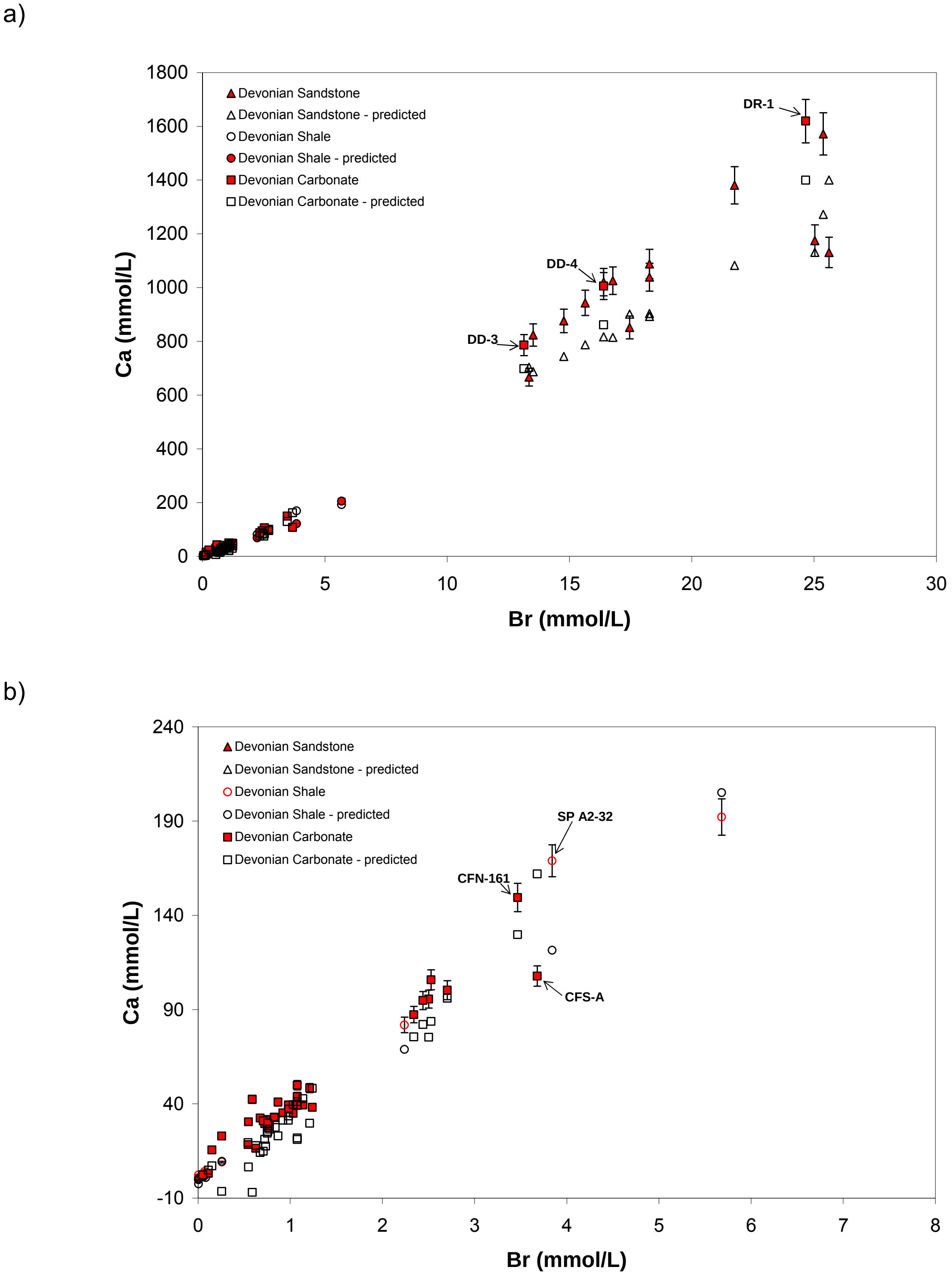


Figure 47: Predicted and measured Ca concentrations versus measured Br concentrations for a) all waters from Devonian-aged formations in the regional geochemical database; and b) waters with Br concentrations of less than 10 mmol/L). The predicted calcium concentrations were calculated using the mass balance approach of Wilson and Long (1993a,b).

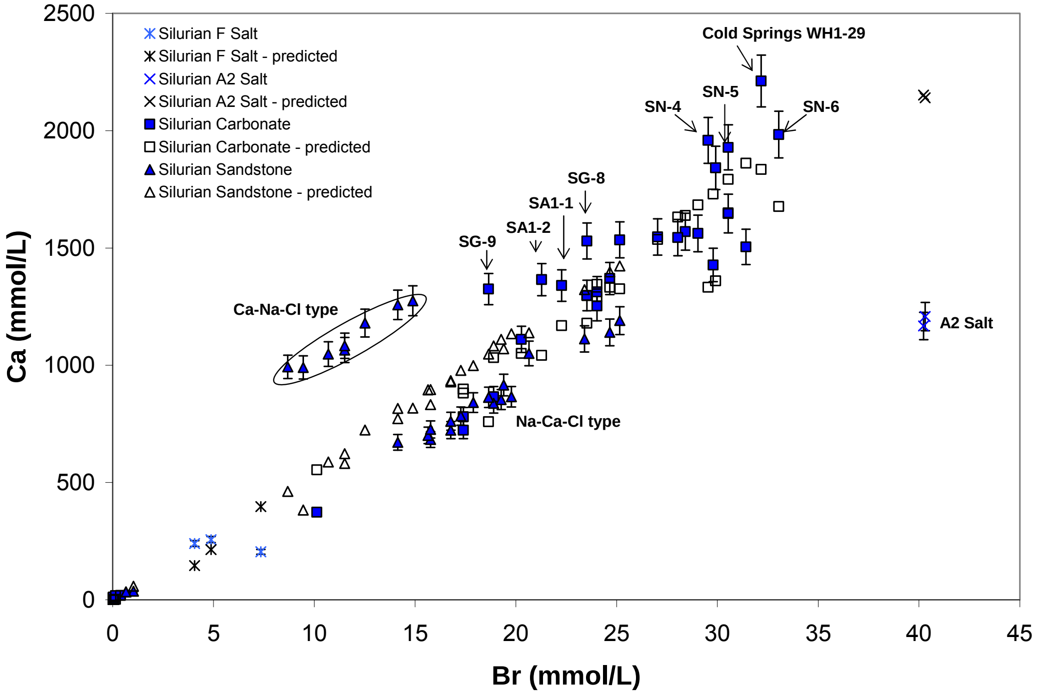


Figure 48. **Predicted and measured Ca concentrations versus measured Br concentrations for waters from Silurian-aged formations in the regional geochemical database. The predicted calcium concentrations were calculated using the mass balance approach of Wilson and Long (1993a,b).**

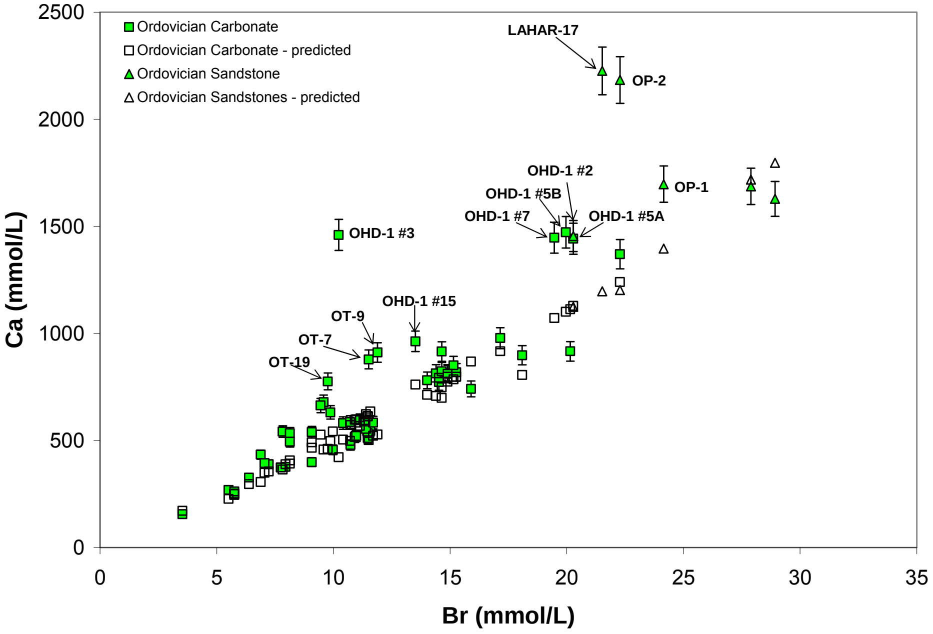


Figure 49: **Predicted and measured Ca concentrations versus measured Br concentrations for waters from Ordovician-aged formations in the regional geochemical database. The predicted calcium concentrations were calculated using the mass balance approach of Wilson and Long (1993a,b).**

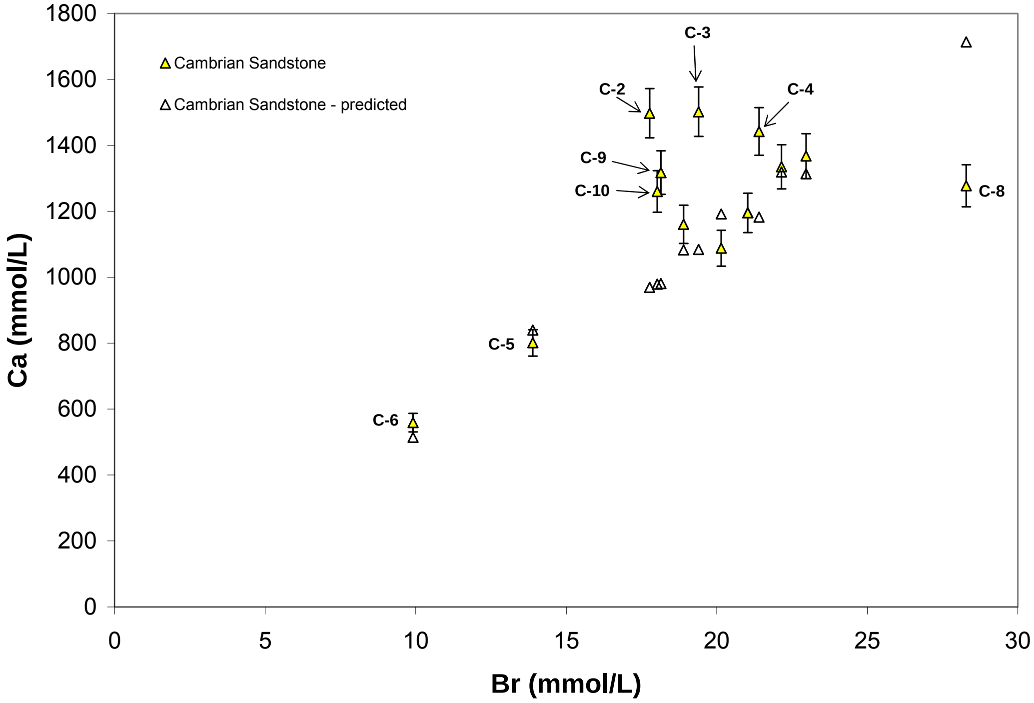


Figure 50: Predicted and measured Ca concentrations versus measured Br concentrations for waters from Cambrian-aged formations in the regional geochemical database. The predicted calcium concentrations were calculated using the mass balance approach of Wilson and Long (1993a,b).

Several general observations are made with respect to this comparison between the measured Ca concentrations in the waters and those predicated by assuming that dolomitization of calcite is the main water-rock interaction process which has influenced the Ca and Mg concentrations in these waters:

- Considering the analytical uncertainty in the measured Ca concentrations (± 5%), the measured and predicated calcium concentrations are in good agreement for the majority of water samples from carbonate formations of all ages;
- The agreement between the predicted and measured Ca concentrations for waters sampled from sandstone formations is not as good as that observed for waters from carbonate formations; and
- The Ca concentrations measured in waters from sandstone formations are most often in excess of those predicted by considering only dolomitization reactions.

In Figure 47, the majority of waters from Devonian-aged sandstones sampled from depths of >700 m and three waters from Devonian-aged carbonate formations (DD-3, DD-4 and DR-1) sampled at depths of greater than 1000 m are observed to have higher Ca concentrations than those predicted as a result of dolomitization.

The Ca-Na-Cl-type waters from the Silurian-aged sandstones also show calcium concentrations which are elevated above those expected if dolomtiziation was the only diagenetic process which had influenced the chemical compositions of these waters (Figure 48). As discussed in section 6.1.2.3, this is also the group of waters which have Cl concentrations which are elevated relative to the Br concentrations expected for evaporated seawater; Mass balance calculations indicate that halite dissolution may account for roughly 30% of the chloride in these samples. In contrast, Na-Ca-Cl type waters within Silurian-aged sandstones have measured Ca concentrations which are lower than the predicted values, as do waters from the A2-Salt.

The majority of waters from Ordovician-aged sandstone and several from carbonate formations also have measured calcium concentrations in excess of the predicated values. The waters which show the most elevated Ca concentrations are from Ordovician-aged sandstone formations sampled in the central Michigan Basin (LAHAR-17, OP-1 and OP-2) from depths of greater than 3000 m. Another group are Ca-Na-Cl waters which were sampled from relatively shallow depths between 180 to 380 m from borehole OHD-1 (Figure 39) and several Na-Ca-Cl type waters sampled from depths of between and in the Ordovician carbonates. Similarly, several waters from the Cambrian-aged formations (samples C-10, C-2, C-3 and C-4) all have measured Ca concentrations in excess of the predicted values, whereas the measured Ca concentration for water C-8 are lower than the predicted values.

As discussed in Chapter 3, reactions of aluminosilicate minerals to form clays (e.g. the formation of albite from plagioclase feldspar) may also result in increased calcium concentrations and decreased Na concentrations relative to evaporated seawater. This process is of particular relevance to waters from the sandstone formations. Other possible reactions leading to elevated calcium include the dissolution of evaporite minerals such as anhydrite and gypsum. For waters from the database such as those identified above containing both elevated Ca concentrations and elevated Cl concentrations relative to Br, dissolution of evaporite minerals may have influenced their chemical compositions. Large-scale dissolution of evaporite minerals is documented in southwestern Ontario, although the timing, source and fluid dynamics of dissolution are unresolved (Hamilton, 1991). Sanford et al. (1985) suggest that this salt dissolution occurred in association with the Calednian Orogeny during the Late Silurian and in association with the Acadian Orogeny during the Mississippian.

More extensive examinations of individual water compositions could be undertaken in an attempt to identify specific water-rock reactions to account for elevated Ca concentrations, as well as for variations in the concentrations of other elements (e.g. K) which deviate from those predicted solely on the basis of seawater evaporation. For the purposes of this study, the general observation considered most important is that the Ca concentrations measured in waters from formations of all ages, particularly carbonate formations agree quite well with those predicted by assuming that i) the waters evolved from seawater by concentration and ii) that dolomitization of calcite is the dominant water-rock reaction influencing the composition of these waters. This interpretation is consistent with the current understanding of diagenetic history of the Paleozoic strata in the Michigan Basin in which dolomitization has been identified as the most significant diagenetic process (Gartner Lee Ltd., 2008b).

The mass balance calculations presented here assume loss of Mg by a 1:1 molar replacement of Ca during dolomitization. In the Silurian and Ordovician formations underlying southern Ontario, evidence from fluid inclusions suggests that hydrothermal fluids ranging in temperature between 65 and 220 °C were involved in dolomitization (section 4.2). A more comprehensive examination of proportion of Ca in the waters attributed to dolomitization reactions would consider the temperature dependence of the equilibrium exchange reaction between calcite and dolomite (Bottomley et al., 2005).

6.1.5 Geochemical Modelling

Geochemical modelling of the water compositions included in the database was beyond the scope of this study. However, it is recommended that in future work a selection of waters chosen to cover the range of water types observed in the database be modelled using the latest version of PHREEQC with the Pitzer database (Parkhurst and Appelo, 1999). The purpose of this modelling will be to determine mineral saturation indices and to use this information to refine interpretations of the soluble minerals and dolomitization as possible controlling water-rock interactions in these waters. Given that some parameters including pH values are not available for the waters, sensitivity analyses to assess the uncertainty in the predicted mineral saturation indices are also recommended.

7. DISCUSSION

A conceptual model for the hydrogeochemistry of the sedimentary formations underlying southwestern Ontario at a regional scale has been developed based on observations made for the geochemical database presented and assessed in the current study. The geology, hydrogeology, structural geology and the diagenetic and thermal history of the Michigan and Appalachian Basins has also been considered, in order to develop a model consistent with the current scientific understanding of the evolution of fluids in sedimentary basins, the driving forces required for migration of these fluids and constraints on the timing of their emplacement.

7.1 Geochemistry of Waters at a Regional-Scale

At a regional-scale, the geochemistry of waters is characterized by a two-layer system consisting of:

i) a shallow groundwater zone occurring at depths of up to approximately 200 m below ground surface containing fresh through brackish waters. Waters in the shallow zone have isotopic compositions of $\delta^{18}O$ and $\delta^{2}H$ suggesting that they are mixtures of dilute, recent or cold-climate waters and more saline waters; and

ii) an intermediate to deep zone at depths greater than 200 m based on waters sampled predominantly from hydrocarbon reservoirs. These waters are characterized by elevated TDS values (200,000-400,000 mg/L) and stable isotopic signatures, which are enriched in $\delta^{18}O$ (-6 and +3 ‰) and $\delta^{2}H$ (-55 and +20 ‰) relative to the GMWL.

The actual sedimentary formation(s) in which the shallow system occurs varies with stratigraphy across southwestern Ontario. As illustrated in Figure 3, the sedimentary formations outcropping in the eastern part of southern Ontario are Ordovician-aged, with progressively younger rocks outcropping to the west towards the centre of the Michigan Basin. The current conceptual model for the hydrogeochemistry of the sedimentary sequence in southwestern Ontario is illustrated in Figure 51. The shallow groundwater zone extends to depths of approximately 200 m in Devonian, Silurian or Ordovician rocks, depending on geographic location in southern Ontario, or an additional 100 m below the zone of occurrence of potable water as illustrated in Figure 51. Waters from depths of greater than 200 m correspond to the intermediate and deep groundwater systems shown in this figure.

Within the sedimentary sequence, four different modes of occurrence for water are recognized:

- Groundwater – defined here as water which can flow under the influence of hydraulic gradients. This includes water within the connected pore space between mineral grains in unconsolidated sediment or in a rock, as well as water in permeable, connected structures in the subsurface. Operationally, groundwater is water which flows into and can be sampled from boreholes, typically over time scales of days to months.

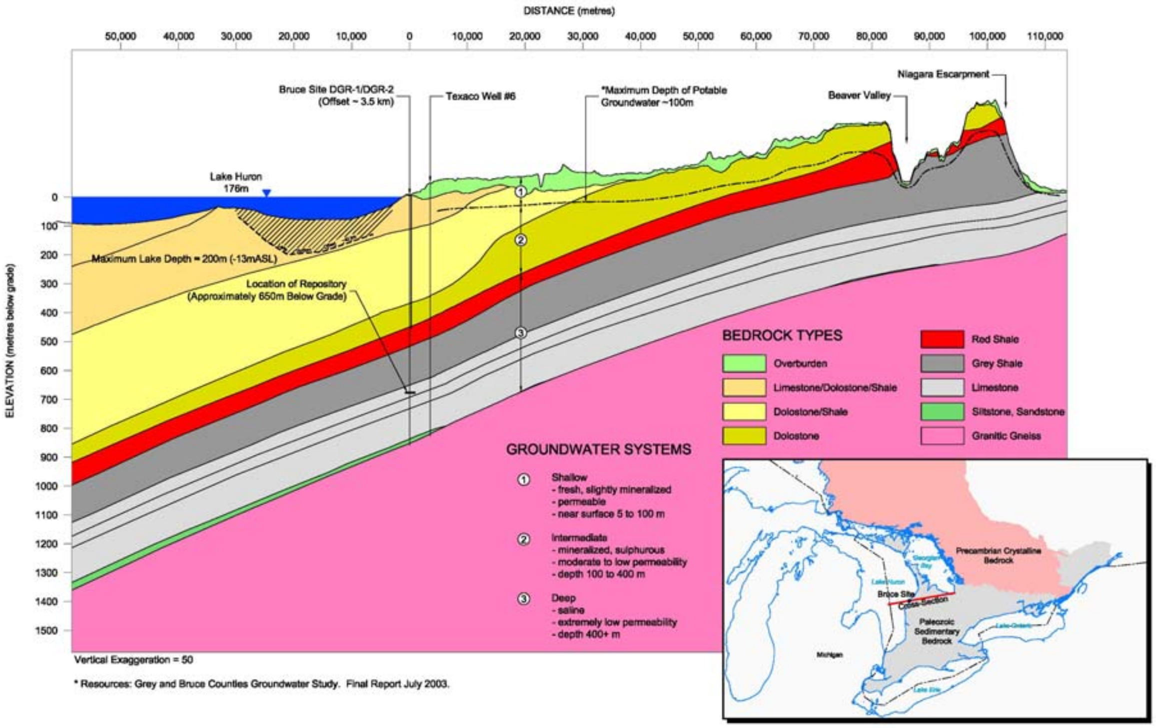


Figure 51: Conceptual model for the geochemical regimes present in the sedimentary formations underlying southwestern Ontario. The shallow system as defined based on the regional geochemical database extends from surface to depths of approximately 200 m; the intermediate to deep system comprises depths >200 m.

