

Chlorine and Bromine Isotopic Analyses of Groundwaters: DGR-3 and DGR-4

NWMO-TR-2015-20

November 2015

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ABSTRACT

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Abstract

This report describes $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ isotopic analyses for groundwaters from confined saline aquifers of Silurian and Cambrian age on the eastern flank of the Michigan Basin within the Huron Domain. In total, six groundwater samples were obtained during opportunistic sampling of the carbonate Salina A1 and Guelph formations and over-pressured Cambrian sandstone during the drilling of deep boreholes DGR-3 and DGR-4 at the Bruce nuclear site, near Kincardine, Ontario. The stable isotopes of Cl and Br, in conjunction with their geochemical parameters, are examined to ascertain the origin of salts and fluids containing these elements, as well as to identify processes that cause isotopic fractionation. Paleohydrogeologic information in the context of regional scale groundwater system dynamics and solute migration is provided by comparing the groundwater halide geochemical and isotopic values determined with other samples from equivalent geologic formations.

Study results reveal that the sampled groundwaters have isotopic and geochemical signatures similar to formation fluids from the same geological units collected in the Niagara tectonic block, southeast of the Algonquin arch. The Salina A1 samples appear to have been altered by halite dissolution and mixing with cold climate recharge. The Salina A1 and Guelph formation groundwaters are both isotopically depleted in $\delta^{81}\text{Br}$. This is similar to other regional groundwaters that are described as having been sourced within the Michigan Basin. In contrast, the Cambrian groundwaters show enriched $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ isotopic signatures. These signatures are similar to those found elsewhere in the Cambrian as it occurs in the Appalachian Basin to the east and south. The halide isotopic signatures of the Cambrian groundwaters suggest that these fluids may be very old as their isotopic compositions have been maintained since emplacement during regional basinal fluid events occurring in the early Paleozoic.

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1. INTRODUCTION

This technical report presents $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ isotopic results from groundwater samples collected from within cored boreholes DGR-3 and DGR-4 that intersect the entire 840 m thick Paleozoic sedimentary sequence occurring beneath the Bruce Nuclear Site near Kincardine, Ontario (Figure 1). In total, six groundwater samples were retrieved by opportunistic sampling of three confined saline bedrock aquifers during drilling. These aquifers include, in descending order, the carbonate Salina A1 and Guelph formations and the lowermost unconformable Cambrian sandstone. The hydrogeochemical and isotopic analyses performed on the groundwater samples are used to assess processes most influencing groundwater origin and evolution. The analyses are also used to compare site specific results against existing isotopic and chemical data from the same sedimentary formations found elsewhere in Ontario and Michigan, with a focus on Cl and Br concentrations and ratios, stable water isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$), and $^{87}\text{Sr}/^{85}\text{Sr}$ ratios. The work described in this report was completed at the University of Waterloo Environmental Isotope Laboratory.

Earlier researchers analyzed and described more than 190 samples of saline waters and brines from sedimentary formations in southern Ontario (Hobbs et al. 2011; Shouakar-Stash 2008). These samples were analyzed for geochemistry and a variety of isotopes including ^{18}O , ^2H , ^{87}Sr , ^{37}Cl , and ^{81}Br . Figures 2a and 2b illustrate sample locations as they occur in the Waterloo Regional Hydrogeochemical Database (WRHD). There are several sources for these samples. Many of the samples are from oil and gas wells, while a smaller number are from wells drilled for research purposes. The larger data set come from a wide range of formations ranging from Cambrian to Mississippian in age, mainly from southern Ontario and primarily from the Niagara tectonic block. A comprehensive review of the chemistry and isotopic signatures of the fluids can be found in Hobbs et al. (2011), and additional information can be found in Shouakar-Stash (2008), Ziegler and Longstaffe (2000a, 2000b), Weaver et al. (1995), Weaver (1994), Dollar (1988), and McNutt et al. (1987). More recently, additional regional hydrochemical and isotopic data was published by Skuce et al. (2015).