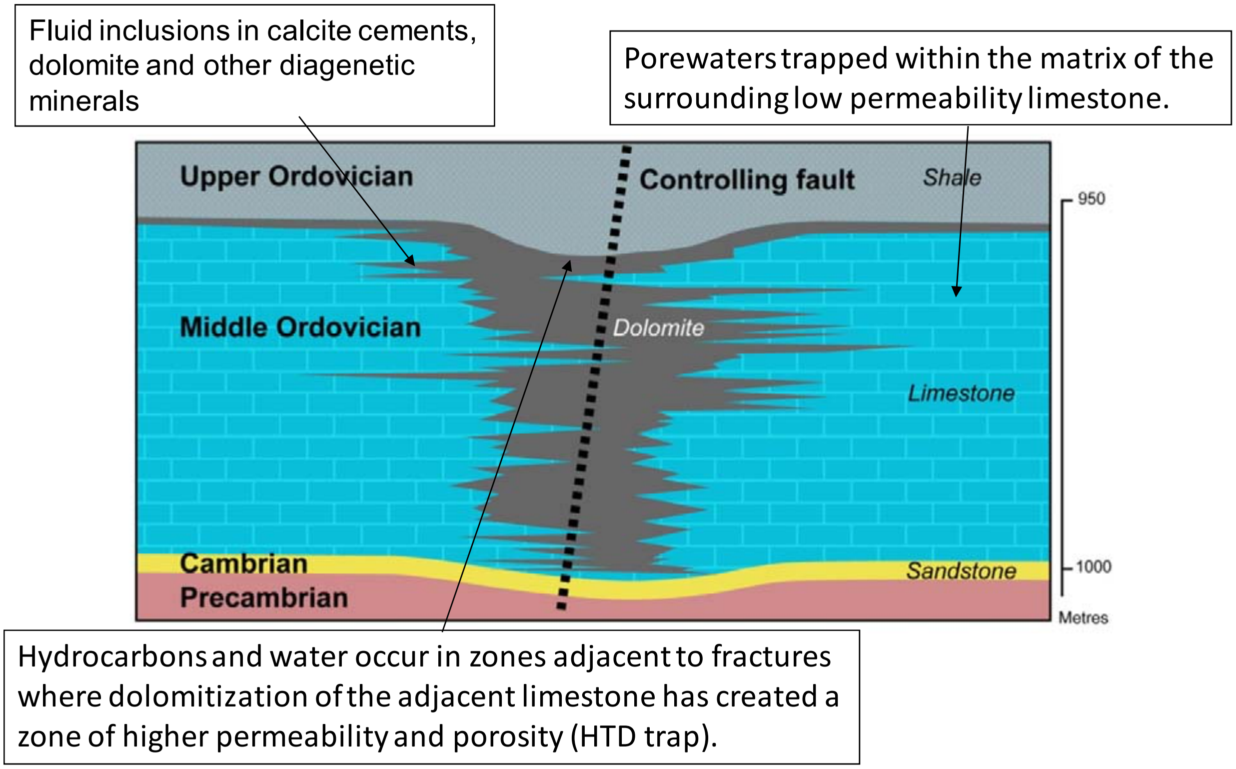
- Waters associated with hydrocarbons and contained in stratigraphic, structural or diagenetic traps. The hydrocarbons occur in discrete, permeable zones which are capped by low-permeability rocks which comprise the trap. These waters are distinguished from relatively shallow, low-salinity groundwaters because the physical conditions required to drive flow in each case are different.

- Porewater - water within the connected pore space between mineral grains in low-permeability sediments or rocks in which flow under the influence of hydraulic gradients is inhibited. Operationally, porewater is water which cannot flow into and be sampled from boreholes over time scales of days to months. Laboratory techniques are generally required to extract porewaters from the sediment or rock matrix.

- Waters trapped as fluid inclusions in dolomite and calcite cements and other diagenetic minerals either in the rock matrix or in fracture infillings.

Within the regional geochemical database discussed here, only groundwaters and waters associated with hydrocarbons are represented; no information on the composition of porewaters within the sedimentary rocks is included in this database. Published literature on dolomitization within Silurian and Ordovician formations in southern Ontario provides information on both the temperature and composition of fluid from which dolomite and calcite cements and other diagenetic minerals formed. The available information on the nature of fluid inclusion fluids is summarized in section 4.2, and is discussed in the context of the intermediate to deep system in section 7.3.

A conceptual model for the occurrence of waters associated with hydrocarbons in fracture-controlled HTD (hydrothermal dolomite) traps within Ordovician-aged rocks is illustrated in Figure 52. Figure 53 illustrates the occurrence of porewaters in clay-rich sedimentary rocks.



Fluid inclusions in calcite cements, dolomite and other diagenetic minerals

Porewaters trapped within the matrix of the surrounding low permeability limestone.

Hydrocarbons and water occur in zones adjacent to fractures where dolomitization of the adjacent limestone has created a zone of higher permeability and porosity (HTD trap).

Figure 52: Example of three different occurrences of waters within sedimentary rocks: i) waters associated with hydrocarbons which occur in traps (in this case, a diagenetic or HTD type trap); ii) waters which occur in the pore spaces between grains within the rock matrix, which are referred to as porewaters (see also Figure 53); and iii) fluid inclusions in diagentic mineral phases.

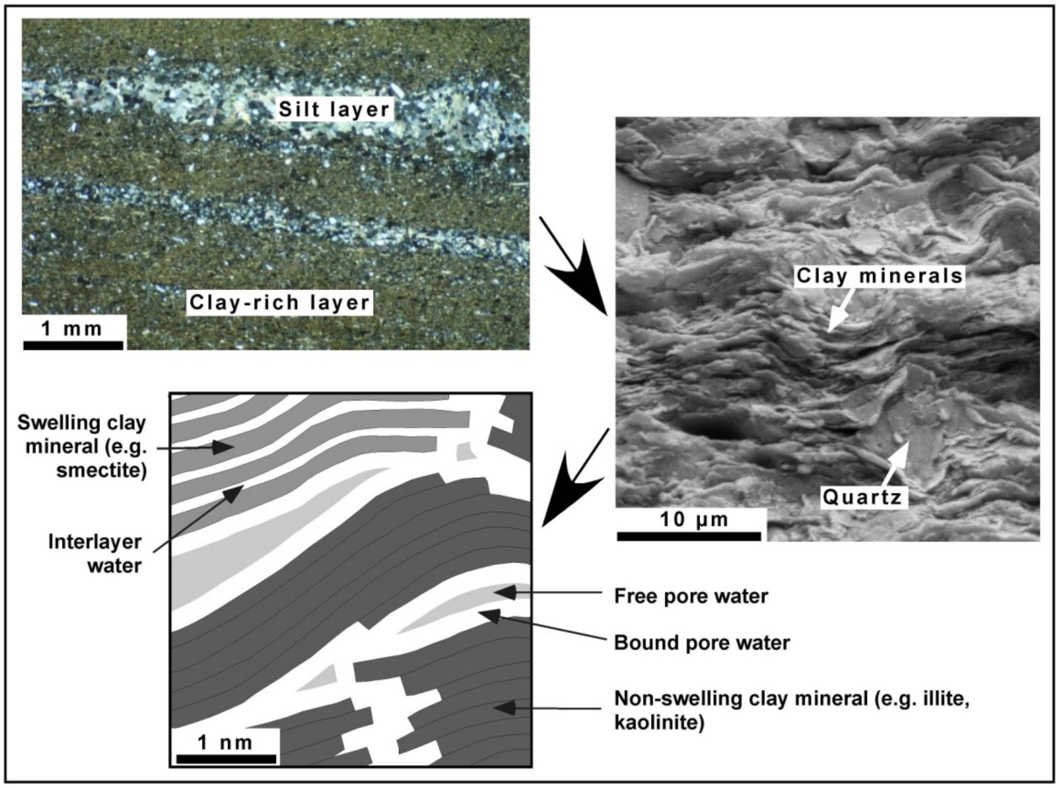


Figure 53: Schematic showing the occurrence of porewater within argillaceous rocks. This particular example is from the Opalinus Clay Formation, Switzerland (From Mazurek et al., 2008).

7.2 Shallow System (<200 m)

Within the regional geochemical database, the shallow system is characterized by waters sampled from Devonian-, Silurian- or Ordovician-aged formations where these formations subcrop or outcrop in southern Ontario. This includes waters associated with hydrocarbons in reservoirs within Devonian-aged carbonates in Lambton County near Sarnia (Weaver, 1994; Weaver et al., 1995) and groundwaters from a limited number of multilevel sampling wells located in: i) Devonian-aged shales and overlying Quaternary sediments in Lambton County (Husain, 1996; Husain et al., 2004); ii) Silurian-aged carbonates and sandstone formations in the Hamilton region (Hanratty, 1996); and iii) Ordovician-aged formations on the eastern margin of the study area (Sherwood Lollar and Frape, 1989).

Waters sampled from Devonian and Silurian-aged formations at depths of up to 200 m below ground surface are generally Na-Cl-type waters with TDS values between 640 and 25,200 mg/L. The exceptions are:

1. Ca-SO_4-type groundwaters sampled in the Silurian-aged Guelph, Lockport or Goat Island formations at depths of between 5 and 65 m in the Hamilton region of southwestern Ontario with TDS values ranging from 480 to 15,100 mg/L (Hanratty, 1996);

2. Na-Ca-Mg-Cl-type waters sampled from hydrocarbon-producing wells within the Devonian-aged Detroit River Group at depths of between 100 and 120 m in Lambton County, Ontario (Weaver 1994). These waters have TDS values ranging from 13,150 to 48,700 mg/L and concentrations of calcium and magnesium which are similar; and

3. Ca-Na-Cl type groundwaters sampled in multilevel wells within Ordovician-aged formations from depths of between 30 and 370 m at Lakeview and Darlington, Ontario (see Figure 6) having TDS values between 44,100 and 305,000 mg/L (Sherwood Lollar and Frape, 1989). These waters are distinct from the Na-Ca-Cl type waters from the Trenton-Black River Group reported by Dollar (1988) and Dollar et al. (1991). The $\delta^{18}O$ and $\delta^{2}H$ signatures of these waters together with their tritium contents indicate that these waters were impacted by mixing with surface water used during drilling.

The Cl and Br and $\delta^{18}O$ and $\delta^{2}H$ isotopic signatures of waters from the Devonian, Silurian and Ordovician Formations were examined in detail in Chapter 6. Considering the distribution of the waters with depth, two important observations were made:

1. The most dilute waters and those with stable isotopic compositions on or close to the GMWL were sampled at depths of 200 m or less, in areas where the formations sub- or outcrop; and

2. On the basis of mass balance calculations, it was shown that the composition of these waters could be derived from waters having Cl and Br concentrations and an isotopic signature that is distinct and characteristic of the waters sampled from within the same formations where they occur at greater depths in the basins by dilution with meteoric water.

In regions where significant petroleum production has occurred, dilution by recently recharged meteoric water may also occur as a result of draw-down due to long-term pumping (over decades), or due to leakage from the surface or shallower formations through improperly sealed and/or abandoned wells. The occurrence of detectable tritium in many of the waters sampled at depths of up to 140 m from Devonian-aged reservoirs in Lambton County (Weaver et al., 1995) strongly supports the interpretation that mixing with recent meteoric waters as a result of activities associated with petroleum production has occurred.

7.2.1 Evidence of Recharge Under Cold-Climate Conditions

In the regional geochemical database, stable isotopic compositions of oxygen and hydrogen consistent with recharge during colder climate (glacial) conditions are observed for five waters sampled at depths of 100 m or less from within Devonian-aged formations. Two of the groundwaters were taken from within the Dundee Formation at the western margin of the Appalachian Basin near Lake Erie (Figure 5). The remaining three were sampled in Lambton County; two were sampled within the Interface aquifer, which occurs between the overlying Quaternary deposits and the underlying Kettle Point shale, and the other was sampled from within the Kettle Point shale (Dollar, 1988; Dollar et al., 1991; Cloutier, 1994, Husain, 1996; Husain et al., 2004). These samples have $\delta^{18}O$ values between -17 and -11‰, which is within the range of $\delta^{18}O$ values estimated for glacial meltwaters within the Great Lakes regions (-25 to -11‰) (e.g., Husain et al., 2004; McIntosh and Walter, 2006). Four samples from the Silurian-aged Guelph/Lockport carbonate and Thorhold sandstone formations sampled at depths between 27 and 73 m below ground surface have δ^{18}O values between -10.9 and -11.5‰, at the upper end of the range of values estimated for glacial meltwaters.

The spatial distribution of waters in southwestern Ontario and Michigan with oxygen and hydrogen isotopic signatures indicative of cold-climate recharge, which are documented in the literature (section 2.2.3) and within this report are summarized in Figure 54. In Ontario, evidence for recharge of cold-climate waters is identified in shallow environments including porewaters within Quaternary-aged till deposits (Desaulniers et al., 1981; Aravena et al., 1995) or shallow bedrock aquifers (Dollar, 1988; McNutt et al., 1987; Dollar et al., 1991; Aravena et al., 1995; Husain, 1996). Within the regional geochemical database, the maximum depth from which glacial waters have been observed in shallow bedrock aquifers is 100 m (Chapter 6); glacial waters have been observed at depths of up to 130 m below ground surface in shallow bedrock wells within the Alliston aquifer (Aravena et al., 1995).

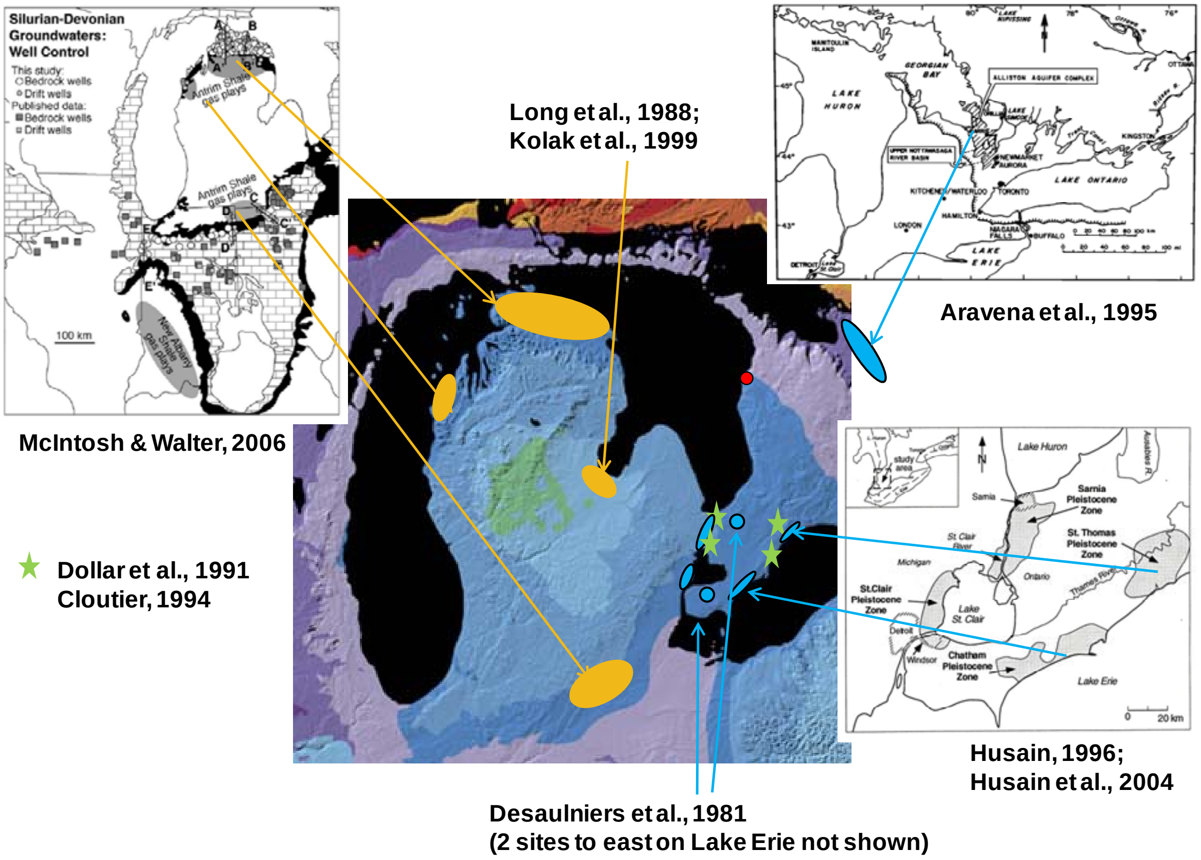


Figure 54: Geologic map of the Michigan Basin showing general locations in Michigan (orange) and Ontario (blue, green) where waters with oxygen and deuterium signatures indicative of glacial meltwater recharge occur, as documented in the literature and in the current study. Red dot indicates location of DGR site.

Along the northern and western margins of the Michigan Basin and the northern margin of the Illinois Basin, glacial recharge has been observed to depths of 300 m below the subcrop of the Antrim (MB) or New Albany (IB) shale formations in waters associated with microbial methane gas reservoirs (McIntosh and Walter, 2006). In these areas, there is evidence for the migration of meteoric waters down into the subsurface via Devonian and Silurian aquifers and then into the overlying shale formations. To date, there is no evidence for significant dilution of formation fluids within the Antrim Shale (or the Kettle Point Formation in Ontario) by meteoric recharge, or for microbial methanogenesis in central Michigan or at the eastern edge of the Michigan Basin (McIntosh et al., 2004).

7.3 Intermediate to Deep System (>200 m)

At depths greater than 200 m in the basin, the majority of waters sampled to date are brines from producing hydrocarbon reservoirs in Devonian-, Silurian-, Ordovician- and Cambrian-aged formations. The only exception is groundwaters sampled at depths of up to 370 m from Ordovician-aged formations in multilevel wells at the eastern edge of the study area (Sherwood Lollar and Frape, 1989). These waters show evidence of mixing with surface water used during drilling, as discussed previously in section 7.2.

The waters in the intermediate to deep system are classified as either Na-Ca-Cl or Ca-Na-Cl type waters based on their major ion concentrations (expressed in meq/L), and have TDS values ranging from 200,000 to 400,000 mg/L. Although the reduction-oxidation potential of the formation waters were not measured in the studies included as part of this geochemical database, the presence of methane gas in oil and gas wells from southwestern Ontario (e.g., Barker and Pollak, 1984; Sherwood Lollar et al., 1994) may provide indirect evidence that the redox conditions in waters from the producing formations are reducing (section 6.1.1.).

The chemical compositions of the waters and in particular, their Cl to Br ratios, provide the strongest line of evidence that they evolved from seawater by evaporation past halite saturation, with evidence for subsequent halite dissolution and/or dilution, as discussed below in section 7.3.1. Reactions between the water and rocks account for changes in non-conservative elements such as Cl (due to precipitation/dissolution of halite), Na, Ca, Mg, K and Sr. Assuming Br behaved conservatively during the evolution of these waters, the waters have been concentrated by up to 40 times relative to present-day seawater. Application of the mass balance approach of Wilson and Long (1993a, b) to waters within the regional database (section 6.1.4) suggests that dolomitization of calcite could account for much of the excess calcium and depletion in Mg observed in the brines relative to that expected for evaporated seawater. Wilson and Long (1993 a,b) also concluded that dolomitization was the dominant water-rock reaction which had influenced the composition of the brines in Devonian- and Silurian-aged formations in the Michigan Basin.

The stable isotopic signatures of oxygen and hydrogen in waters within the intermediate to deep system are significantly enriched relative to the Global Meteoric Water Line; a common characteristic of sedimentary basin fluids, which is thought to develop as a result of the evaporation of seawater and/or extensive water-rock interactions over geologic time. However, interpretation of the evolution of the brines based on the stable isotopic compositions of oxygen and hydrogen as a result of seawater evaporation is not unequivocal, in part because the δ^{18}O and δ^{2}H signature of seawater throughout geologic time is not well-defined and because a number of water-rock reactions can influence the isotopic signatures. Stable isotope data for waters from producing hydrocarbon wells in Devonian and Silurian-aged formations in central

Michigan was presented by Wilson and Long (1993a, b). The evolution of the isotopic composition ($\delta^{18}O$ and $\delta^{2}H$) of these waters was shown to be consistent with evaporation of seawater and possibly isotopic equilibrium with carbonate minerals (Wilson and Long, 1993a,b).

In several of the previous research studies on data included within the regional geochemical database, including Dollar (1988), Dollar et al. (1991) and Frape et al. (1989), it was observed that waters sampled from oil and gas-producing intervals in formations of a specific age and/or general rock type have stable water isotopic signatures ($\delta^{18}O$ and $\delta^{2}H$), which are clustered and unique, with little overlap in the ranges (Figure 25). The exception is overlap observed between a small number of waters from within the Ordovician carbonates and Cambrian sandstone reservoirs and is discussed further in the context of cross-formational flow in section 7.6.2.

The majority of waters from the Devonian-aged carbonates have strontium isotopic ratios within the range observed for Devonian-aged seawater (0.70780 to 0.70870). Waters sampled from within the Silurian salts (F salt and A2 salt) and from the Silurian Niagaran Formation in central Michigan have strontium isotopic signatures consistent with seawater during the Silurian (0.70800 to 0.70875); only three waters from Ordovician formations have $^{87}Sr/^{86}Sr$ values within the range for Ordovician seawater (0.70780 to 0.70900). The remaining waters from formations throughout the stratigraphic section have signatures which are enriched in $^{87}Sr/^{86}Sr$ relative to seawater at the time the formations were deposited. This enrichment was also observed by McNutt et al. (1987) for a sub-set of the waters included in the current database (details are provided in section 6.1.2). These authors concluded that the original seawater strontium isotopic signatures were modified by subsequent water-rock reactions, although a source for the radiogenic Sr was not identified. McNutt et al. (1987) observed that the $^{87}Sr/^{86}Sr$, $\delta^{18}O$ and $\delta^{2}H$ isotopic signatures of brines sampled from within Ordovician formations at the edge of the Michigan Basin in Ontario are similar to those sampled from the same formations deeper in the basin. This supports a model in which brine migration occurred over a distance of approximately two hundred kilometers, similar to models described for migration of hydrocarbons and fluids associated with MVT Pb-Zn deposits in other sedimentary basins (McNutt et al., 1987).

McNutt et al. (1987) also examined the strontium isotopic compositions of brines, the rock matrix and several late-stage diagenetic phases coexisting with the brines for core and brine samples from within the Cambrian (1 location) and the Ordovician-aged Trenton Formation in Ontario (3 locations). The rock matrix sample from the Cambrian had a $^{87}Sr/^{86}Sr$ ratio of 0.7330, whereas diagenetic calcite had a ratio of 0.7096, which is identical to the brine sampled from the same location. This indicates Sr isotopic equilibrium between the brine and the late-stage diagenetic phases, but not with the rock matrix. Matrix dolomite samples from three boreholes within the Ordovician Trenton Formation had strontium isotopic signatures within the range of Ordovician seawater; late stage dolomite, anhydrite and calcite were found to have $^{87}Sr/^{86}Sr$ ratios which were the same as those measured in the matrix dolomite. The exception was the brine which is currently present in the borehole, which has a distinct $^{87}Sr/^{86}Sr$ ratio. In this case, the whole-rock and diagenetic mineral phases have an Ordovician seawater Sr isotopic signature, suggesting that these phases may have equilibrated during burial diagenesis; whereas the brine is not in equilibrium with strontium in the rock matrix and diagenetic minerals. This disequilibrium suggests that the brine was emplaced after the formation of the diagenetic minerals.

7.3.1 Evidence for Halite Dissolution and Dilution

The potential for meteoric recharge into the sedimentary sequence has existed in the geologic past during erosional events in which different formations were exposed to meteoric conditions.

These erosional events are recorded as gaps in the sedimentary sequence underlying southwestern Ontario and correlate with orogenic events associated with plate tectonic activity (e.g. Mazurek, 2004). The most recent tectonic event in this region of North America was the Alleghenian Orogeny, which occurred between approximately 350 and 250 Ma BP (see also Figure 57).

Evidence for regional-scale dissolution of the Silurian-aged evaporites in southern Ontario was presented by Sanford et al. (1985). These authors suggest that dissolution of the evaporites began during the Late Silurian at the outer margins of the Michigan Basin. The most extensive period of salt dissolution is thought to have occurred near the end of the Late Silurian, coincident with Caledonian orogenic activity at the eastern margin of the North American continent (Sanford et al., 1985). Although there is evidence within the database for halite dissolution as described below, it is not known whether or not regional-scale salt dissolution during the Silurian contributed to the elevated Cl concentrations observed in the waters from the hydrocarbon reservoirs underlying southwestern Ontario. If the sedimentary formations themselves contain (or contained) halite as a primary or secondary mineral phase, dissolution of this halite would comprise a potential source for the excess Cl relative to Br in waters within the geochemical database, relative to the concentrations expected in evaporated seawater.

The evidence within the regional geochemical database for halite dissolution and dilution based on the major ion and stable isotopic compositions of waters within both the shallow and intermediate to deep systems is discussed below.

7.3.1.1 Shallow System

Within the shallow system, several waters sampled from the Devonian-aged Kettle Point and Hamilton shales and Devonian-aged carbonates at depths between 40 and 140 m in southwestern Ontario have Na:Cl molar ratios close to 1, suggesting that dissolution of halite may be the primary source for Na and Cl in these waters (section 6.1.2.2). These waters also have isotopic signatures which are typical of present-day meteoric water, plotting along the GMWL. In waters sampled from the Devonian-aged Antrim Shale at the northern margin of the Michigan Basin, McIntosh and Walter (2005) observed elevated Na and Cl concentrations relative to Br concentrations in seawater concentrated by evaporation. The authors propose that these waters likely evolved from meteoric waters by dissolution of halite and mixing with remnant Silurian-Devonian brines, as proposed for waters within the Illinois Basin by Walter et al. (1990). The observed Cl:Br and Na:Br relationships and stable isotopic signatures ($\delta^{18}O$, $\delta^{2}H$) of waters from the Kettle Point and Hamilton shales and from the Devonian carbonates in southwestern Ontario with Na:Cl molar ratios close to unity are consistent with a similar evolutionary model.

7.3.1.2 Intermediate to Deep Groundwater System

In Figure 55, chloride concentrations measured in the waters are plotted on a linear scale against the measured Br concentrations (mg/L). In this figure, chloride concentrations above those expected for seawater concentrated by evaporation past halite saturation are observed for many waters within the intermediate to deep groundwater system (>200 m bgs). This includes waters sampled from hydrocarbon reservoirs within the Devonian-aged sandstone (Berea Formation, Central Michigan), almost all waters from the Silurian carbonate formations and several from within Silurian-aged sandstones, waters from the Silurian F and A2 salts, several waters from the Ordovician carbonates and sandstones and three waters sampled from the

Cambrian sandstones. This observed excess of Cl relative to Br compared to that expected for evaporated seawater could be explained by dissolution of halite by the evaporated brines. However, unlike the waters from the shallow systems, the Na to Cl molar ratios in the deep waters are below the 1:1 ratio expected if the dominant source of Cl in these waters was from halite dissolution (Figure 56). Assuming the excess chloride (relative to evaporated seawater) in these waters originated by halite dissolution, the Na concentrations in waters from the intermediate to deep system have been reduced, likely as a result of water-rock reactions (section 3.1.2) over long residence times.

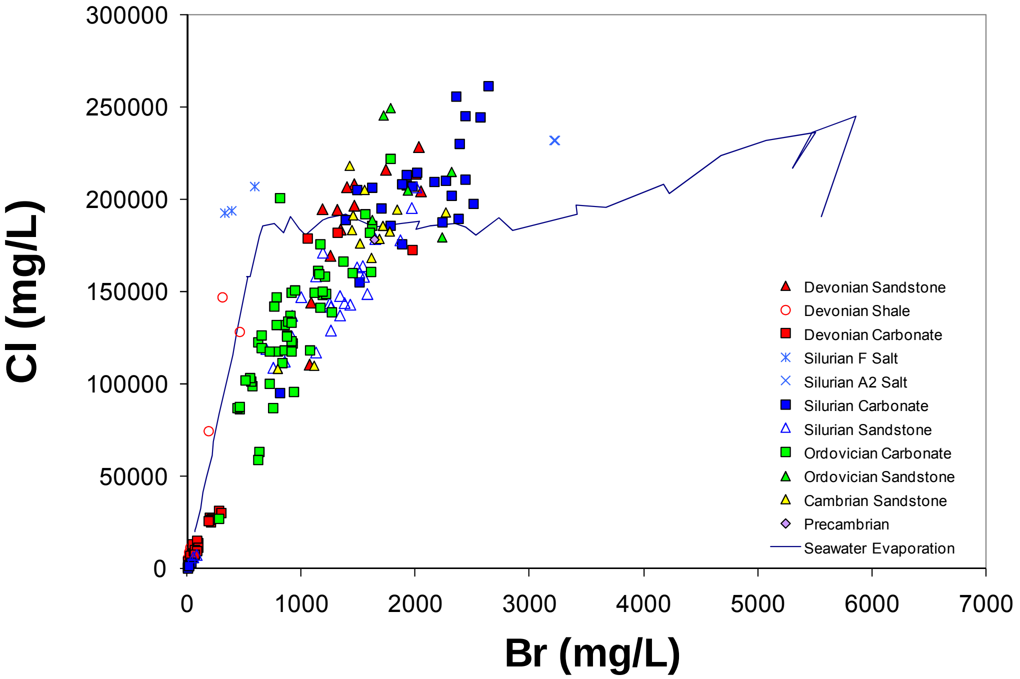


Figure 55: Concentrations of Cl and Br in mg/L measured for waters in the geochemical database, plotted on a linear scale.

The Cl and Br compositions of several waters from within the intermediate to deep system can be simulated using mass balance calculations by assuming evolution from an end-member brine (seawater concentrated by evaporation) and subsequent dilution with seawater or meteoric water, with or without a portion of total Cl from the dissolution of halite, as described in detail in sections 6.1.2.3 and 6.1.2.4. For a series of Na-Ca-Cl type waters sampled from Silurian sandstones in the Appalachian Basin (center and east end of Lake Erie in Figure 5), a maximum degree of dilution of 60% was calculated based on Cl and Br concentrations. For Ca-Na-Cl type waters sampled from within the same formations, it was shown that mixing of a brine-end member with a maximum of 50% meteoric water can be used to simulate the Cl and Br concentrations in the waters, if 30% of the Cl is assumed to originate from halite. However, although the range of δ^{18}O values observed in waters from the sandstone formations could be consistent with dilution by meteoric waters, the δ^{2}H values in the measured waters are enriched in ^{2}H relative to those expected for mixing with even the most enriched present-day meteoric waters (δ^{2}H = -50‰). The reason for the observed enrichment in δ^{2}H in these waters is not known.

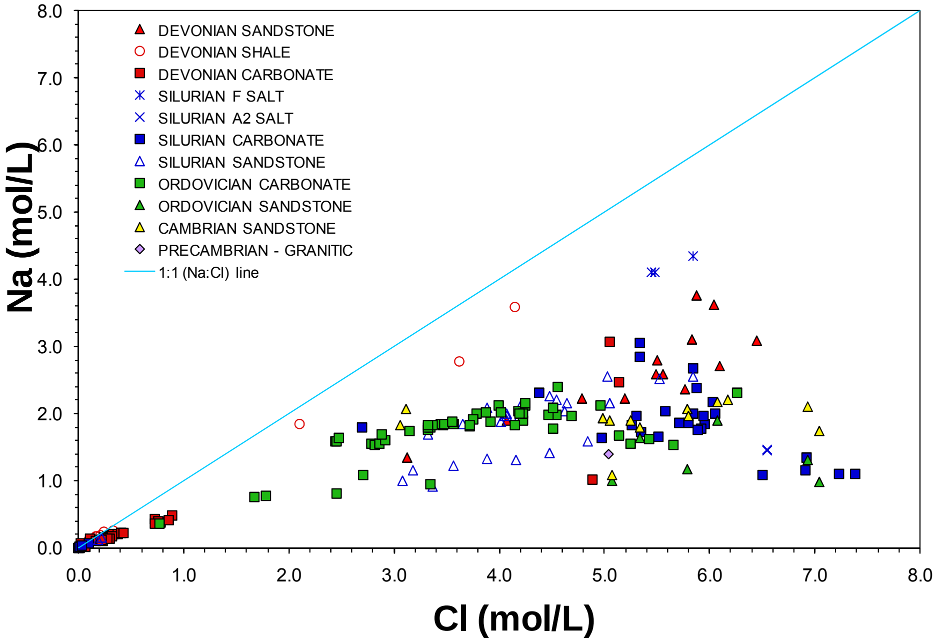


Figure 56: Sodium versus chloride concentrations (in moles/L) measured in waters within the geochemical database. The 1:1 Na:Cl line shows the expected Na concentrations for a given chloride concentration assuming congruent dissolution of halite.

Similarly, for several waters sampled from the Ordovician carbonates, Cl and Br concentrations could be predicted by mixing of an end-member brine with a maximum of 40% meteoric water, or by dilution of an end-member brine with a maximum 50% meteoric water and assuming 20% of the total Cl in these waters is from halite. Only five of the waters sampled in southeastern Michigan (OT-21, OT-39, OT-40, OT-41 and OT-42) have oxygen and hydrogen isotopic signatures which are shifted slightly towards the meteoric water line. The mass balance calculations indicated that this observed shift could result from mixing with less than 10% meteoric water. For these samples, mixing of this small percentage of meteoric waters with the brines as a result of hydrocarbon production cannot be discounted. The remainder of the waters in these apparent dilution trends have δ^{18}O and δ^{2}H signatures which are clustered together with the concentrated, “end-member” waters from the Ordovician carbonates, which are enriched relative to the Global Meteoric Water Line (Figure 38). This suggests that dilution occurred in the geologic past, perhaps in association with erosional events. The oxygen and hydrogen stable isotopic signatures of these waters have since been altered by water-rock interactions (section 7.3) over long groundwater residence times.

7.3.2 Major Ion Composition and Source Formation

An examination of the water types given in Table 7 illustrates that a specific formation or group of formations are not generally characterized by the occurrence a single water type, with the following exceptions:

- Na-Ca-Cl type waters in the Devonian Berea Formation
- Ca-Na-Cl type waters in the Devonian Richfield Formation (one sample)
- Na-Cl type waters in the Salina F Salt (3 samples)

- Ca-Na-Mg-Cl type waters in the Salina A2 Salt (2 samples)
- Ca-Na-Cl type waters in the Silurian Whirlpool and Salina A1 Carbonate
- Na-Ca-Cl type waters in the Thorhold Formation

In Ordovician-aged formations of the Trenton-Black River Group, waters associated with hydrocarbons are predominantly Na-Ca-Cl type, with several exceptions:

- Ca-Na-Cl type waters sampled in southcentral Michigan (OT-30)
- Ca-Cl type waters from the Prairie du Chien sandstone (OP-1 and OP-2) sampled at depths of approximately 3300 m
- Waters sampled at depths of 50 and 85 m from packered intervals in the Lindsay and Veralum formations in the UN-2 and OHD-1 wells at the eastern edge of the study area. Both Na-Ca-Cl and Ca-Na-Cl type waters were sampled from the Veralum formation; Ca-Na-Mg-Cl water was sampled from the Bobcaygeon formation.

Waters sampled from the Cambrian-aged formations are associated with hydrocarbons and are Ca-Na-Cl type waters, with the exception of one sample (C-6 in Table 7), which is a Na-Ca-Cl type water. The occurrence of a given water type, particularly Na-Ca-Cl or Ca-Na-Cl type waters does not appear to be related to the general lithology of the reservoir, for example sandstone versus carbonate lithology.

7.4 Comparison to Hydrogeologic Models

In North America, the zone of active groundwater flow in sedimentary basins occurs predominantly in glacial drift aquifers and in shallow fractured rock (Person et al., 2007). The relatively low topographic relief in many sedimentary basins and consequently, low hydraulic gradients limits groundwater flow depths of 50 to 100 m (McIntosh and Walter, 2005). In addition, the presence of groundwaters with elevated salinities at greater depths and the resulting density gradient inhibits groundwater flow into deeper units (Mazurek, 2004). The general, two-layer conceptual model proposed in this study for the regional scale is consistent with the conceptual hydrogeologic model suggested by Mazurek (2004), in which the bands along which formations outcrop (Figure 3) represent the potential recharge or discharge areas in shallow bedrock aquifers.

At the sub-regional scale, a three-layer hydrogeologic model is proposed (Sykes et al., 2008), which includes shallow, intermediate and deep groundwater zones. The shallow groundwater system is considered to include the Devonian- and Upper Silurian-aged carbonates, which occur at depths of up to approximately 180 m (to the top of the Salina F-shale) in the sub-regional study area defined by Sykes et al. (2008). This is consistent with the shallow groundwater zone defined at the regional scale by the geochemical data presented here, although at a regional scale, the formations which comprise this shallow zone will be progressively older towards the east in Ontario as a result of the changing stratigraphy (section 7.1).

Sykes et al. (2008) further defined an intermediate and a deep groundwater zone in the sub-regional study area which consist of Silurian-aged strata and Ordovician through Cambrian strata, respectively. In the regional geochemical database, the majority of information on the chemical compositions of waters in the intermediate to deep zone at greater than 200 m is for waters associated with producing hydrocarbon reservoirs. Reservoirs within particular formations are often concentrated in particular areas of southwestern Ontario, as a result of the geologic (stratigraphic and structural) controls on their occurrence. Although the regional geochemical database provides information on the spatial distribution of waters and their occurrence as a function of depth across southwestern Ontario, it does not provide information down through the stratigraphic section in one specific location or sub-regional area. In general terms, the intermediate to deep system defined on the basis of the regional geochemical data base encompasses both the intermediate and deep groundwater zones as defined by Sykes et al. (2008).

7.5 Stability of the Intermediate to Deep System

7.5.1 Origin of Waters

The majority of waters in the intermediate to deep system at depths of greater than 200 m are brines (>100,000 mg/L TDS) associated with hydrocarbons which were sampled from producing reservoirs. The presence of these reservoirs is a result of the local occurrence of structural or stratigraphic (Ordovician-Cambrian aged) reservoirs, pinnacle-reefs (Silurian-aged), or collapse structures (Devonian-aged formations) which contain zones of enhanced permeability in which these fluids have accumulated, and which have been trapped by overylying and adjcent rocks of low permeability (e.g. Sanford et al., 1985; Carter et al., 1996).

The chemical compositions of waters in the intermediate to deep system are predominantly either Ca-Na-Cl or Na-Ca-Cl type. Based on evidence from fluid inclusions, the fluids involved in dolomitization in the Ordovician formations are NaCl-$MgCl_2$-$CaCl_2$ type fluids, with salinities in the range of 16 to 41 wt. % NaCl (Coniglio et al., 1994). The temperatures of between 70 and 220 °C determined for primary fluid inclusions indicate that these fluids were hydrothermal (i.e. temperatures > 100 °C). In Silurian-aged formations, fluid inclusions suggest that dolomitizing fluids were Na-Ca-Mg-Cl brines with salinities between 14 and 30 wt.% NaCl and temperatures between 65 and 130 °C (Coniglio et al., 2003). The general similarity in the range of salinities and the composition of the fluids involved in dolomitization with the compositions of the Na-Ca-Cl, Na-Ca-Mg-Cl or Na-Mg-Ca-Cl type waters occurring in association with hydrocarbons in the subsurface is an additional line of evidence supporting the interpretation of these waters as diagenetic in origin.

Sherwood Lollar et al. (1994) suggested that elevated He concentrations and $^{3}He/^{4}He$ ratios in gases from Ordovician and Cambrian reservoirs may indicate a source of methane from within the underlying crystalline basement. This raises the question of whether there is geochemical evidence in the chemical or isotopic composition of the waters from within these hydrocarbon reservoirs for mixing with other fluids from within Precambrian basement. Deep groundwaters sampled from crystalline rocks of the Canadian Shield are typically Ca-Na-Cl brines (Frape and Fritz, 1987; Frape et al., 1984), while waters associated with hydrocarbons in sedimentary systems are typically Na-Ca-Cl type (Kharaka and Thordsen, 1992), although Ca-Na-Cl type waters also occur. Waters from both environments may have Br/Cl ratios which are elevated compared to those predicted for evaporated seawater. However, brines from within crystalline rocks of the Canadian Shield have $\delta^{18}O$ and $\delta^{2}H$ signatures which are enriched in $\delta^{2}H$ (or depleted in $\delta^{18}O$) relative to the GMWL. These waters plot above and to the left of the GMWL. Based on extrapolations of measured isotopic compositions, Frape and Fritz (1987) estimated that the concentrated end-member brine in the crystalline shield would have $\delta^{18}O$ values between -10 and +7‰ and $\delta^{2}H$ values between -20 and 0‰. Assuming halite saturation in the brines, Pearson (1987) refined these estimated ranges to between -8.3 and -9.1‰ for $\delta^{18}O$ and $\delta^{2}H$ values between +10 and -10‰ and demonstrated that these values could result from an approach to water-rock equilibrium with silicate rocks at 25 °C. Waters associated with hydrocarbons in the sedimentary formations underlying southwestern Ontario are more enriched in $\delta^{18}O$, with values between -6 and +3‰, plotting below and to the right of the GMWL. On the basis of their enriched $\delta^{18}O$ signatures, waters in the geochemical database reported here are consistent with typical brines from within sedimentary basins. However, in the case of waters sampled from Cambrian-aged formations, the δ^{18}O are depleted (or δ^{2}H values are enriched) relative to those observed for waters from the Ordovician-formations, plotting closer to the meteoric water line (e.g. Figure 37), which may suggest that mixing with brines characteristic of the underlying Precambrian crystalline rock has influcenced their stable isotopic composition (δ^{18}O, δ^{2}H).