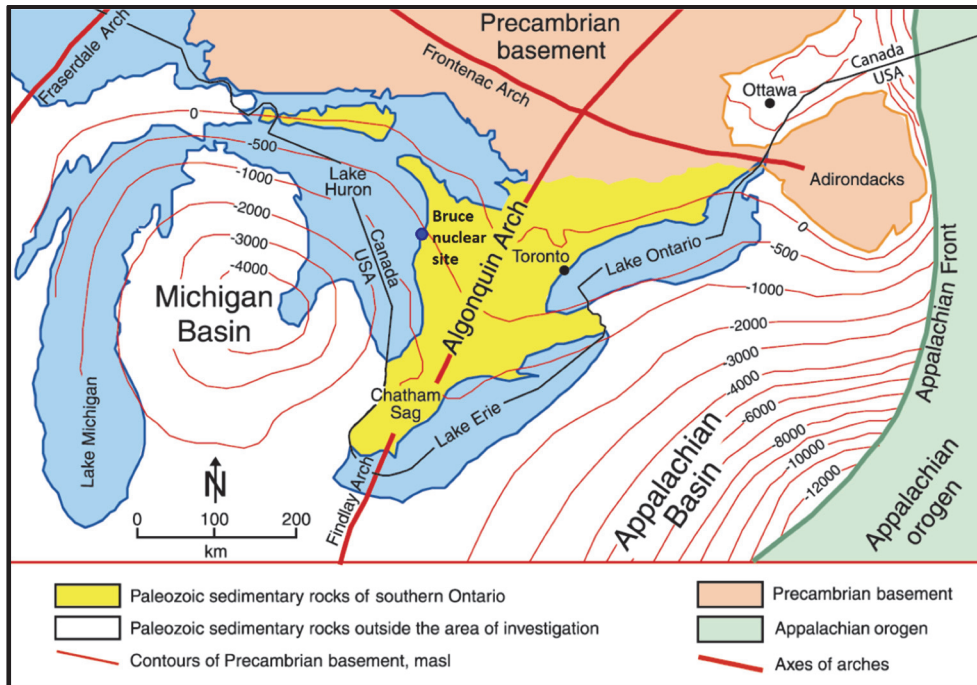


Figure 1: Large-scale Tectonic Elements in Southern Ontario and Location of the Bruce Nuclear Site (Adapted from Johnson et al. 1992 (from Mazurek 2004))

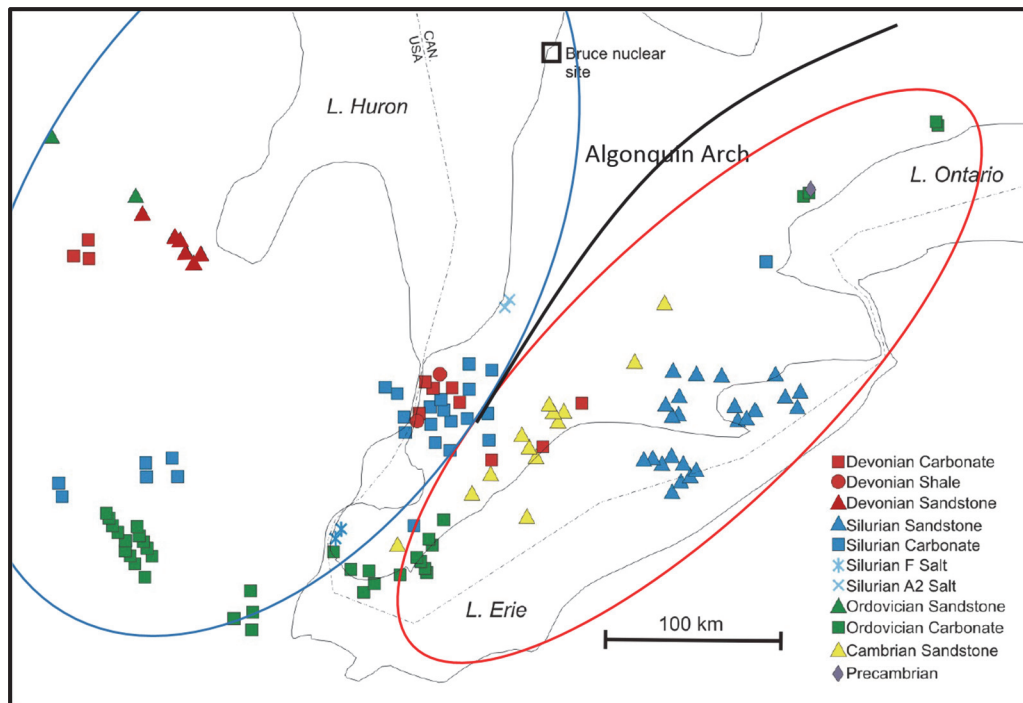


Figure 2a: Location of Regional Samples Collected from the Sedimentary Formations in Southwestern Ontario and in Central and Eastern Michigan, USA. Adapted from Hobbs et al. 2011 (from Frapet et al. 1989)