The working hypothesis for waters associated with hydrocarbons in the intermediate to deep system is that they are diagenetic fluids. There are two different evolutionary histories for these waters which could be considered consistent with the geochemical evidence:

1. The waters formed in-situ as the result of extensive seawater evaporation in the basin, which lead to entrapment of waters in the rocks either during sedimentation or compaction. The compositions of these waters were altered by water-rock interactions during diagenesis; or
2. The waters are remnants of hydrothermal fluids from deeper within the sedimentary basin(s) which migrated into the stratigraphic or structural traps along permeable pathways (permeable sandstone formations, fractures or other areas of enhanced porosity such as reef-structures in Silurian carbonates).

In the current scientific understanding of the emplacement of diagenetic fluids associated with dolomitization, MVT massive sulphide deposits and hydrocarbons, the presence of driving forces which are sufficient to transport dense brines from deep within the sedimentary basins to the margins along regional aquifers and other permeable pathways such as fractures or faults is a key constraint on the timing of fluid movement. Although various conceptual models for fluid flow have been proposed (section 4.5.3), a common element is that the majority of the proposed driving forces are associated with tectonic or orogenic events. As illustrated in Figure 57, the most recent tectonic event in this region of North America was the Alleghenian Orogeny, which occurred between approximately 350 and 250 Ma BP.

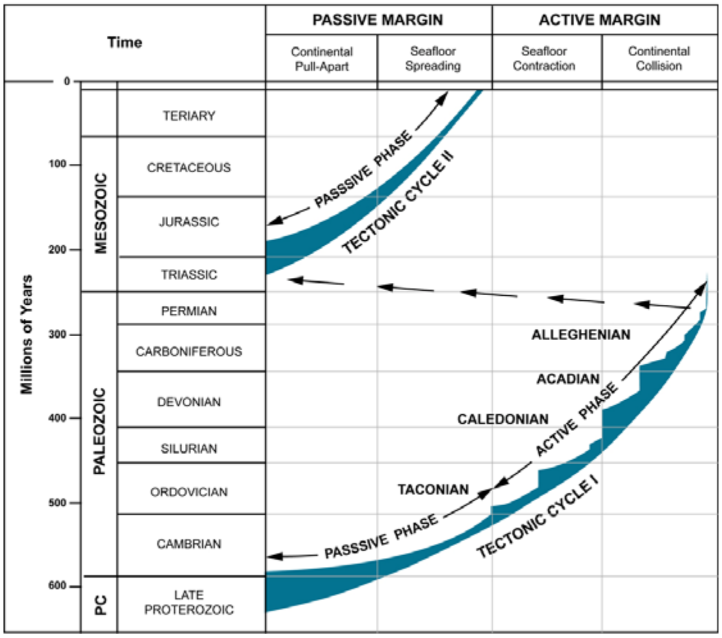


Figure 57: Phanerozoic Tectonic Cycles. The band widths represent relative tectonic intensity (Sanford, 1993).

A Late Paleozoic to Early Mesozoic (350 to 250 Ma BP) time-frame has been proposed for both the emplacment of MVT Pb-Zn deposits in Silurian strata in southern Ontario (Farquhar et al., 1987) and for the formation of fracture-related dolomitization and hydrocarbon migration in the Michigan Basin in Ordovician formations, likely as a result of Alleghenian deformation and thrusting events (Prouty 1988; Hurley and Budros 1990; Budai and Wilson 1991). Coniglio et al. (1994) observed solid hydrocarbons coating saddle dolomite and late-stage calcite cement, supporting a close association between hydrocarbon migration into the Ordovician reservoir rocks in Ontario and these late-stage diagenetic phases. This is also consistent with the findings of Budai and Wilson (1991) for samples from the Trenton and Black River Groups in the central Michigan Basin.

The observation that hydrocarbons within Ordovician-aged reservoirs have remained trapped since emplacement approximately 250 Ma BP provides a strong argument for the stability of intermediate to deep system over geologic time frames. The distinct ranges of $\delta^{18}O$ and $\delta^{2}H$ signatures observed for waters from reservoirs of different ages and/or lithologies may reflect varying degrees of equilibration of the emplaced brines with the surrounding rock matrix. The persistence of these distinct isotopic signatures suggests that at a regional-scale, equilibration between reservoirs (for example, via diffusion-dominated transport) has not been achieved across the stratigraphic section.

7.5.2 Evidence for Cross-Formation Flow

The majority of evidence for flow between formations in southern Ontario involves fluids associated with diagenesis within the Michigan and Appalachian Basins (section 4.0). The exception is localized occurrences of hydrocarbons and associated brines within the Pleistocene glacial tills (Weaver et al., 1992), which likely occurred either during the later stages of the Wisconsian glaciations, or during or after deglaciation approximately 10,000 BP.

Evidence for cross-formational flow of diagenetic fluids includes clay alteration of the upper most Precambrian basement rocks and overlying Cambrian and Ordovician rocks, calcite veins precipitated in the Lockport dolomite, dolomitization of Ordovician and Silurian formations, Mississippi-type sulphide deposits and emplacement of hydrocarbons within structural, stratigraphic or diagenetic (HTD) type traps in formations of Cambrian, Ordovician, Silurian or Devonian age. Direct dating of K-feldspars associated with the oldest observed clay alteration dates this event at approximately 444 Ma ago (Harper et al., 1995). Based on textural evidence, hydrocarbon emplacement post-dates dolomitization in the Silurian reservoirs of southwestern Ontario and was essentially the last process to occur after halite and anhydrite deposition, with the exception of some localized pressure-dissolution and re-precipitation of evaporites that post-dates hydrocarbon emplacement in some areas (Coniglio et al., 2003). The formation of fracture-related dolomitization and hydrocarbon migration in the Michigan Basin in the Ordovician formations are considered to be contemporaneous, and were likely the result of the Alleghenian deformation and thrusting events taking place in the east during the Late Paleozoic to Early Mesozoic between 350 and 250 Ma BP (Prouty, 1989; Hurley and Budros 1990; Budai and Wilson 1991). Coniglio et al. (1994) observed solid hydrocarbons coating saddle dolomite and late-stage calcite cement, supporting a close association between hydrocarbon migration into the Ordovician reservoir rocks and these late-stage diagenetic phases. This is also consistent with the findings of Budai and Wilson (1991) for samples from the Trenton and Black River Groups in the central Michigan Basin.

Frape et al. (1989) observed that waters from producing hydrocarbon reservoirs have distinctive $\delta^{18}O$ and $\delta^{2}H$ isotopic signatures depending on the geologic unit which hosts the reservoir. The only overlap observed was between waters from the Cambrian-aged sandstones, Ordovician-aged carbonates and a limited number waters from Silurian-aged sandstones or carbonates. In the geochemical database, the two waters from Cambrian reservoirs which fall within the isotopic range observed for waters from Ordovician formations are samples C-6 and C-11 (Appendix B). Water sample C-6 is the only Na-Ca-Cl type water; the remaining waters from Cambrian reservoirs are Ca-Na-Cl type. The overlap in the isotopic compositions of waters sampled from Cambrian and Ordovician reservoirs observed by Frape et al. (1989) is generally consistent with examinations of the oil compositions by Powell et al. (1984), in which oil from Cambrian and Ordovician formations could not be distinguished. Based on the Ca/Na ratios and Total Dissolved Solids of the brines, Frape et al. (1989) proposed large-scale migration of a Na-Ca-Cl brine (TDS 150 g/L) from the south into both the Michigan and Appalachian basins, perhaps along large fracture systems or basement highs, which mixed with Ca-Na-Cl type fluids present in these two basins. These authors also noted a correspondence between the major trends for ingress of the Na-Ca-Cl waters and the largest producing hydrocarbon reservoirs in Ordovician- and Cambrian-aged formations. Frape et al. (1989) orginally proposed that the dilute Na-Ca-Cl brines had mixed across all units, including Ordovician carbonates, Cambrian and Silurian sandstones and Silurian carbonates. The observed limited overlap between the isotopic compositions of the waters from different formations as reported by Frape et al. (1989) and in this report suggests that mixing across these formations was limited and localized.

Although oils from reservoirs within the Cambrian-Ordovician, Silurian and Devonian-aged formations are reported to have distinct compositions (Powell et al., 1984), anomalies were identified for reservoirs within the Silurian-aged A1-Carbonate. Oil in the Fletcher Reservoir was identified as belonging to the Cambro-Ordovician family, and oil in the Mosa Reservoir was found to be a mixture of Cambro-Ordovician and Silurian oils. Obermajer et al. (1999) also reported evidence for cross-formational flow between the Ordovician and Silurian units and possibly some relationship between the overlying Devonian oils and the Ordovician source rocks. The presence of Cambrian-Ordovician oils in Silurian reservoirs suggests that at least locally, some cross-formational flow of hydrocarbons occurred between reservoirs. Although the timing of these cross-formational flow events is not directly known, the requirement for sufficient driving forces for movement of these fluids suggests that these events occurred in association with tectonic or orogenic events; the most recent event being the Alleghenian Orogeny, which ended approximately 250 Ma BP.

The occurrence of hydrocarbons and saline waters within the Pleistocene clay-rich glacial deposits which overlie the sedimentary bedrock formations in Ontario demonstrates that flow of these fluids occurred either during the later stages of, or after the Wisconsinan glaciation. Weaver et al. (1995) presented indirect evidence for localized mixing between waters similar (but more dilute) than those from the Silurian A2 Evaporite unit with a glacial recharge water to explain the observed chemical and isotopic signature of groundwaters from the Oil Springs field sampled within the Devonian-aged Dundee carbonate. Weaver et al. (1995) proposed a conceptual model in which isostatic rebound led to the creation of new fractures or reactivated or enlarged existing fractures in Paleozoic formations. In this model, meteoric water with low δ^2H and δ^{18}O values (cold-climate waters) could enter Devonian- or Silurian-aged formations where they subcropped during glaciation or deglaciation and mix with Silurian brines along fracture pathways (Weaver et al., 1995). In a second stage of mixing, the previously mixed, saline waters with depleted δ^2H isotopic signatures derived from the underlying Silurian salt formations migrated vertically from depths of several hundred meters into the oil-bearing Devonian formations. Weaver et al. (1995) note that the limited occurence of the low δ^2H, high TDS fluids suggests that migration of the mixed brine/glacial fluid probably occurred along discrete fractures.

7.6 Transferability to the Regional Study Area

Within the regional study area (Figure 3), the potential for hydrocarbon resources in Devonian, Silurian, Ordovician and Cambrian formations is considered to be low (Gartner Lee Limited, 2008b). This is related in part to the fact that all the hydrocarbon trapping styles are associated with or controlled by faults and fractures and to date, there is no evidence in the regional study area (RSA) to suggest the presence of active faults or the potential for reactivation of pre-existing faults in the Precambrian basement or in the Paleozoic cover (Gartner Lee Limited, 2008b). Consequently, groundwaters, porewaters within the rock matrix and fluid inclusions from diagenetic mineral phases are expected to be the dominant sources for information on chemical and isotopic compositions of waters in the sedimentary sequence within the RSA, rather than waters associated with hydrocarbons, as is the case in southwestern Ontario and in the geochemical database presented within this report. There are two lines of reasoning which suggest that the geochemical database presented in this report provides a reasonable starting point for the interpretation of site-specific geochemical data:

- Waters sampled from isolated intervals in multilevel wells completed within Ordovician-aged formations at Lakeview and Darlington (Sherwood Lollar and Frape, 1989) are Na-Ca-Cl or Ca-Na-Cl type with TDS values (uncorrected for drilling fluid contamination) of between 44,000 and 304,000 mg/L. Mass balance calculations for Cl/Br and δ^{18}O and δ^{2}H show that the chemical and isotopic compositions of these waters could be derived from waters typical of these formations where they occur deeper in the basin by dilution with surface waters used during drilling. The good agreement between the chemical composition and salinities of these groundwaters and those sampled within producing hydrocarbon wells suggests that waters associated with hydrocarbons can be used to estimate the compositions of groundwaters sampled from the same formations elsewhere in the basin, where hydrocarbons are absent.

- It is expected that diagenetic processes, such as dolomitization, identified as important influences on water compositions in the sedimentary sequence underlying southwestern Ontario (this study) and elsewhere in the Michigan Basin (Wilson and Long, 1993a,b) will also be dominant influences on the chemical and isotopic compositions of the porewaters and deep groundwaters in the RSA. It is therefore anticipated that the chemical and isotopic information on waters from the regional geochemical database will provide a reasonable basis for comparison with site-specific data generated within the RSA.

Demonstration of the transferability of the regional hydrogeochemical information to the regional study area will require comparison to site-specific groundwater data from the DGR site-characterization activities, which are currently underway.

8. CONCLUSIONS

In this study, a regional database of chemical and isotopic water compositions has been assembled, which includes published and previously unpublished data from research conducted over 25 years at the University of Waterloo, Ontario, Canada. The database contains information on 202 waters sampled from depths between 40 and 3500 m below ground surface in southern Ontario and in Michigan. The shallow wells included in this study are limited to research wells which intersect bedrock, because much of the original research was focused on understanding the nature and origin of saline waters deeper in the sedimentary sequence.

From an assessment of this database, two geochemical systems are recognized at the regional-scale:

i) A shallow system (<200 m) m below ground surface containing fresh through brackish waters classified as Na-Cl, Na-Mg-Ca-Cl or Ca-SO_4 type based on major ion concentrations. Waters in this system have stable isotopic compositions of $\delta^{18}O$ and $\delta^{2}H$ consistent with mixing of dilute recent or cold-climate (glacial) waters with more saline waters;

ii) An intermediate to deep system (>200 m) containing brines associated with hydrocarbons in reservoirs which are characterized primarily by Na-Ca-Cl or Ca-Na-Cl type waters with elevated TDS values (200,000-400,000 mg/L). The stable oxygen and hydrogen values of these waters are typical of sedimentary basin brines in that they are enriched relative to the GMWL ($\delta^{18}O$ values between -6 and +3 ‰ and $\delta^{2}H$ values between -55 and +20 ‰).

On the basis of mass balance calculations, it was shown that the composition of waters within the shallow system could be derived from waters having Cl and Br concentrations and isotopic signatures which are distinct and characteristic of the waters sampled from within the same formations where they occur at greater depths in the basins by dilution with meteoric water (recent or glacial meltwater).

The maximum depth at which waters with isotopic signatures indicative of present-day meteoric origin are observed in the database is 140 m below ground surface. In Ontario, the maximum depth from which glacial waters have been observed in shallow bedrock aquifers is 130 m below ground surface in wells of the Alliston aquifer (Aravena et al., 1995). Within the regional geochemical database, the maximum depth at which glacial waters are observed is 100 m below ground surface. Along the northern and western margins of the Michigan Basin and the northern margin of the Illinois Basin, glacial recharge has been observed to depths of 300 m below the subcrop of the Antrim (MB) or New Albany (IB) shale formations in groundwaters associated with microbial methane gas reservoirs (McIntosh and Walter, 2006). There is no evidence for significant dilution of formation fluids within the Antrim Shale (or the Kettle Point Formation in Ontario) by meteoric recharge, or for microbial methanogenesis in central Michigan or at the eastern margin of the Michigan Basin (McIntosh et al., 2004).

The chemical compositions of waters in the intermediate to deep system are predominantly either Ca-Na-Cl or Na-Ca-Cl type. The presence of methane gas in hydrocarbon reservoirs suggests that the redox conditions are reducing in this system. The major ion composition of waters from the intermediate to deep system, in particular Cl and Br concentrations support the interpretation that these waters evolved from seawater by evaporation past halite saturation, with limited evidence for recent dilution by meteoric or glacial waters. Increased Ca concentrations and decreased Mg concentrations relative to seawater are consistent with dolomitization reactions between these waters and calcite within the carbonate formations. This finding is consistent with the interpretation of Wilson and Long (1993 a,b) for waters from Devonian and Silurian formations in central Michigan, where dolomitization was identified as the dominant water-rock reaction influencing the evolution of waters associated with hydrocarbons. Dolomitization is also identified as the most significant diagenetic influence on the Paleozoic strata to have occurred post-lithification (Gartner Lee Limited, 2008b).

Based on evidence from fluid inclusions, the fluids involved in dolomitization in the Ordovician formations are $NaCl$-$MgCl_2$-$CaCl_2$ type fluids, with salinities in the range of 16 to 41 wt. % NaCl (Coniglio et al., 1994). The temperatures of between 70 and 220 °C determined for primary fluid inclusions indicate that these fluids were hydrothermal (i.e. temperatures > 100 °C). In Silurian-aged formations, fluid inclusions suggest that dolomitizing fluids were Na-Ca-Mg-Cl brines with salinities between 14 and 30 wt.% NaCl and temperatures between 65 and 130 °C (Coniglio et al., 2003). The general similarity in the range of salinities and the composition of the fluids involved in dolomitization with the compositions of waters occurring in association with hydrocarbons in the subsurface is an additional line of evidence supporting the interpretation of these waters as diagenetic in origin. An initial study of fluid inclusions in fluorite from the Silurian-aged Lockport formation suggest that the mineralizing fluids associated with MVT deposits in southern Ontario had temperatures within the range of 132 to 142 °C (Kinsland, 1977). These temperatures are consistent with the upper range of temperatures reported for fluids associated with dolomitization in Silurian-aged formations (Coniglio et al., 2003). Elevated temperatures may have been generated in the basin due to deep burial by Carboniferous and Permian sediments which have since been eroded. At the basin margins, at least 1,000 m of sdiement has been eroded. However, even burial depths of 2,000 m would have produced burial temperatures of <70 °C in southwestern Ontario (Gartner Lee Limited, 2000b). The interpretation that hydrothermal fluids were involved in both dolomitization and the formation of MVT deposits in Silurian-aged formations is therefore considered more consistent with the thermal and burial history of the sedimentary sequence.

In the intermediate to deep system, waters that occur in association with hydrocarbons are interpreted as diagenetic fluids. There are two different evolutionary histories for these waters that are considered consistent with the geochemical evidence:

1. The waters formed in-situ as the result of extensive seawater evaporation in the basin, which lead to entrapment of waters in the rocks either during sedimentation or compaction during burial; or
2. The waters are remnants of hydrothermal fluids formed deeper within the sedimentary basin(s) that migrated into the stratigraphic or structural traps along permeable pathways (permeable sandstone formations, fractures or other areas of enhanced porosity e.g. reef-structures in Silurian carbonates).

In the current scientific understanding of the emplacement of diagenetic fluids associated with dolomitization, MVT massive sulphide deposits or hydrocarbons, the presence of driving forces which are sufficient to transport dense, hydrothermal brines from deep within the sedimentary basins to the margins along regional aquifers and other permeable pathways such as fractures or faults is a key constraint on the timing of fluid movement. The majority of the driving forces proposed for basin-scale fluid flow were present during diagenesis (e.g. compaction-driven flow, gas generation) or were associated with orogenic events (e.g. topographically-driven flow, thermal convection). In the Michigan and Applachaian basins, the most recent orogenic event was the Alleghanian Orogeny between approximately 350 and 250 Ma BP. A Late Paleozoic to Early Mesozoic (350 to 250 Ma BP) time-frame has been proposed for both the emplacment of MVT Pb-Zn deposits in Silurian strata in southern Ontario (Farquhar et al., 1987) and for the formation of fracture-related dolomitization and hydrocarbon migration in the Michigan Basin in Ordovician formations, likely as a result of Alleghenian deformation and thrusting events (Prouty 1988; Hurley and Budros 1990; Budai and Wilson 1991).

The most recent evidence for cross-formation flow is the localized occurrences in the shallow system of hydrocarbons and associated brines within the Pleistocene glacial tills in Lambton County, Ontario (Weaver et al., 1992). The fact that oil occurs in the glacial tills constrains the timing of this fluid movement to the later stages of the Wisconsian glaciation, or after deglaciation approximately 10,000 BP. Indirect evidence for localized mixing between waters similar (but more dilute) than those from the Silurian A2 Evaporite unit with a glacial recharge water was presented by Weaver et al. (1995) to explain the observed chemical and isotopic signature of waters from the Oil Springs field sampled within the Devonian-aged Dundee carbonate. These authors proposed that previously mixed, saline waters with depleted δ^2H isotopic signatures derived from the underlying Silurian salt formations migrated vertically along local fracture networks from depths of several hundred meters into the oil-bearing Devonian formation during or after the last deglaciation.

In the intermediate to deep system, evidence for cross-formational flow is associated with fluid movement during diagenesis. This includes fluids involved in clay alteration of the upper most Precambrian basement rocks and in the overlying Cambrian and Ordovician rocks, calcite veins precipitated in the Lockport dolomite, dolomitization of Ordovician and Silurian formations, Mississippi-type sulphide deposits and emplacement of hydrocarbons within structural, stratigraphic or diagenetic (HTD) type traps in formations of Cambrian, Ordovician, Silurian or Devonian age. The presence of Cambrian-Ordovician oils in a limited number of Silurian reservoirs suggests that at least locally, some cross-formational flow of hydrocarbons occurred between reservoirs. Although the timing of these cross-formational flow events is not directly known, the requirement for sufficient driving forces for movement of these fluids suggests that these events occurred in association with tectonic or orogenic events; the most recent event being the Alleghenian Orogeny, which ended approximately 250 Ma BP.

The observation that hydrocarbons in Ordovician-aged formations have remained trapped since emplacement over 250 Ma BP provides a strong argument for the stability of the intermediate to deep system in the sedimentary sequence underlying southern Ontario. Although it is not possible to interpret with certainty the various processes which have influenced the stable isotopic compositions of oxygen and hydrogen during the evolution of the brines, the δ^{18}O and δ^2H signatures of brines from reservoirs from formations of different ages and lithologies (e.g. carbonate versus sandstone) are observed to cluster in distinct ranges (Dollar et al., 1991; Frape et al., 1989; Dollar, 1988). The persistence of these distinct isotopic signatures at a regional-scale suggests that the brines and associated hydrocarbons have remained isolated from one another over geologic time frames.

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APPENDIX A: Technical Procedures for Analysis of Stable Isotopes

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A.1 Chlorine-37

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DEPARTMENT OF EARTH SCIENCES
UNIVERSITY OF WATERLOO

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DEPARTMENT OF EARTH SCIENCES
UNIVERSITY OF WATERLOO

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A.3 Oxygen-18

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A.4 Hydrogen-2

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APPENDIX B: Regional Geochemical Database

Table 1

Author	Sample ID	AGE - FORMATION	Rock Type	Water Type$^+$	Depth m	pH	Temp. °C	DIC mg/L	DOC mg/L	Fluid Density g/cm^3	Spec .Conduct. mhos	Charge Error (%)*	Ca mg/L	Na mg/L	Mg mg/L	K mg/L	Sr mg/L	Cl mg/L	Br mg/L
Dollar (1988)	MB-1	DEVONIAN - BEREA	Sandstone	Na-Ca-Cl	746	-	-	-	-	-	-	-1.48	41000	51000	8800	800	1540	184000	1340
Dollar (1988)	MB-2	DEVONIAN - BEREA	Sandstone	Na-Ca-Cl	760	-	-	-	-	-	-	-0.03	44000	59000	9200	860	1750	197000	1460
Dollar (1988)	MB-3	DEVONIAN - BEREA	Sandstone	Na-Ca-Cl	738	-	-	-	-	-	-	-0.38	38000	51000	7500	730	1530	170000	1250
Dollar (1988)	MB-4	DEVONIAN - BEREA	Sandstone	Na-Ca-Cl	737	-	-	-	-	-	-	0.12	33000	44000	6300	550	1340	144000	1080
Dollar (1988)	MB-5	DEVONIAN - BEREA	Sandstone	Na-Ca-Cl	728	-	-	-	-	-	-	-1.45	41000	60000	8100	700	1570	194000	1310
Dollar (1988)	MB-6	DEVONIAN - BEREA	Sandstone	Na-Ca-Cl	723	-	-	-	-	-	-	-3.10	35000	64000	7100	800	1210	195000	1180
Walter (Pers. Comm.)	BRENNAN 122	DEVONIAN - BEREA	Sandstone	Na-Ca-Cl		-	-	-	-	-	-	-2.85	45000	54000	9600	690	1740	200000	2000
Walter (Pers. Comm.)	CAMPBELL #7	DEVONIAN - BEREA	Sandstone	Ca-Na-Cl		-	-	-	-	-	-	6.08	63000	71000	12300	710	2200	230000	2000
Walter (Pers. Comm.)	CAMPBELL #9	DEVONIAN - BEREA	Sandstone	Ca-Na-Cl		-	-	-	-	-	-	2.68	55000	62000	10700	2400	2100	220000	1740
Walter (Pers. Comm.)	CANNELL #1	DEVONIAN - BEREA	Sandstone	Na-Ca-Cl		-	-	-	-	-	-	6.15	42000	87000	9400	630	1660	210000	1460
Walter (Pers. Comm.)	CARTER	DEVONIAN - BEREA	Sandstone	Na-Ca-Cl		-	-	-	-	-	-	9.24	47000	83000	15100	720	2700	210000	2000
Walter (Pers. Comm.)	JAMES 122	DEVONIAN - BEREA	Sandstone	Na-Ca-Cl		-	-	-	-	-	-	0.48	27000	31000	5600	430	1030	111000	1070
Walter (Pers. Comm.)	NKERN #1	DEVONIAN - BEREA	Sandstone	Na-Ca-Cl		-	-	-	-	-	-	-2.95	34000	72000	7800	1090	1260	210000	1390
Cloutier (1994)	LD-90-3-5	DEVONIAN - KETTLE POINT	Shale	Na-Cl	52	-	-	-	-	-	-	-1.95	127	5400	120	31	5.3	8600	6.6
Cloutier (1994)	DOW-90-3-4	DEVONIAN - KETTLE POINT	Shale	Na-Cl-HCO$_3$	44	-	-	-	-	-	-	12.38	8.4	189	0.097	72	0.47	164	0.69
Husain (1996)	BRP-143	DEVONIAN - KETTLE POINT	Shale	Na-Cl-HCO$_3$	44	-	-	-	-	-	-	2.90**	40	280	14.0	4.6	0.83	390	0.39
Husain (1996)	BRP-151	DEVONIAN - KETTLE POINT	Shale	Na-Cl-HCO$_3$	46	8.10	-	-	-	-	-	8.83**	27	340	11.7	9.2	0.50	390	0.28
Martini et al. (1998)	SP A2-32	DEVONIAN - ANTRIM	Shale	Na-Cl		6.20	17.8	-	-	1.15700	-	1.14	6800	83000	3600	670	320	147000	310
Martini et al. (1998)	WSMC2-10	DEVONIAN - ANTRIM	Shale	Na-Cl		5.90	15.5	-	-	-	-	-1.03	7700	64000	4700	490	420	128000	450
Martini et al. (1998)	HGR D4-6	DEVONIAN - ANTRIM	Shale	Na-Cl		6.60	15.0	-	-	-	-	1.78	3300	42000	2100	370	220	74000	179
Cloutier (1994)	LD-90-3-4	DEVONIAN - HAMILTON	Shale	Na-Cl	68	-	-	-	-	-	-	1.50	122	3800	68	29	3.1	5800	4.7
Cloutier (1994)	LD-90-3-3	DEVONIAN - HAMILTON	Shale	Na-Cl	89	-	-	-	-	-	-	0.77	104	2600	59	47	4.2	3500	5.5
Cloutier (1994)	LD-90-3-2	DEVONIAN - HAMILTON	Shale	Na-Cl	131	-	-	-	-	-	-	-3.90	200	4200	137	41	13.8	7300	0
Cloutier (1994)	DOW-90-3-3	DEVONIAN - HAMILTON	Shale	Na-Cl	77	-	-	-	-	-	-	-1.04	164	3800	75	47	3.1	6100	5.7
Cloutier (1994)	DOW-90-3-2	DEVONIAN - HAMILTON	Shale	Na-Cl	106	-	-	-	-	-	-	-7.43	370	5900	210	67	8.0	11500	21
Cloutier (1994)	DOW-90-3-1	DEVONIAN - DUNDEE	Carbonate	Na-Cl	142	-	-	-	-	-	-	2.02	127	2900	70	48	2.8	3900	8.9
Cloutier (1994)	LD-90-3-1	DEVONIAN - DUNDEE	Carbonate	Na-SO$_4$-Cl	142	-	-	-	-	-	-	5.50	92	1510	29	136	2.3	790	4.1
Dollar (1988)	DD-1	DEVONIAN - DUNDEE	Carbonate	Na-Cl	108	-	-	-	-	-	-	-10.10	660	3700	630	85	29	10000	50
Dollar (1988)	DD-2	DEVONIAN - DUNDEE	Carbonate	Ca-Na-Cl	97	-	-	-	-	-	-	-1.66	620	410	83	19.0	12.0	2000	12.0
Dollar (1988)	DD-3	DEVONIAN - DUNDEE	Carbonate	Na-Mg-Ca-Cl	1131	-	-	-	-	-	-	0.97	32000	71000	5400	3000	750	179000	1050
Dollar (1988)	DD-4	DEVONIAN - DUNDEE	Carbonate	Na-Mg-Ca-Cl	1128	-	-	-	-	-	-	-0.10	40000	57000	7000	3400	1120	182000	1310
Weaver (1994)	PD-COCH	DEVONIAN - DUNDEE	Carbonate	Na-Ca-Mg-Cl		6.50	21.0	105.00	20.37	1.01170	23.5	-2.33**	1180	3500	720	91	23	8700	58
Weaver (1994)	PD-NORTH	DEVONIAN - DUNDEE	Carbonate	Na-Mg-Ca-Cl		6.40	18.0	89.00	22.63	1.01610	28.5	-3.21**	1580	4800	900	115	29	12000	91
Weaver (1994)	PD-RAL	DEVONIAN - DUNDEE	Carbonate	Na-Mg-Ca-Cl		6.50	-	91.20	20.46	-	-	-0.64**	1580	4400	910	117	30	10900	78
Weaver (1994)	PD-WEST	DEVONIAN - DUNDEE	Carbonate	Na-Mg-Ca-Cl		6.50	-	99.20	34.12	-	-	-2.97**	1400	3900	790	105	26	9900	82
Weaver (1994)	RA-N	DEVONIAN - DUNDEE	Carbonate	Na-Mg-Ca-Cl		6.50	21.5	108.00	28.70	1.01160	23.0	-3.92**	1140	3400	680	85	24	8900	62
Weaver (1994)	RA-NE	DEVONIAN - DUNDEE	Carbonate	Na-Ca-Cl		6.45	21.0	96.90	37.12	1.01470	29.0	-4.57**	1410	4400	810	105	28	11300	74
Weaver (1994)	RA-SE	DEVONIAN - DUNDEE	Carbonate	Na-Ca-Cl		6.35	20.0	87.80	20.89	1.01520	29.5	-3.51**	1490	4500	860	111	28	11500	79
Weaver (1994)	RA-SW	DEVONIAN - DUNDEE	Carbonate	Na-Ca-Cl		6.50	17.5	101.00	23.33	1.01330	23.5	-3.48**	1320	4000	760	100	25	10100	67
Weaver (1994)	LAI-1	DEVONIAN - DUNDEE	Carbonate	Na-Mg-Ca-Cl		6.35	21.0	99.20	21.27	1.01300	25.3	-3.63**	1270	3700	820	103	25	9500	59
Weaver (1994)	LAI-2	DEVONIAN - DUNDEE	Carbonate	Na-Mg-Ca-Cl		6.40	21.0	86.70	21.59	1.01260	25.0	-2.91**	1300	3500	800	102	26	9000	54
Weaver (1994)	LAI-3	DEVONIAN - DUNDEE	Carbonate	Na-Mg-Ca-Cl		6.35	18.0	84.40	9.73	1.01200	22.5	-1.63**	1220	3400	770	107	23	8200	44
Weaver (1994)	WB-11	DEVONIAN - DUNDEE	Carbonate	Na-Mg-Ca-Cl		6.73	19.0	121.00	15.53	1.00740	14.8	-5.22**	740	2100	450	62	51	5700	43
Weaver (1994)	WB-2	DEVONIAN - DUNDEE	Carbonate	Na-Mg-Ca-Cl		6.54	19.0	117.00	11.56	1.00930	18.3	-4.15**	920	2600	590	76	21	7200	21
Weaver (1994)	WB-7	DEVONIAN - DUNDEE	Carbonate	Na-Mg-Ca-Cl		6.54	18.0	104.00	17.20	1.01110	16.0	-5.03**	1100	3100	690	88	22	8500	60
Weaver (1994)	WB-8	DEVONIAN - DUNDEE	Carbonate	Na-Mg-Ca-Cl		6.40	17.0	106.00	10.18	1.01270	17.3	-3.21**	1240	3600	840	111	27	9800	57
Weaver (1994)	LBH-1	DEVONIAN - DUNDEE	Carbonate	Na-Mg-Ca-Cl		6.74	16.0	67.40	6.46	1.01630	29.2	-3.24**	1700	4500	1170	152	32	13200	47
Weaver (1994)	LBH-2	DEVONIAN - DUNDEE	Carbonate	Na-Mg-Ca-Cl		6.87	18.0	43.60	8.75	1.01850	32.7	-2.81**	2000	5000	1320	156	34	14300	86
Weaver (1994)	LBH-3	DEVONIAN - DUNDEE	Carbonate	Na-Mg-Ca-Cl		6.65	16.0	44.70	10.72	1.01810	33.3	-2.10**	1940	4900	1340	169	36	14100	97
Weaver (1994)	LBH-4	DEVONIAN - DUNDEE	Carbonate	Na-Mg-Ca-Cl		6.76	15.0	64.00	15.92	1.01820	32.0	-3.14**	1760	5200	1300	171	36	15000	86
Weaver (1994)	LBO-2	DEVONIAN - DETROIT RIVER	Carbonate	Na-Mg-Ca-Cl		6.65	19.0	1.37	34.91	1.01460	26.2	0.47**	1530	4000	940	131	34	11300	99
Weaver (1994)	LBO-3	DEVONIAN - DETROIT RIVER	Carbonate	Na-Ca-Mg-Cl		7.05	18.0	11.90	29.87	1.01240	24.8	-1.90**	1640	3100	920	125	35	10400	69
Weaver (1994)	CFN-14	DEVONIAN - DETROIT RIVER	Carbonate	Na-Ca-Mg-Cl		6.05	23.0	126.00	26.90	1.00980	20.5	-5.16**	1310	2400	610	85	29	8000	66
Weaver (1994)	CFN-A	DEVONIAN - DETROIT RIVER	Carbonate	Na-Ca-Mg-Cl		6.30	21.0	98.00	27.73	1.01190	25.3	-0.23**	1570	3200	830	123	35	9500	86
Weaver (1994)	CFN-B	DEVONIAN - DETROIT RIVER	Carbonate	Na-Ca-Mg-Cl		6.40	21.0	110.00	27.90	1.00940	20.5	-0.79**	1190	2600	670	98	27	7800	61
Weaver (1994)	CFN-161	DEVONIAN - DETROIT RIVER	Carbonate	Na-Ca-Mg-Cl		5.95	18.0	60.60	6.64	1.04000	80.0	4.79**	6000	10900	2800	450	100	31000	280
Weaver (1994)	CFN-C	DEVONIAN - DETROIT RIVER	Carbonate	Na-Mg-Ca-Cl		6.10	16.0	81.00	23.40	1.03270	61.0	-1.04**	3800	8700	2400	310	70	27000	200
Weaver (1994)	CFN-E	DEVONIAN - DETROIT RIVER	Carbonate	Na-Ca-Mg-Cl		5.95	21.0	73.10	8.75	1.03220	68.0	-2.69**	4000	8000	2300	290	67	27000	220
Weaver (1994)	CFS-A	DEVONIAN - DETROIT RIVER	Carbonate	Na-Ca-Mg-Cl		6.00	23.0	72.00	13.82	1.03620	78.0	-4.10**	4300	9300	2300	310	70	30000	290
Weaver (1994)	CFS-B	DEVONIAN - DETROIT RIVER	Carbonate	Na-Ca-Mg-Cl		5.95	18.0	62.90	8.19	1.03260	71.0	4.91**	4200	9700	2300	330	67	26000	200
Weaver (1994)	CFS-C	DEVONIAN - DETROIT RIVER	Carbonate	Na-Ca-Mg-Cl		6.09	22.0	70.80	14.40	1.03210	70.0	-0.74**	3800	8900	2200	310	67	27000	195
Weaver (1994)	CFS-D	DEVONIAN - DETROIT RIVER	Carbonate	Na-Mg-Ca-Cl		6.05	17.0	72.00	16.94	1.03080	59.0	-1.93**	3500	8300	2200	300	67	26000	187
Dollar (1988)	DR-1	DEVONIAN - RICHFIELD	Carbonate	Ca-Na-Cl	1445	-	-	-	-	-	-	2.39	65000	23000	8000	8300	2100	173000	1970

- = not measured

*charge error (%) calculated in this study, unless otherwise indicated

**charge error reported in original reference

$^+$ water type calculated based on ion concentrations in meq/L

Table 1 continued

Author	**Sample ID**	**SO_4** **mg/L**	**HCO_3** **mg/L**	**F** **mg/L**	**^{18}O** **‰**	**^{2}H** **‰**	**^{3}H** **TU**	**Sr(87/86)**	**^{37}Cl**	**TDS** **mg / L**	**Classification** **Davis 1964**
Dollar (1988)	MB-1	53	<7.0	3.6	-1.5	-32	-	0.70893	-	288600	brine
Dollar (1988)	MB-2	<15.0	<7.0	12.2	0.3	-24	-	0.70899	0.1	312900	brine
Dollar (1988)	MB-3	<15.0	<7.0	12.0	-2.1	-45	-	0.70904	0.0	269400	brine
Dollar (1988)	MB-4	18	<7.0	9.60	-3.9	-52	-	0.70915	-	230100	brine
Dollar (1988)	MB-5	<15.0	<7.0	8.60	0.2	-31	-	0.70905	-	306500	brine
Dollar (1988)	MB-6	66	<7.0	-	0.5	-25	-	0.70807	0.1	304500	brine
Walter (Pers. Comm.)	BRENNAN 122	26	-	-	-	-	-	-	-0.2	**313056**	**brine**
Walter (Pers. Comm.)	CAMPBELL #7	38	-	-	-	-	-	-	-0.4	**381248**	**brine**
Walter (Pers. Comm.)	CAMPBELL #9	20	-	-	-	-	-	-	-0.4	**353960**	**brine**
Walter (Pers. Comm.)	CANNELL #1	72	-	-	-	-	-	-	0.0	**352222**	**brine**
Walter (Pers. Comm.)	CARTER	26	-	-	-	-	-	-	-0.3	**360546**	**brine**
Walter (Pers. Comm.)	JAMES 122	14.2	-	-	-	-	-	-	-0.3	**177144**	**brine**
Walter (Pers. Comm.)	NKERN #1	70	-	-	-	-	-	-	-0.2	**327610**	**brine**
Cloutier (1994)	LD-90-3-5	1.20	1210	-	-11.1	-69	-	-	1.8	**14291**	**saline**
Cloutier (1994)	DOW-90-3-4	42	164	-	-8.5	-61	-	-	-	**477**	**freshwater**
Husain (1996)	BRP-143	10.0	194	-	-16.9	-122	-	-	0.0	**740**	**freshwater**
Husain (1996)	BRP-151	5.6	200	-	-16.9	-122	-	-	0.2	**784**	**freshwater**
Martini et al. (1998)	SP A2-32	<5.0	4.9	-	-4.6	-28	-	0.71000	-0.4	**241700**	**brine**
Martini et al. (1998)	WSMC2-10	-	15.6	-	-6.7	-40	-	-	-1.1	**205760**	**brine**
Martini et al. (1998)	HGR D4-6	-	24	-	-10.2	-64	-	-	-0.4	**122169**	**brine**
Cloutier (1994)	LD-90-3-4	350	200	-	-7.5	-52	-	-	0.9	**10177**	**saline**
Cloutier (1994)	LD-90-3-3	780	380	-	-7.2	-51	-	-	0.7	**7100**	**brackish**
Cloutier (1994)	LD-90-3-2	320	720	-	-6.9	-47	-	-	0.2	**12212**	**brackish**
Cloutier (1994)	DOW-90-3-3	380	210	-	-7.1	-57	-	-	0.0	**10575**	**saline**
Cloutier (1994)	DOW-90-3-2	570	400	-	-6.8	-50	-	-	0.0	**18646**	**saline**
Cloutier (1994)	DOW-90-3-1	820	500	-	-6.9	-51	-	-	-0.7	**7877**	**brackish**
Cloutier (1994)	LD-90-3-1	1830	470	-	-7.2	-54	-	-	-	**4393**	**brackish**
Dollar (1988)	DD-1	800	290	-	-11.4	-86	-	0.70852	0.1	15940	saline
Dollar (1988)	DD-2	98	<7.0	-	-15.7	-120	-	0.70949	-	3260	brackish
Dollar (1988)	DD-3	166	<7.0	17.3	-	-	-	0.70816	-0.2^{+}	291500	brine
Dollar (1988)	DD-4	150	90	10.3	-0.9	-34	-	0.70823	-0.3^{+}	292000	brine
Weaver (1994)	PD-COCH	1700	260	-	-7.5	-48	-	0.70822	-	16155	saline
Weaver (1994)	PD-NORTH	2200	330	-	-6.9	-41	-	-	0.9	22073	saline
Weaver (1994)	PD-RAL	2000	158	-	-6.8	-43	2.4	0.70820	-	20166	saline
Weaver (1994)	PD-WEST	1940	260	-	-7.1	-46	-	-	-	18399	saline
Weaver (1994)	RA-N	1380	250	-	-7.6	-49	7.1	-	-	16008	saline
Weaver (1994)	RA-NE	1810	500	-	-6.8	-46	-	0.70820	1.1	20145	saline
Weaver (1994)	RA-SE	1920	320	-	-7.2	-45	-	-	1.0	20840	saline
Weaver (1994)	RA-SW	1690	310	-	-7.3	-49	-	-	-	18342	saline
Weaver (1994)	LAI-1	1790	590	-	-6.6	-36	-	-	-	17828	saline
Weaver (1994)	LAI-2	2000	550	-	-6.5	-43	-	0.70821	1.0	17346	saline
Weaver (1994)	LAI-3	2100	560	-	-6.4	-37	0.8	-	-	16512	saline
Weaver (1994)	WB-11	750	570	-	-8.5	-55	-	0.70813	1.2	10470	saline
Weaver (1994)	WB-2	790	600	-	-8.2	-49	7.2	-	-	12829	saline
Weaver (1994)	WB-7	1320	510	-	-7.6	-48	-	-	1.3	15334	saline
Weaver (1994)	WB-8	1230	540	-	-6.9	-42	-	0.70820	-	17388	saline
Weaver (1994)	LBH-1	1400	157	-	-8.7	-59	-	-	-	22314	saline
Weaver (1994)	LBH-2	2300	5.0	-	-8.8	-62	-	-	0.4	25194	saline
Weaver (1994)	LBH-3	2100	5.0	-	-8.2	-59	0.8	0.70827	-	24731	saline
Weaver (1994)	LBH-4	1220	112	-	-8.1	-57	-	-	0.3	24839	saline
Weaver (1994)	LBO-2	450	40	-	-7.5	-53	-	-	0.7	18556	saline
Weaver (1994)	LBO-3	630	113	-	-7.2	-54	-	-	-	17066	saline
Weaver (1994)	CFN-14	800	220	-	-9.5	-63	-	0.70833	0.5	13500	saline
Weaver (1994)	CFN-A	920	171	-	-9.0	-60	-	-	0.3^{+}	16365	saline
Weaver (1994)	CFN-B	400	300	-	-9.1	-60	37.7	-	-	13148	saline
Weaver (1994)	CFN-161	1240	330	-	-6.3	-84	1.1	0.70825	0.6	53400	saline
Weaver (1994)	CFN-C	760	220	-	-6.3	-38	0.8	0.70827	0.8	43912	saline
Weaver (1994)	CFN-E	1220	330	-	-5.9	-56	-	0.70826	0.9	43304	saline
Weaver (1994)	CFS-A	1390	350	-	-6.0	-76	-	-	0.7	48694	saline
Weaver (1994)	CFS-B	1350	148	-	-6.3	-49	0.8	-	0.5	43805	saline
Weaver (1994)	CFS-C	940	210	-	-6.4	-48	-	-	0.7	43192	saline
Weaver (1994)	CFS-D	810	420	-	-6.3	-68	-	-	0.3*	41456	saline
Dollar (1988)	DR-1	210	260	14.4	0.2	-55	-	0.70913	-0.5*	281900	brine

- = not measured

*includes original measurements as well as new measurements on archived samples; some as old as 1989

$^{+}$new measurements on archived samples; some as old as 1989

TDS in **bold** indicates a calculated value (not measured)

Table 2

Author	Sample ID	AGE FORMATION	Rock Type	Water Type$^+$	Depth m	pH	Temp. °C	DIC mg/L	DOC mg/L	Fluid Density g/cm^3	Spec. Conduct. mhos	Charge Error (%)*	Ca mg/L	Na mg/L	Mg mg/L	K mg/L	Sr mg/L	Cl mg/L	Br mg/L
Dollar (1988)	SF-1	SILURIAN - F SALT	Salt	Na-Cl	150	-	-	-	-	-	-	-7.29	8200	100000	2900	2600	210	210000	590
Dollar (1988)	SF-2	SILURIAN - F SALT	Salt	Na-Cl	150	-	-	-	-	-	-	-5.13	10300	95000	3100	2800	197	194000	390
Dollar (1988)	SF-3	SILURIAN - F SALT	Salt	Na-Cl	150	-	-	-	-	-	-	-5.05	9600	94000	3400	2600	158	193000	330
Dollar (1988)	SA2-1	SILURIAN - A2 SALT	Salt	Ca-Na-Mg-Cl	250	-	-	-	-	-	-	-9.91	48000	33000	16600	5000	1620	230000	3200
Dollar (1988)	SA2-2	SILURIAN - A2 SALT	Salt	Ca-Na-Mg-Cl	250	-	-	-	-	-	-	-10.54	47000	34000	16200	6400	1620	230000	3200
Dollar (1988)	SG-1	SILURIAN - GUELPH	Carbonate	Na-Ca-Cl	354	-	-	-	-	-	-	0.13	15000	41000	3800	1430	260	96000	810
Dollar (1988)	SG-2	SILURIAN - GUELPH	Carbonate	Na-Ca-Cl	448	-	-	-	-	-	-	-2.46	31000	66000	7800	1880	440	189000	1390
Dollar (1988)	SG-3	SILURIAN - GUELPH	Carbonate	Na-Ca-Cl	553	-	-	-	-	-	-	-1.28	45000	61000	9000	2700	600	210000	1620
Dollar (1988)	SG-4	SILURIAN - GUELPH	Carbonate	Ca-Na-Cl	614	-	-	-	-	-	-	1.81	60000	47000	8300	3000	1220	198000	2500
Dollar (1988)	SG-5	SILURIAN - GUELPH	Carbonate	Na-Ca-Cl	571	-	-	-	-	-	-	-1.29	29000	70000	8200	2000	450	189000	1390
Dollar (1988)	SG-6	SILURIAN - GUELPH	Carbonate	Ca-Na-Cl	646	-	-	-	-	-	-	0.98	54000	42000	9500	3200	740	186000	1780
Dollar (1988)	SG-7	SILURIAN - GUELPH	Carbonate	Ca-Na-Cl	749	-	-	-	-	-	-	-0.46	66000	42000	8400	3300	1120	210000	2400
Dollar (1988)	SG-8	SILURIAN - GUELPH	Carbonate	Ca-Na-Cl	695	-	-	-	-	-	-	-0.23	62000	46000	10600	3400	1000	210000	2000
Dollar (1988)	SG-9	SILURIAN - GUELPH	Carbonate	Ca-Na-Cl	770	-	-	-	-	-	-	-1.29	53000	43000	13300	2200	580	210000	1490
Dollar (1988)	SG-10	SILURIAN - GUELPH	Carbonate	Ca-Na-Cl	726	-	-	-	-	-	-	0.15	57000	39000	8700	3300	1220	190000	2400
Dollar (1988)	SG-11	SILURIAN - GUELPH	Carbonate	Ca-Na-Cl	518	-	-	-	-	-	-	-2.91	53000	50000	9500	4800	700	210000	1920
Dollar (1988)	SG-12	SILURIAN - GUELPH	Carbonate	Na-Ca-Cl	597	-	-	-	-	-	-	2.98	35000	53000	7100	2400	570	155000	1510
Dollar (1988)	SG-13	SILURIAN - GUELPH	Carbonate	Ca-Na-Cl	670	-	-	-	-	-	-	-2.21	50000	55000	8200	2800	680	210000	1920
Dollar (1988)	SA1-1	SILURIAN - A1 CARBONATE	Carbonate	Ca-Na-Cl	645	-	-	-	-	-	-	3.04	52000	38000	11400	4500	740	176000	1880
Dollar (1988)	SA1-2	SILURIAN - A1 CARBONATE	Carbonate	Ca-Na-Cl	649	-	-	-	-	-	-	-1.05	55000	38000	10900	4800	970	195000	1700
Dollar (1988)	SN-1	SILURIAN - NIAGARAN	Carbonate	Ca-Na-Cl	892	-	-	-	-	-	-	-4.12	62000	41000	8700	6100	1270	210000	2200
Dollar (1988)	SN-2	SILURIAN - NIAGARAN	Carbonate	Ca-Na-Cl	895	-	-	-	-	-	-	-4.26	61000	40000	8500	5900	1270	210000	1880
Dollar (1988)	SN-3	SILURIAN - NIAGARAN	Carbonate	Ca-Mg-Cl	1161	-	-	-	-	-	-	-0.23	74000	25000	17900	8600	2000	230000	2400
Dollar (1988)	SN-4	SILURIAN - NIAGARAN	Carbonate	Ca-Mg-Cl	1272	-	-	-	-	-	-	-3.41	79000	25000	17900	9300	2200	260000	2400
Dollar (1988)	SN-5	SILURIAN - NIAGARAN	Carbonate	Ca-Na-Cl	1305	-	-	-	-	-	-	-3.39	77000	31000	11900	10300	2000	250000	2400
Dollar (1988)	SN-6	SILURIAN - NIAGARAN	Carbonate	Ca-Cl	1264	-	-	-	-	-	-	-5.48	80000	25000	15500	9800	2500	260000	2600
Dollar (1988)	SN-7	SILURIAN - NIAGARAN	Carbonate	Ca-Na-Cl	1010	-	-	-	-	-	-	-0.27	63000	45000	8600	4300	1160	210000	2300
Dollar (1988)	SN-8	SILURIAN - NIAGARAN	Carbonate	Ca-Na-Cl	1001	-	-	-	-	-	-	4.51	62000	45000	8100	3900	1190	188000	2200
Dollar (1988)	SN-9	SILURIAN - NIAGARAN	Carbonate	Ca-Na-Cl	713	-	-	-	-	-	-	-1.96	55000	46000	9600	3600	920	210000	1970
Dollar (1988)	SN-10	SILURIAN - NIAGARAN	Carbonate	Ca-Na-Cl	717	-	-	-	-	-	-	0.34	63000	43000	8500	3400	1060	200000	2300
Walter (Pers. Comm.)	COLD SPRINGS WH1-29	SILURIAN - NIAGARAN	Carbonate	Ca-Cl		-	-	-	-	-	-	0.09	89000	26000	10200	18300	3700	240000	2600
Hanratty (1996)	87-2-5	MIDDLE SILURIAN - GUELPH/LOCKPORT	Carbonate	Ca-Mg-SO_4	5^{++}	-	-	-	-	-	1973.3	-0.76	300	70	94	4.1	15.3	125	0.38
Hanratty (1996)	87-2-4	MIDDLE SILURIAN - LOCKPORT	Carbonate	Ca-Mg-SO_4	14^{++}	-	-	-	-	-	1955.0	-2.57	360	30.0	84	7.8	13.8	63	1.64
Hanratty (1996)	87-2-3	MIDDLE SILURIAN - GOAT ISLAND	Carbonate	Ca-Na-Mg-SO_4-Cl	32^{++}	-	-	-	-	-	2962.5	-1.91	320	210	107	15.6	21	540	5.3
Hanratty (1996)	87-2-2	MIDDLE SILURIAN - GASPORT	Carbonate	Na-Ca-Cl	45^{++}	-	-	-	-	-	9885.0	-1.71	770	1270	200	63	22	3200	31
Hanratty (1996)	88-1-5	MIDDLE SILURIAN - GUELPH/LOCKPORT	Carbonate	Ca-Mg-HCO_3	27^{++}	-	-	-	-	-	620.7	-2.71	100	11.3	22.0	1.20	0.50	18.8	1.22
Hanratty (1996)	88-1-4	MIDDLE SILURIAN - LOCKPORT	Carbonate	Ca-Mg-SO_4	35^{++}	-	-	-	-	-	1188.0	2.41	192	31.0	50	4.0	7.2	34	2.5
Hanratty (1996)	88-1-3	MIDDLE SILURIAN - GOAT ISLAND	Carbonate	Ca-Mg-SO_4	55^{++}	-	-	-	-	-	3150.0	-0.16	470	129	152	19.3	13.2	260	3.2
Hanratty (1996)	88-1-2	MIDDLE SILURIAN - GASPORT	Carbonate	Ca-Na-Mg-SO_4-Cl	67^{++}	-	-	-	-	-	5687.5	4.26	740	470	183	33	13.9	1110	11.4
Hanratty (1996)	88-1-1	MIDDLE SILURIAN - THOROLD	Sandstone	Na-Ca-Cl	73^{++}	-	-	-	-	-	21700.0	-1.10	1490	3400	340	112	24	7800	82
Hanratty (1996)	87-2-1	MIDDLE SILURIAN - THOROLD	Sandstone	Na-Ca-Cl	53^{++}	-	-	-	-	-	18000.0	-1.53	1370	2700	300	107	29	6500	53
Dollar (1988)	STGr-1	LOWER SILURIAN - GRIMSBY	Sandstone	Na-Ca-Cl	431	-	-	-	-	-	-	2.03	29000	48000	6000	1000	460	138000	1340
Dollar (1988)	STGr-2	LOWER SILURIAN - GRIMSBY	Sandstone	Na-Ca-Cl	380	-	-	-	-	-	-	2.41	37000	52000	7000	1410	610	159000	1550
Dollar (1988)	STGr-3	LOWER SILURIAN - GRIMSBY	Sandstone	Na-Ca-Cl	374	-	-	-	-	-	-	1.42	27000	42000	6600	900	460	129000	1260
Dollar (1988)	STGr-4	LOWER SILURIAN - GRIMSBY	Sandstone	Na-Ca-Cl	414	-	-	-	-	-	-	2.14	35000	49000	6100	980	540	149000	1580
Dollar (1988)	ST-5	LOWER SILURIAN - THORHOLD	Sandstone	Na-Ca-Cl	292	-	-	-	-	-	-	-2.79	31000	45000	5800	1010	490	148000	1340
Dollar (1988)	ST-6	LOWER SILURIAN - THORHOLD	Sandstone	Na-Ca-Cl	408	-	-	-	-	-	-	1.55	34000	45000	6200	1040	540	143000	1430
Dollar (1988)	SGr-7	LOWER SILURIAN - GRIMSBY	Sandstone	Na-Ca-Cl	424	-	-	-	-	-	-	-1.81	34000	51000	5900	1010	530	161000	1510
Dollar (1988)	SGr-8	LOWER SILURIAN - GRIMSBY	Sandstone	Na-Ca-Cl	426	-	-	-	-	-	-	-3.09	34000	50000	5800	1130	520	164000	1540
Dollar (1988)	STGr-9	LOWER SILURIAN - GRIMSBY	Sandstone	Na-Ca-Cl	522	-	-	-	-	-	-	-1.47	42000	50000	7500	1260	700	179000	1650
Dollar (1988)	STGr-10	LOWER SILURIAN - GRIMSBY	Sandstone	Na-Ca-Cl	524	-	-	-	-	-	-	-0.32	46000	58000	8000	1390	780	196000	1970
Dollar (1988)	SGr-11	LOWER SILURIAN - GRIMSBY	Sandstone	Na-Ca-Cl	512	-	-	-	-	-	-	3.90	45000	59000	7700	1450	750	178000	1870
Dollar (1988)	SGr-12	LOWER SILURIAN - GRIMSBY	Sandstone	Na-Ca-Cl	524	-	-	-	-	-	-	2.37	27000	39000	5300	880	460	118000	1130
Dollar (1988)	STGr-13	LOWER SILURIAN - THORHOLD/GRIMSBY	Sandstone	Na-Ca-Cl	547	-	-	-	-	-	-	-.087	31000	45000	5600	880	510	144000	1380
Dollar (1988)	STGr-14	LOWER SILURIAN - THORHOLD/GRIMSBY	Sandstone	Na-Ca-Cl	541	-	-	-	-	-	-	-1.77	48000	59000	8200	1400	880	210000	2000
Dollar (1988)	SGr-15	LOWER SILURIAN - GRIMSBY	Sandstone	Na-Ca-Cl	554	-	-	-	-	-	-	-3.59	35000	47000	6300	930	560	164000	1490
Dollar (1988)	SGr-16	LOWER SILURIAN - GRIMSBY	Sandstone	Na-Ca-Cl	572	-	-	-	-	-	-	-3.35	28000	46000	4900	910	450	144000	1250
Dollar (1988)	STGr-17	LOWER SILURIAN - THORHOLD/GRIMSBY	Sandstone	Na-Ca-Cl	544	-	-	-	-	-	-	-3.20	29000	43000	5100	850	480	142000	1260
Dollar (1988)	SGr-18	LOWER SILURIAN - GRIMSBY	Sandstone	Ca-Na-Cl	289	-	-	-	-	-	-	6.83	40000	23000	6800	660	350	109000	760
Dollar (1988)	SGr-19	LOWER SILURIAN - GRIMSBY	Sandstone	Ca-Na-Cl	335	-	-	-	-	-	-	-2.59	40000	21000	3500	640	360	119000	690
Dollar (1988)	SGr-20	LOWER SILURIAN - GRIMSBY	Sandstone	Ca-Na-Cl	365	-	-	-	-	-	-	0.45	43000	30000	5500	820	480	137000	920
Dollar (1988)	SGr-21	LOWER SILURIAN - GRIMSBY	Sandstone	Ca-Na-Cl	410	-	-	-	-	-	-	5.92	42000	26000	3900	710	430	113000	860
Dollar (1988)	SW-1	LOWER SILURIAN - WHIRLPOOL	Sandstone	Ca-Na-Cl	361	-	-	-	-	-	-	-2.31	50000	32000	4300	780	490	159000	1130
Dollar (1988)	SW-2	LOWER SILURIAN - WHIRLPOOL	Sandstone	Ca-Na-Cl	422	-	-	-	-	-	-	-2.27	47000	30000	3700	760	450	148000	1000
Dollar (1988)	SW-3	LOWER SILURIAN - WHIRLPOOL	Sandstone	Ca-Na-Cl	422	-	-	-	-	-	-	-2.56	51000	36000	5500	870	510	172000	1190
Dollar (1988)	SW-4	LOWER SILURIAN - WHIRLPOOL	Sandstone	Ca-Na-Cl	459	-	-	-	-	-	-	2.87	43000	28000	4500	770	420	126000	920

- = not measured

$^{++}$Sample depth is masl, not depth in borehole

*charge error (%) calculated in this study

$^+$ water type calculated based on ion concentrations in meq/L

Table 2 continued

Author	Sample ID	SO_4	HCO_3	F	^{18}O	^{2}H	^{3}H	Sr(87/86)	^{37}Cl	TDS	Classification
		mg/L	mg/L	mg/L	‰	‰	TU			mg / L	Davis 1964
Dollar (1988)	SF-1	750	-	-	-5.5	-55	-	0.70866	-0.2	322200	brine
Dollar (1988)	SF-2	510	73	-	-	-	-	-	-	305900	brine
Dollar (1988)	SF-3	600	76	-	-4.7	-52	-	-	-	304000	brine
Dollar (1988)	SA2-1	110	-	-	2.9	-52	-	0.70853	-	340400	brine
Dollar (1988)	SA2-2	106	-	-	3.2	-48	-	0.70866	-	340000	brine
Dollar (1988)	SG-1	810	127	164	-4.7	-42	-	0.71029	-	158800	brine
Dollar (1988)	SG-2	250	69	8.0	-	-	-	0.70931	-	297600	brine
Dollar (1988)	SG-3	127	43	-	-0.8	-43	-	-	-0.4	326800	brine
Dollar (1988)	SG-4	119	<7.0	-	-	-	-	0.70915	-0.2^{+}	319800	brine
Dollar (1988)	SG-5	260	84	8.0	-	-	-	0.70934	-	300400	brine
Dollar (1988)	SG-6	230	<7.0	8.0	-	-	-	0.70889	-	297600	brine
Dollar (1988)	SG-7	240	<7.0	8.0	-	-	-	0.70946	-0.4^{+}	334700	brine
Dollar (1988)	SG-8	61	<7.0	-	-0.4	-44	-	0.70908	-0.5*	339200	brine
Dollar (1988)	SG-9	200	<7.0	8.0	-	-	-	0.70929	-	319200	brine
Dollar (1988)	SG-10	172	<7.0	-	-	-	-	0.70902	-0.3^{+}	301900	brine
Dollar (1988)	SG-11	170	250	-	-	-	-	0.70893	-	333300	brine
Dollar (1988)	SG-12	300	<7.0	27	-	-	-	0.70931	-	255000	brine
Dollar (1988)	SG-13	170	77	8.0	-	-	-	0.70907	-	327000	brine
Dollar (1988)	SA1-1	167	76	-	-	-	-	-	-0.4	284400	brine
Dollar (1988)	SA1-2	193	18.0	-	-1.1	-47	-	0.70849	-0.4	306400	brine
Dollar (1988)	SN-1	79	<7.0	320	0.2	-42	-	0.70833	-1.0*	330800	brine
Dollar (1988)	SN-2	79	<7.0	300	-1.4	-48	-	-	-	327800	brine
Dollar (1988)	SN-3	59	<7.0	-	-2.9	-50	-	-	-0.3^{+}	359900	brine
Dollar (1988)	SN-4	38	<7.0	-	-4.9	-46	-	0.70861	-0.6^{+}	391700	brine
Dollar (1988)	SN-5	42	<7.0	-	1.2	-40	-	-	-0.2^{+}	380300	brine
Dollar (1988)	SN-6	49	<7.0	-	-1.0	-47	-	0.70848	-0.3*	397000	brine
Dollar (1988)	SN-7	94	<7.0	8.4	0.2	-43	-	0.70935	-0.3	335300	brine
Dollar (1988)	SN-8	105	<7.0	10.5	-0.5	-41	-	0.70939	-0.3	310300	brine
Dollar (1988)	SN-9	89	<7.0	-	-0.4	-43	-	0.70909	-	324100	brine
Dollar (1988)	SN-10	89	<7.0	7.8	-0.1	-47	-	0.70929	-0.4^{+}	323100	brine
Walter (Pers. Comm.)	COLD SPRINGS WH1-29	36	-	-	-	-	-	-	-0.4	**300836**	**brine**
Hanratty (1996)	87-2-5	790	158**	1.50	-10.0	-66	21.8	-	0.1	**1098**	brackish
Hanratty (1996)	87-2-4	960	154**	1.30	-10.3	-68	14.1	-	0.2	**1160**	brackish
Hanratty (1996)	87-2-3	750	147**	0.80	-10.5	-68	0.8	-	-0.4	**1649**	brackish
Hanratty (1996)	87-2-2	1050	127**	0.70	-10.8	-75	0.8	-	-0.1	**5836**	brackish
Hanratty (1996)	88-1-5	37	177**	0.70	-11.5	-75	25.0	-	-0.2	**92**	freshwater
Hanratty (1996)	88-1-4	370	163**	1.00	-10.4	-69	20.9	-	-0.2	**499**	freshwater
Hanratty (1996)	88-1-3	1440	122**	1.10	-10.6	-69	1.4	-	-0.3	**2016**	brackish
Hanratty (1996)	88-1-2	1660	117**	0.70	-11.1	-75	0.8	-	-0.4	**3482**	brackish
Hanratty (1996)	88-1-1	1730	82**	0.60	-11.2	-76	1.0	-	-0.3	**13488**	saline
Hanratty (1996)	87-2-1	1400	105**	0.60	-10.9	-73	0.8	-	-0.1	**11089**	saline
Dollar (1988)	STGr-1	390	<7.0	-	-3.5	-43	-	-	-	223900	brine
Dollar (1988)	STGr-2	260	<7.0	-	-2.9	-34	-	0.70977	-	258000	brine
Dollar (1988)	STGr-3	450	<7.0	-	-4.2	-44	-	-	-	208700	brine
Dollar (1988)	STGr-4	320	<7.0	-	-2.9	-43	-	-	-	242800	brine
Dollar (1988)	ST-5	410	<7.0	-	-4.1	-46	-	0.71014	0.8	232200	brine
Dollar (1988)	ST-6	340	<7.0	-	-3.4	-44	-	-	-	231900	brine
Dollar (1988)	SGr-7	330	<7.0	-	-3.3	-43	-	-	-	254300	brine
Dollar (1988)	SGr-8	350	<7.0	-	-3.0	-42	-	-	-	257400	brine
Dollar (1988)	STGr-9	370	<7.0	-	-2.8	-44	-	-	-	282200	brine
Dollar (1988)	STGr-10	164	<7.0	-	-1.9	-42	-	-	0.1^{+}	311800	brine
Dollar (1988)	SGr-11	174	<7.0	-	-1.7	-41	-	-	0.4^{+}	293500	brine
Dollar (1988)	SGr-12	660	<7.0	-	-3.9	-40	-	-	-	191700	brine
Dollar (1988)	STGr-13	420	<7.0	-	-3.4	-41	-	-	0.4	229600	brine
Dollar (1988)	STGr-14	123	<7.0	-	-1.7	-46	-	0.71018	0.2*	325900	brine
Dollar (1988)	SGr-15	400	<7.0	-	-3.5	-39	-	-	-	254800	brine
Dollar (1988)	SGr-16	530	<7.0	-	-3.4	-35	-	0.71076	-	226100	brine
Dollar (1988)	STGr-17	450	<7.0	-	-2.9	-41	-	-	0.1	222700	brine
Dollar (1988)	SGr-18	560	<7.0	-	-4.3	-44	-	-	-	180800	brine
Dollar (1988)	SGr-19	240	<7.0	-	-4.5	-44	-	0.71092	0.4	185600	brine
Dollar (1988)	SGr-20	410	<7.0	-	-3.7	-38	-	0.71036	0.5*	218500	brine
Dollar (1988)	SGr-21	330	<7.0	-	-3.8	-43	-	-	0.5^{+}	187300	brine
Dollar (1988)	SW-1	320	47	8.4	-3.0	-39	-	0.71103	0.9*	248600	brine
Dollar (1988)	SW-2	380	60	-	-3.7	-41	-	0.71107	0.6*	231000	brine
Dollar (1988)	SW-3	380	<7.0	-	-2.5	-39	-	-	0.6^{+}	267500	brine
Dollar (1988)	SW-4	430	<7.0	-	-3.8	-42	-	0.71112	-	204700	brine

- = not measured

*includes original measurements as well as new measurements on archived samples; some as old as 1989

$^{+}$new measurements on archived samples; some as old as 1989

**measurements were converted from mg/L $CaCO_3$ to mg/L HCO_3

TDS in **bold** indicates a calculated value (not measured)

Table 3

Author	Sample ID	AGE FORMATION	Rock Type	Water Type$^+$	Depth m	pH	Temp. °C	DIC mg/L	DOC mg/L	Fluid Density g/cm^3	Spec. Conduct. mhos	Charge Error (%)*	Ca mg/L	Na mg/L	Mg mg/L	K mg/L	Sr mg/L	Cl mg/L	Br mg/L
Dollar (1988)	OT-1	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	647	-	-	-	-	-	-	-2.14	15600	36000	3700	1600	530	99000	580
Dollar (1988)	OT-2	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	657	-	-	-	-	-	-	-2.98	16000	35000	3500	1600	540	100000	730
Dollar (1988)	OT-3	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	645	-	-	-	-	-	-	-3.42	15800	36000	3500	1630	470	101000	560
Dollar (1988)	OT-4	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	738	-	-	-	-	-	-	3.59	23000	40000	5500	1970	400	111000	830
Dollar (1988)	OT-5	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	743	-	-	-	-	-	-	-2.58	24000	41000	6100	2100	740	132000	860
Dollar (1988)	OT-6	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	771	-	-	-	-	-	-	-0.85	17400	37000	4300	1690	570	103000	550
Dollar (1988)	OT-7	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	790	-	-	-	-	-	-	1.19	35000	44000	7400	2300	610	150000	920
Dollar (1988)	OT-8	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	775	-	-	-	-	-	-	0.86	33000	47000	6500	2400	530	148000	1190
Dollar (1988)	OT-9	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	786	-	-	-	-	-	-	4.09	37000	49000	7400	2300	610	151000	950
Dollar (1988)	OT-10	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	784	-	-	-	-	-	-	-3.16	37000	49000	7900	2300	630	176000	1170
Dollar (1988)	OT-11	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	804	-	-	-	-	-	-	-0.76	37000	46000	7300	2300	730	161000	1610
Dollar (1988)	OT-12	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	779	-	-	-	-	-	-	-1.54	39000	45000	6900	2100	730	166000	1370
Dollar (1988)	OT-13	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	791	-	-	-	-	-	-	1.45	33000	55000	7300	2400	580	161000	1150
Dollar (1988)	OT-14	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	782	-	-	-	-	-	-	4.47	33000	49000	6800	2400	550	141000	1170
Dollar (1988)	OT-15	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	787	-	-	-	-	-	-	-0.86	31000	46000	6500	2300	530	150000	1120
Dollar (1988)	OT-16	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	778	-	-	-	-	-	-	0.45	33000	46000	6600	2700	530	149000	1220
Dollar (1988)	OT-17	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	781	-	-	-	-	-	-	-0.17	30000	43000	6000	2200	570	139000	1270
Dollar (1988)	OT-18	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	786	-	-	-	-	-	-	-2.11	34000	45000	6700	2300	660	158000	1210
Dollar (1988)	OT-19	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	844	-	-	-	-	-	-	-3.35	31000	42000	5400	2200	520	147000	780
Dollar (1988)	OT-20	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl		-	-	-	-	-	-	-2.09	27000	47000	5200	2100	470	142000	770
Dollar (1988)	OT-21	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	854	-	-	-	-	-	-	-1.88	33000	50000	6000	2100	620	150000	1190
Dollar (1988)	OT-22	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	1225	-	-	-	-	-	-	-1.68	22000	42000	4500	3200	490	123000	630
Dollar (1988)	OT-23	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	1140	-	-	-	-	-	-	-3.98	31000	48000	5500	3400	600	160000	1160
Dollar (1988)	OT-24	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	1247	-	-	-	-	-	-	-3.71	22000	42000	4300	3100	490	122000	930
Dollar (1988)	OT-25	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	1238	-	-	-	-	-	-	-6.60	18300	40000	3800	3100	450	118000	800
Dollar (1988)	OT-26	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	1203	-	-	-	-	-	-	-4.76	19200	41000	4400	3300	490	119000	860
Dollar (1988)	OT-27	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	1287	-	-	-	-	-	-	-4.63	21000	43000	4600	3500	510	123000	920
Dollar (1988)	OT-28	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	1299	-	-	-	-	-	-	-1.91	19800	42000	4300	3500	490	119000	650
Dollar (1988)	OT-29	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	1278	-	-	-	-	-	-	-2.68	21000	41000	4700	3500	510	118000	920
Dollar (1988)	OT-30	ORDOVICIAN - TRENTON	Carbonate	Ca-Na-Cl	1280	-	-	-	-	-	-	-3.67	55000	53000	7800	5300	1060	220000	1780
Dollar (1988)	OT-31	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	1279	-	-	-	-	-	-	-2.30	24000	46000	5100	4000	560	137000	910
Dollar (1988)	OT-32	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	1259	-	-	-	-	-	-	-9.63	24000	46000	5200	3800	550	134000	890
Dollar (1988)	OT-33	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	1289	-	-	-	-	-	-	0.13	22000	42000	4100	3900	520	180000	730
Dollar (1988)	OT-34	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	1290	-	-	-	-	-	-	-3.95	22000	44000	4300	4000	550	133000	910
Dollar (1988)	OT-35	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	1292	-	-	-	-	-	-	-3.96	21000	43000	4100	3700	510	126000	870
Dollar (1988)	OT-36	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	1292	-	-	-	-	-	-	-3.39	21000	43000	4000	3800	480	126000	650
Dollar (1988)	OT-37	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	1288	-	-	-	-	-	-	-3.09	21000	43000	4100	3800	510	126000	880
Dollar (1988)	OT-38	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	1293	-	-	-	-	-	-	-2.47	25000	42000	4700	3300	480	132000	790
Dollar (1988)	OT-39	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	637	-	-	-	-	-	-	-3.30	13100	39000	3700	2000	470	102000	510
Dollar (1988)	OT-40	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	308	-	-	-	-	-	-	-0.22	9900	36000	3700	1840	520	87000	460
Dollar (1988)	OT-41	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	310	-	-	-	-	-	-	0.70	10800	36000	3900	1850	500	87000	440
Dollar (1988)	OT-42	ORDOVICIAN - TRENTON	Carbonate	Na-Ca-Cl	614	-	-	-	-	-	-	0.86	10500	38000	3700	1880	570	88000	460
Sherwood Lollar & Frape (1989)	OHD-1 #15	UPPER ORDOVICIAN - BLUE MTN	Carbonate	Ca-Na-Cl	173	-	-	-	-	-	-	-1.22	39000	22000	4500	400	700	118000	1080
Sherwood Lollar & Frape (1989)	UN-2 #13	UPPER ORDOVICIAN - LINDSAY	Carbonate	Na-Ca-Cl	50	-	-	-	-	-	-	3.61	6300	8100	1840	141	280	27000	280
Sherwood Lollar & Frape (1989)	OHD-1 #13	UPPER ORDOVICIAN - LINDSAY	Carbonate	Ca-Na-Cl	204	-	-	-	-	-	-	-0.83	27000	18400	3300	320	520	87000	760
Sherwood Lollar & Frape (1989)	UN-2 #11	ORDOVICIAN - VERALUM	Carbonate	Na-Ca-Cl	85	-	-	-	-	-	-	2.71	15100	17900	4100	270	710	63000	640
Sherwood Lollar & Frape (1989)	OHD-1 #7	ORDOVICIAN - BOBCAYGEON	Carbonate	Ca-Na-Cl	30	-	-	-	-	-	-	-2.88	58000	37000	7100	640	1210	192000	1560
Sherwood Lollar & Frape (1989)	UN-2 #5	ORDOVICIAN - BOBCAYGEON	Carbonate	Ca-Na-Mg-Cl	175	-	-	-	-	-	-	0.05	36000	41000	11200	710	1130	160000	1450
Sherwood Lollar & Frape (1989)	OHD-1 #5A	ORDOVICIAN - BOBCAYGEON	Carbonate	Ca-Na-Cl	326	-	-	-	-	-	-	-1.98	58000	36000	7100	640	1200	186000	1620
Sherwood Lollar & Frape (1989)	OHD-1 #5B	ORDOVICIAN - BOBCAYGEON	Carbonate	Ca-Na-Cl	326	-	-	-	-	-	-	0.98	59000	39000	7200	650	1220	182000	1600
Sherwood Lollar & Frape (1989)	OHD-1 #3	ORDOVICIAN -GULL RIVER	Carbonate	Ca-Na-Cl	353	-	-	-	-	-	-	-5.49	59000	35000	7200	650	1220	200000	820
Sherwood Lollar & Frape (1989)	UN-2 #2	ORDOVICIAN -GULL RIVER	Carbonate	Ca-Na-Cl	210	-	-	-	-	-	-	4.89	15000	17400	4100	320	340	59000	620
Sherwood Lollar & Frape (1989)	UN-2 #4	ORDOVICIAN -GULL RIVER	Carbonate	Ca-Na-Cl	190	-	-	-	-	-	-	2.46	23000	25000	7200	470	490	96000	940
Sherwood Lollar & Frape (1989)	OHD-1 #2	ORDOVICIAN -SHADOW LAKE	Sandstone	Ca-Na-Cl	368	-	-	-	-	-	-	-1.64	58000	38000	7200	660	1220	189000	1620
Dollar (1988)	OP-1	ORDOVICIAN - PRAIRIE DU CHIEN	Sandstone	Ca-Na-Cl	3425	-	-	-	-	-	-	-2.14	68000	27000	7200	14200	2400	210000	1930
Walter (Pers. Comm.)	LAHAR 1-7	ORDOVICIAN - PRAIRIE DU CHIEN	Sandstone	Ca-Cl	-	-	-	-	-	-	-	-1.17	89000	30000	7600	12700	3600	250000	1720
Walter (Pers. Comm.)	FOSTER 1-21	ORDOVICIAN - PRAIRIE DU CHIEN	Sandstone	Ca-Na-Cl	-	-	-	-	-	-	-	-1.51	65000	44000	5600	9500	2900	220000	2300
Walter (Pers. Comm.)	PRASS 1-12	ORDOVICIAN - PRAIRIE DU CHIEN	Sandstone	Ca-Cl	-	-	-	-	-	-	-	0.73	68000	23000	5700	10600	2900	180000	2200
Dollar (1988)	OP-2	ORDOVICIAN - PRAIRIE DU CHIEN	Sandstone	Ca-Cl	-	-	-	-	-	-	-	-3.40	88000	23000	8700	18400	2900	250000	1780

- = not measured
* = charge error (%) calculated in this study
$^+$ water type calculated based on ion concentrations in meq/L

Table 3 continued

Author	**Sample ID**	**SO_4 mg/L**	**HCO_3 mg/L**	**F mg/L**	**^{18}O ‰**	**^{2}H ‰**	**^{3}H TU**	**Sr(87/86)**	**^{37}Cl**	**TDS mg / L**	**Classification Davis 1964**
Dollar (1988)	OT-1	450	<7.0	4.3	-2.1	-31	-	0.70978	-0.4	156900	brine
Dollar (1988)	OT-2	740	34	-	-1.7	-23	-	0.70980	0.0	158200	brine
Dollar (1988)	OT-3	580	<7.0	5.4	-1.9	-31	-	0.70976	0.3	159400	brine
Dollar (1988)	OT-4	630	<7.0	5.7	-1.7	-30	-	0.70996	-	183700	brine
Dollar (1988)	OT-5	152	<7.0	5.6	-1.9	-29	-	0.70973	-0.6	206700	brine
Dollar (1988)	OT-6	410	58	4.0	-2.2	-28	-	0.70982	-0.3	165000	brine
Dollar (1988)	OT-7	260	17.0	-	-	-	-	-	-	239800	brine
Dollar (1988)	OT-8	350	33	-	-2.1	-30	-	0.71041	-	238500	brine
Dollar (1988)	OT-9	260	<7.0	-	-2.1	-27	-	0.70900	-0.6[+]	247300	brine
Dollar (1988)	OT-10	260	-	-	-2.3	-31	-	0.71029	-0.6[+]	273600	brine
Dollar (1988)	OT-11	270	-	-	-1.9	-26	-	0.71030	-0.6[+]	255500	brine
Dollar (1988)	OT-12	320	-	-	-2.0	-29	-	0.71030	-0.5*	262100	brine
Dollar (1988)	OT-13	320	32	-	-2.1	-27	-	0.71007	-0.5	260700	brine
Dollar (1988)	OT-14	360	<7.0	8.0	-2.0	-33	-	0.71036	-0.5[+]	234300	brine
Dollar (1988)	OT-15	380	60	8.0	-2.2	-27	-	0.71023	-0.4	237800	brine
Dollar (1988)	OT-16	350	49	13.0	-2.1	-36	-	0.71034	-0.6	238900	brine
Dollar (1988)	OT-17	370	<7.0	-	-	-	-	0.71036	-	221800	brine
Dollar (1988)	OT-18	350	-	-	-	-	-	0.71036	-0.3[+]	249000	brine
Dollar (1988)	OT-19	390	12.0	-	-1.8	-24	-	-	-0.7	229400	brine
Dollar (1988)	OT-20	490	45	-	-2.0	-23	-	-	-	225000	brine
Dollar (1988)	OT-21	340	<7.0	250	-3.1	-32	-	0.71045	-0.4[+]	242700	brine
Dollar (1988)	OT-22	620	49	-	-	-	-	0.70962	-	195700	brine
Dollar (1988)	OT-23	330	86	-	-1.3	-45	-	0.70887	-0.7*	249700	brine
Dollar (1988)	OT-24	400	66	168	-1.7	-27	-	0.70958	-1.1	195300	brine
Dollar (1988)	OT-25	540	90	160	-2.0	-27	-	0.71000	-	184800	brine
Dollar (1988)	OT-26	260	81	171	-2.1	-27	-	0.70991	-	188300	brine
Dollar (1988)	OT-27	310	69	184	-1.9	-26	-	0.70977	-	196000	brine
Dollar (1988)	OT-28	620	48	7.9	-	-	-	0.70980	-	190700	brine
Dollar (1988)	OT-29	420	66	191	-1.6	-24	-	0.70985	-	190200	brine
Dollar (1988)	OT-30	129	95	10.4	0.4	-35	-	0.70827	-0.3	346100	brine
Dollar (1988)	OT-31	410	73	10.4	-1.7	-20	-	0.70992	-1.3	218200	brine
Dollar (1988)	OT-32	400	61	710	-1.5	-25	-	-	-	214600	brine
Dollar (1988)	OT-33	460	57	7.1	-	-	-	-	-	190700	brine
Dollar (1988)	OT-34	470	71	6.3	-1.8	-29	-	0.71027	-	209500	brine
Dollar (1988)	OT-35	540	96	7.9	-1.8	-25	-	0.71010	-	199300	brine
Dollar (1988)	OT-36	510	48	8.4	-	-	-	-	-	199400	brine
Dollar (1988)	OT-37	490	75	7.2	-1.5	-33	-	0.71003	-	199400	brine
Dollar (1988)	OT-38	510	<7.0	6.6	-2.4	-34	-	0.70994	-	208700	brine
Dollar (1988)	OT-39	420	61	-	-2.7	-26	-	0.70958	-	160900	brine
Dollar (1988)	OT-40	66	66	-	-3.0	-28	-	0.70929	-1.1	139500	brine
Dollar (1988)	OT-41	66	137	-	-2.8	-28	-	0.70938	-0.6	140900	brine
Dollar (1988)	OT-42	<15.0	76	-	-2.6	-28	-	0.70929	-	142100	brine
Sherwood Lollar & Frape (1989)	OHD-1 #15	120	44	-	-5.6	-46	26.0	0.70986	0.1[+]	185570	brine
Sherwood Lollar & Frape (1989)	UN-2 #13	175	53	-	-6.4	-52	69.0	0.71057	-0.3*	44113	saline
Sherwood Lollar & Frape (1989)	OHD-1 #13	125	41	-	-6.1	-52	22.0	0.70993	0.1*	136737	brine
Sherwood Lollar & Frape (1989)	UN-2 #11	210	32	-	-5.7	-47	50.0	0.71060	-0.3*	101983	brine
Sherwood Lollar & Frape (1989)	OHD-1 #7	140	<7.0	-	-4.8	-41	<6.0	0.70981	0.1*	297766	brine
Sherwood Lollar & Frape (1989)	UN-2 #5	165	26	-	-6.0	-46	<6.0	0.71042	-0.1*	251375	brine
Sherwood Lollar & Frape (1989)	OHD-1 #5A	145	29	-	-4.8	-42	<6.0	-	-	290235	brine
Sherwood Lollar & Frape (1989)	OHD-1 #5B	155	<7.0	-	-4.6	-42	<6.0	-	0.3	290351	brine
Sherwood Lollar & Frape (1989)	OHD-1 #3	150	<7.0	-	-4.6	-41	<6.0	0.70979	0.1*	304086	brine
Sherwood Lollar & Frape (1989)	UN-2 #2	580	44	-	-6.7	-49	32.0	0.71027	0.0*	97385	saline
Sherwood Lollar & Frape (1989)	UN-2 #4	520	45	-	-5.2	-47	25.0	0.71038	-0.1*	153987	brine
Sherwood Lollar & Frape (1989)	OHD-1 #2	155	<7.0	-	-4.5	-42	<6.0	0.70981	0.1*	295752	brine
Dollar (1988)	OP-1	63	<7.0	-	-1.6	-50	-	0.70930	1.0*	325400	brine
Walter (Pers. Comm.)	LAHAR 1-7	83	-	-	-	-	-	-	-0.3	**394703**	**brine**
Walter (Pers. Comm.)	FOSTER 1-21	43	-	-	-	-	-	-	-0.2	**349343**	**brine**
Walter (Pers. Comm.)	PRASS 1-12	91	-	-	-	-	-	-	-0.3	**292491**	**brine**
Dollar (1988)	OP-2	<30	<7.0	-	-	-	-	0.70923	-1.0[+]	391500	brine

- = not measured

*includes original measurements as well as new measurements on archived samples; some as old as 1989

[+] new measurements on archived samples; some as old as 1989

TDS in **bold** indicates a calculated value (not measured)

Table 4

Author	Sample ID	AGE FORMATION	Rock Type	Water Type^{+}	Depth m	pH	Temp. °C	DIC mg/L	DOC mg/L	Fluid Density g/cm^3	Spec. Conduct. mhos	Charge Error (%)*	Ca mg/L	Na mg/L	Mg mg/L	K mg/L	Sr mg/L	Cl mg/L	Br mg/L
Dollar (1988)	C-1	CAMBRIAN	Sandstone	Ca-Na-Cl	1217	-	-	-	-	-	-	-2.87	48000	41000	6800	1410	1210	179000	1680
Dollar (1988)	C-2	CAMBRIAN	Sandstone	Ca-Na-Cl	1095	-	-	-	-	-	-	-4.17	60000	48000	6700	1340	1640	220000	1420
Dollar (1988)	C-3	CAMBRIAN	Sandstone	Ca-Na-Cl	1097	-	-	-	-	-	-	-0.73	60000	49000	6700	1330	1690	210000	1550
Dollar (1988)	C-4	CAMBRIAN	Sandstone	Ca-Na-Cl	1212	-	-	-	-	-	-	4.27	58000	50000	7700	1480	1170	186000	1710
Dollar (1988)	C-5	CAMBRIAN	Sandstone	Ca-Na-Cl	1070	-	-	-	-	-	-	-2.43	32000	25000	3200	650	1010	110000	1110
Dollar (1988)	C-6	CAMBRIAN	Sandstone	Na-Ca-Cl	1011	-	-	-	-	-	-	3.02	22000	40000	4400	2100	420	108000	790
Dollar (1988)	C-7	CAMBRIAN	Sandstone	Ca-Na-Cl	1209	-	-	-	-	-	-	-2.55	47000	43000	5900	1380	1210	177000	1510
Dollar (1988)	C-8	CAMBRIAN	Sandstone	Ca-Na-Cl	1264	-	-	-	-	-	-	-1.01	51000	51000	6500	1810	1320	193000	2300
Dollar (1988)	C-9	CAMBRIAN	Sandstone	Ca-Na-Cl	1201	-	-	-	-	-	-	-1.77	53000	45000	7100	1560	1290	192000	1450
Dollar (1988)	C-10	CAMBRIAN	Sandstone	Ca-Na-Cl	1203	-	-	-	-	-	-	-1.51	51000	44000	6900	1550	1210	184000	1440
Dollar (1988)	C-11	CAMBRIAN	Sandstone	Ca-Na-Cl	1149	-	-	-	-	-	-	-0.28	44000	48000	5300	1570	1130	169000	1610
Dollar (1988)	C-12	CAMBRIAN	Sandstone	Ca-Na-Cl	1087	-	-	-	-	-	-	-1.58	54000	42000	5700	1150	1230	183000	1770
Dollar (1988)	C-13	CAMBRIAN	Sandstone	Ca-Na-Cl	887	-	-	-	-	-	-	-2.07	55000	44000	7200	940	1210	195000	1840
Sherwood Lollar & Frape (1989)	OHD-1 #1	PRECAMBRIAN	Granitic	Ca-Na-Cl	380	-	-	-	-	-	-	2.15	69000	32000	5000	500	1400	178000	1640

- = not measured
* = charge error (%) calculated in this study
$^{+}$ water type calculated based on ion concentrations in meq/L

Table 4 continued

Author	Sample ID	SO_4 mg/L	HCO_3 mg/L	F mg/L	^{18}O ‰	^{2}H ‰	^{3}H TU	Sr(87/86)	^{37}Cl	TDS mg / L	Classification Davis 1964
Dollar (1988)	C-1	280	<7.0	-	-4.0	-29	-	0.71028	-0.2	279200	brine
Dollar (1988)	C-2	52	21	-	-4.4	-28	-	0.71002	-0.2*	337600	brine
Dollar (1988)	C-3	47	19.0	-	-4.6	-28	-	-	-0.2^{+}	325600	brine
Dollar (1988)	C-4	96	<7.0	10.5	-4.6	-35	-	0.70990	-0.2*	306000	brine
Dollar (1988)	C-5	980	<7.0	-	-4.1	-36	-	0.70957	0.2	174100	brine
Dollar (1988)	C-6	650	<7.0	11.4	-1.4	-28	-	0.71007	-0.5	179200	brine
Dollar (1988)	C-7	250	<7.0	-	-3.3	-21	-	0.70986	-	276600	brine
Dollar (1988)	C-8	134	<7.0	-	-3.3	-28	-	0.70990	-0.3*	307400	brine
Dollar (1988)	C-9	131	17.0	-	-3.6	-29	-	0.70980	-0.1^{+}	301100	brine
Dollar (1988)	C-10	169	17.0	-	-3.8	-32	-	-	-0.1	289200	brine
Dollar (1988)	C-11	210	<7.0	-	-2.0	-24	-	0.71029	-0.4	269900	brine
Dollar (1988)	C-12	138	<7.0	-	-	-	-	-	-	288600	brine
Dollar (1988)	C-13	146	<7.0	-	-	-	-	0.70951	-0.1^{+}	305200	brine
Sherwood Lollar & Frape (1989)	OHD-1 #1	143	<7.0	-	-5.3	-44	8.0	-	0.3	287807	brine

- = not measured
*includes original measurements as well as new measurements on archived samples; some as old as 1989
$^{+}$new measurements on archived samples; some as old as 1989

Table 5

Author	Sample Number	Depth m	Sampling procedure	Sample Quality Production only	Explanation
Dollar (1988)	MB-1	746	Well head bleeder valve	Good	-
Dollar (1988)	MB-2	760	Well head bleeder valve	Good	-
Dollar (1988)	MB-3	738	Well head bleeder valve	Good	-
Dollar (1988)	MB-4	737	Well head bleeder valve	Good	-
Dollar (1988)	MB-5	728	Well head bleeder valve	Good	-
Dollar (1988)	MB-6	723	Well head bleeder valve	Good	-
Walter (Pers. Comm.)	BRENNAN 122		Well head bleeder valve	Good	-
Walter (Pers. Comm.)	CAMPBELL #7		Well head bleeder valve	Good	-
Walter (Pers. Comm.)	CAMPBELL #9		Well head bleeder valve	Good	-
Walter (Pers. Comm.)	CANNELL #1		Well head bleeder valve	Good	-
Walter (Pers. Comm.)	CARTER		Well head bleeder valve	Good	-
Walter (Pers. Comm.)	JAMES 122		Well head bleeder valve	Good	-
Walter (Pers. Comm.)	NKERN #1		Well head bleeder valve	Good	-
Cloutier (1994)	LD-90-3-5	51.66	Well head bleeder valve	Good	-
Cloutier (1994)	DOW-90-3-4	43.9	Well head bleeder valve	Good	-
Husain (1996)	BRP-143	43.66	Multilevel monitoring well	Good	-
Husain (1996)	BRP-151	45.89	Multilevel monitoring well	Good	-
Martini et al. (1998)	SP A2-32		Well head bleeder valve	Good	-
Martini et al. (1998)	WSMC2-10		Well head bleeder valve	Good	-
Martini et al. (1998)	HGR D4-6		Well head bleeder valve	Good	-
Cloutier (1994)	LD-90-3-4	67.67	Multilevel monitoring well	Good	-
Cloutier (1994)	LD-90-3-3	89.42	Multilevel monitoring well	Good	-
Cloutier (1994)	LD-90-3-2	131.06	Multilevel monitoring well	Good	-
Cloutier (1994)	DOW-90-3-3	76.7	Multilevel monitoring well	Good	-
Cloutier (1994)	DOW-90-3-2	106	Multilevel monitoring well	Good	-
Cloutier (1994)	DOW-90-3-1	142.32	Multilevel monitoring well	Good	-
Cloutier (1994)	LD-90-3-1	141.99	Multilevel monitoring well	Good	-
Dollar (1988)	DD-1	108	Well head bleeder valve	uncertain	long production history, many fields water flooded
Dollar (1988)	DD-2	97	Well head bleeder valve	uncertain	long production history, many fields water flooded
Dollar (1988)	DD-3	1131	Well head bleeder valve	uncertain	long production history, many fields water flooded
Dollar (1988)	DD-4	1128	Well head bleeder valve	uncertain	long production history, many fields water flooded
Weaver (1994)	PD-COCH		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	PD-NORTH		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	PD-RAL		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	PD-WEST		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	RA-N		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	RA-NE		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	RA-SE		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	RA-SW		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	LAI-1		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	LAI-2		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	LAI-3		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	WB-11		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	WB-2		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	WB-7		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	WB-8		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	LBH-1		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	LBH-2		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	LBH-3		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	LBH-4		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	LBO-2		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	LBO-3		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	CFN-14		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	CFN-A		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	CFN-B		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	CFN-161		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	CFN-C		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	CFN-E		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	CFS-A		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	CFS-B		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	CFS-C		Well head or well outlet pipe entering collection tank	Good	-
Weaver (1994)	CFS-D		Well head or well outlet pipe entering collection tank	Good	-
Dollar (1988)	DR-1	1445	Well head bleeder valve	Good	-

Table 6

Author	Sample Number	Depth m	Sampling procedure	Sample Quality Production only	Explanation
Dollar (1988)	SF-1	150	Well head bleeder valve	Good	-
Dollar (1988)	SF-2	150	Well head bleeder valve	Good	-
Dollar (1988)	SF-3	150	Well head bleeder valve	Good	-
Dollar (1988)	SA2-1	250	Well head bleeder valve	Good	-
Dollar (1988)	SA2-2	250	Well head bleeder valve	Good	-
Dollar (1988)	SG-1	354	Well head bleeder valve	Good	-
Dollar (1988)	SG-2	448	Well head bleeder valve	Good	-
Dollar (1988)	SG-3	553	Well head bleeder valve	Good	-
Dollar (1988)	SG-4	614	Well head bleeder valve	Good	-
Dollar (1988)	SG-5	571	Well head bleeder valve	Good	-
Dollar (1988)	SG-6	646	Well head bleeder valve	Good	-
Dollar (1988)	SG-7	749	Well head bleeder valve	Good	-
Dollar (1988)	SG-8	695	Well head bleeder valve	Good	-
Dollar (1988)	SG-9	770	Well head bleeder valve	Good	-
Dollar (1988)	SG-10	726	Well head bleeder valve	Good	-
Dollar (1988)	SG-11	518	Well head bleeder valve	Good	-
Dollar (1988)	SG-12	597	Well head bleeder valve	Good	-
Dollar (1988)	SG-13	670	Well head bleeder valve	Good	-
Dollar (1988)	SA1-1	645	Well head bleeder valve	Good	-
Dollar (1988)	SA1-2	649	Well head bleeder valve	Good	-
Dollar (1988)	SN-1	892	Well head bleeder valve	Good	-
Dollar (1988)	SN-2	895	Well head bleeder valve	Good	-
Dollar (1988)	SN-3	1161	Well head bleeder valve	Good	-
Dollar (1988)	SN-4	1272	Well head bleeder valve	Good	-
Dollar (1988)	SN-5	1305	Well head bleeder valve	Good	-
Dollar (1988)	SN-6	1264	Well head bleeder valve	Good	-
Dollar (1988)	SN-7	1010	Well head bleeder valve	Good	-
Dollar (1988)	SN-8	1001	Well head bleeder valve	Good	-
Dollar (1988)	SN-9	713	Well head bleeder valve	Good	-
Dollar (1988)	SN-10	717	Well head bleeder valve	Good	-
Walter (Pers. Comm.)	COLD SPRINGS WH1-29		Well head bleeder valve	Good	-
Hanratty (1996)	87-2-5	230*	Multilevel monitoring well	Good	-
Hanratty (1996)	87-2-4	221*	Multilevel monitoring well	Good	-
Hanratty (1996)	87-2-3	203*	Multilevel monitoring well	Good	-
Hanratty (1996)	87-2-2	190*	Multilevel monitoring well	Good	-
Hanratty (1996)	88-1-5	239*	Multilevel monitoring well	Good	-
Hanratty (1996)	88-1-4	231*	Multilevel monitoring well	Good	-
Hanratty (1996)	88-1-3	211*	Multilevel monitoring well	Good	-
Hanratty (1996)	88-1-2	199*	Multilevel monitoring well	Good	-
Hanratty (1996)	88-1-1	193*	Multilevel monitoring well	Good	-
Hanratty (1996)	87-2-1	182*	Multilevel monitoring well	Good	-
Dollar (1988)	STGr-1	431	Well head bleeder valve	Good	-
Dollar (1988)	STGr-2	380	Well head bleeder valve	Good	-
Dollar (1988)	STGr-3	374	Well head bleeder valve	Good	-
Dollar (1988)	STGr-4	414	Well head bleeder valve	Good	-
Dollar (1988)	ST-5	292	Well head bleeder valve	Good	-
Dollar (1988)	ST-6	408	Well head bleeder valve	Good	-
Dollar (1988)	SGr-7	424	Well head bleeder valve	Good	-
Dollar (1988)	SGr-8	426	Well head bleeder valve	Good	-
Dollar (1988)	STGr-9	522	Well head bleeder valve	Good	-
Dollar (1988)	STGr-10	524	Well head bleeder valve	Good	-
Dollar (1988)	SGr-11	512	Well head bleeder valve	Good	-
Dollar (1988)	SGr-12	524	Well head bleeder valve	Good	-
Dollar (1988)	STGr-13	547	Well head bleeder valve	Good	-
Dollar (1988)	STGr-14	541	Well head bleeder valve	Good	-
Dollar (1988)	SGr-15	554	Well head bleeder valve	Good	-
Dollar (1988)	SGr-16	572	Well head bleeder valve	Good	-
Dollar (1988)	STGr-17	544	Well head bleeder valve	Good	-
Dollar (1988)	SGr-18	289	Well head bleeder valve	Good	-
Dollar (1988)	SGr-19	335	Well head bleeder valve	Good	-
Dollar (1988)	SGr-20	365	Well head bleeder valve	Good	-
Dollar (1988)	SGr-21	410	Well head bleeder valve	Good	-
Dollar (1988)	SW-1	361	Well head bleeder valve	Good	-
Dollar (1988)	SW-2	422	Well head bleeder valve	Good	-
Dollar (1988)	SW-3	422	Well head bleeder valve	Good	-
Dollar (1988)	SW-4	459	Well head bleeder valve	Good	-

*masl, not depth in borehole

Table 7

Author	**Sample Number**	**Depth m**	**Sampling procedure**	**Sample Quality Production only**	**Explanation**
Dollar (1988)	OT-1	647	Well head bleeder valve	Good	-
Dollar (1988)	OT-2	657	Well head bleeder valve	Good	-
Dollar (1988)	OT-3	645	Well head bleeder valve	Good	-
Dollar (1988)	OT-4	738	Well head bleeder valve	Good	-
Dollar (1988)	OT-5	743	Well head bleeder valve	Good	-
Dollar (1988)	OT-6	771	Well head bleeder valve	Good	-
Dollar (1988)	OT-7	790	Well head bleeder valve	Good	-
Dollar (1988)	OT-8	775	Well head bleeder valve	Good	-
Dollar (1988)	OT-9	786	Well head bleeder valve	Good	-
Dollar (1988)	OT-10	784	Well head bleeder valve	Good	-
Dollar (1988)	OT-11	804	Well head bleeder valve	Good	-
Dollar (1988)	OT-12	779	Well head bleeder valve	Good	-
Dollar (1988)	OT-13	791	Well head bleeder valve	Good	-
Dollar (1988)	OT-14	782	Well head bleeder valve	Good	-
Dollar (1988)	OT-15	787	Well head bleeder valve	Good	-
Dollar (1988)	OT-16	778	Well head bleeder valve	Good	-
Dollar (1988)	OT-17	781	Well head bleeder valve	Good	-
Dollar (1988)	OT-18	786	Well head bleeder valve	Good	-
Dollar (1988)	OT-19	844	Well head bleeder valve	Good	-
Dollar (1988)	OT-20		Well head bleeder valve	Good	-
Dollar (1988)	OT-21	854	Well head bleeder valve	Good	-
Dollar (1988)	OT-22	1225	Well head bleeder valve	Good	-
Dollar (1988)	OT-23	1140	Well head bleeder valve	Good	-
Dollar (1988)	OT-24	1247	Well head bleeder valve	Good	-
Dollar (1988)	OT-25	1238	Well head bleeder valve	Good	-
Dollar (1988)	OT-26	1203	Well head bleeder valve	Good	-
Dollar (1988)	OT-27	1287	Well head bleeder valve	Good	-
Dollar (1988)	OT-28	1299	Well head bleeder valve	Good	-
Dollar (1988)	OT-29	1278	Well head bleeder valve	Good	-
Dollar (1988)	OT-30	1280	Well head bleeder valve	Good	-
Dollar (1988)	OT-31	1279	Well head bleeder valve	Good	-
Dollar (1988)	OT-32	1259	Well head bleeder valve	Good	-
Dollar (1988)	OT-33	1289	Well head bleeder valve	Good	-
Dollar (1988)	OT-34	1290	Well head bleeder valve	Good	-
Dollar (1988)	OT-35	1292	Well head bleeder valve	Good	-
Dollar (1988)	OT-36	1292	Well head bleeder valve	Good	-
Dollar (1988)	OT-37	1288	Well head bleeder valve	Good	-
Dollar (1988)	OT-38	1293	Well head bleeder valve	Good	-
Dollar (1988)	OT-39	637	Well head bleeder valve	Good	-
Dollar (1988)	OT-40	308	Well head bleeder valve	Good	-
Dollar (1988)	OT-41	310	Well head bleeder valve	Good	-
Dollar (1988)	OT-42	614	Well head bleeder valve	Good	-
Sherwood Lollar & Frape (1989)	OHD-1 #15	172.5	Westbay packer system	Good	-
Sherwood Lollar & Frape (1989)	UN-2 #13	50	Westbay packer system	Good	-
Sherwood Lollar & Frape (1989)	OHD-1 #13	204	Westbay packer system	Good	-
Sherwood Lollar & Frape (1989)	UN-2 #11	85	Westbay packer system	Good	-
Sherwood Lollar & Frape (1989)	OHD-1 #7	29.5	Westbay packer system	Good	-
Sherwood Lollar & Frape (1989)	UN-2 #5	175	Westbay packer system	Good	-
Sherwood Lollar & Frape (1989)	OHD-1 #5A	325.5	Westbay packer system	Good	-
Sherwood Lollar & Frape (1989)	OHD-1 #5B	325.5	Westbay packer system	Good	-
Sherwood Lollar & Frape (1989)	OHD-1 #3	352.5	Westbay packer system	Good	-
Sherwood Lollar & Frape (1989)	UN-2 #2	210	Westbay packer system	Good	-
Sherwood Lollar & Frape (1989)	UN-2 #4	190	Westbay packer system	Good	-
Sherwood Lollar & Frape (1989)	OHD-1 #2	368	Westbay packer system	Good	-
Dollar (1988)	OP-1	3425	separator	uncertain	necessary due to high pressures & low daily brine volumes
Walter (Pers. Comm.)	LAHAR 1-7		Well head bleeder valve	Good	-
Walter (Pers. Comm.)	FOSTER 1-21		Well head bleeder valve	Good	-
Walter (Pers. Comm.)	PRASS 1-12		Well head bleeder valve	Good	-
Dollar (1988)	OP-2		separator	uncertain	necessary due to high pressures & low daily brine volumes

Table 8

Author	Sample Number	Depth m	Sampling procedure	Sample Quality Production only	Explanation
Dollar (1988)	C-1	1217	Well head bleeder valve	Good	-
Dollar (1988)	C-2	1095	Well head bleeder valve	Good	-
Dollar (1988)	C-3	1097	Well head bleeder valve	Good	-
Dollar (1988)	C-4	1212	Well head bleeder valve	Good	-
Dollar (1988)	C-5	1070	Well head bleeder valve	Good	-
Dollar (1988)	C-6	1011	Well head bleeder valve	Good	-
Dollar (1988)	C-7	1209	Well head bleeder valve	Good	-
Dollar (1988)	C-8	1264	Well head bleeder valve	Good	-
Dollar (1988)	C-9	1201	Well head bleeder valve	Good	-
Dollar (1988)	C-10	1203	Well head bleeder valve	Good	-
Dollar (1988)	C-11	1149	Well head bleeder valve	Good	-
Dollar (1988)	C-12	1087	Well head bleeder valve	Good	-
Dollar (1988)	C-13	887	Well head bleeder valve	Good	-
Sherwood Lollar & Frape (1989)	OHD-1 #1	380	Well head bleeder valve	Good	-