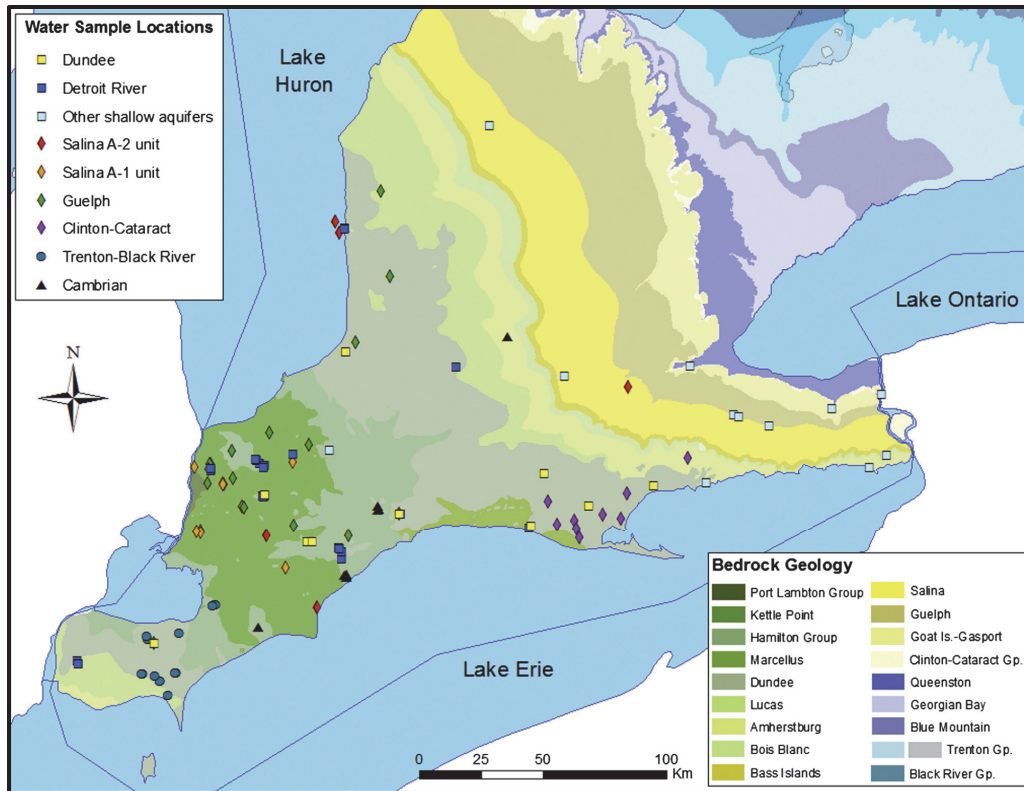


Figure 2b: Bedrock Geology Map of Southwestern Ontario and Locations of Water Samples Collected in the Study by Skuce et al. (2015)

2. OBJECTIVE

The objective of this study is to ‘fingerprint’ the halide isotopic signature of the saline groundwaters occurring within confined sedimentary aquifers beneath the Bruce nuclear site to further assess groundwater mobility and origin at the site and regional basin scales. Shouakar-Stash (2008) found that both $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ yielded distinctive signatures for individual sedimentary units of the Michigan Basin. $\delta^{81}\text{Br}$ isotopic results for samples to the east of the Algonquin Arch (Figure 1) were more enriched than the seawater standard (SMOB, 0‰) while samples from the Waterloo regional data set to the west of the Arch and associated with the Michigan Basin were almost always depleted relative to SMOB.

As such, a comparison of these regional results with groundwaters occurring beneath the Bruce nuclear site would further explore the ability to uniquely identify groundwaters test notions of groundwater system stability, lateral migration and depth of penetration.

3. METHODOLOGY AND SAMPLE LOCATION

The formation fluids analyzed consisted of archived opportunistic groundwater samples from boreholes DRG-3 and DGR-4 at the Bruce nuclear site near Kincardine, Ontario. Analytical results for geochemistry and stable water isotopes were provided by NWMO for each groundwater sample in order to i) assess and compare the chemistry in the context of the $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ isotopic results obtained, and ii) assess groundwater origin, evolution and potential for cross-formational mixing.

3.1 LOCATION OF THE DGR GROUNDWATER SAMPLES

The six groundwater samples from the site come from two deep vertical bedrock boreholes (DGR-3 and DGR-4). DGR-3 groundwater samples were collected at depths of 339.66 mbgs, 389.99 mbgs, and 860.53 mbgs, in the Salina A1 Member, the Guelph Formation, and the Cambrian, respectively (Figure 3). Likewise, similar samples from the same bedrock horizons were obtained at depths of 327.08 mbgs, 377.42 mbgs, and 848.50 mbgs in DGR-4.

The geology of the DGR-3 and DGR-4 boreholes are described in detail by Intera (2011) and NWMO (2011) (see Figure 3). The formation groundwater samples in the DGR-3 borehole at 339.66 m and in DGR-4 at 327.08 m are from the Salina A1 Unit (Upper Silurian), consisting of argillaceous dolostone and anhydritic dolostone. The formation fluid samples in DGR-3 at 389.99 m and in DGR-4 at 377.42 m are from the Guelph Formation (Middle Silurian), which consists of porous dolostone and dolomitic limestone. The formation fluid samples in DGR-3 at 860.53 m and in DGR-4 at 848.50 m are from the Cambrian Formation, consisting primarily of sandstone and dolostone.

3.2 LOCATION OF THE FORMATION FLUIDS FROM SEDIMENTARY UNITS IN SOUTHERN ONTARIO AND MICHIGAN

Over 190 samples of saline waters and brines included in the Waterloo Regional Hydrogeochemistry Database are from sedimentary formations in southwestern Ontario (Figure 2a). These samples were collected from northwest and southeast of the Algonquin Arch (Figure 1). These samples include a large range of formations from Precambrian to Devonian age (Figure 2a). The sample locations range in depth from near ground surface to almost four kilometres depth. Several researchers, including Dollar (1988), Cloutier (1994), Husain (1996), Weaver (1994), and Sherwood-Lollar and Frappe (1989), collected the samples over the past 30 years.

Sampling methods described by Lico et al. (1982) and Kharaka et al. (1987) were used to collect the samples, with slight modifications in certain situations. Weaver et al. (1995) and Hobbs et al. (2011) reported the specific procedures used for sample collection and handling.

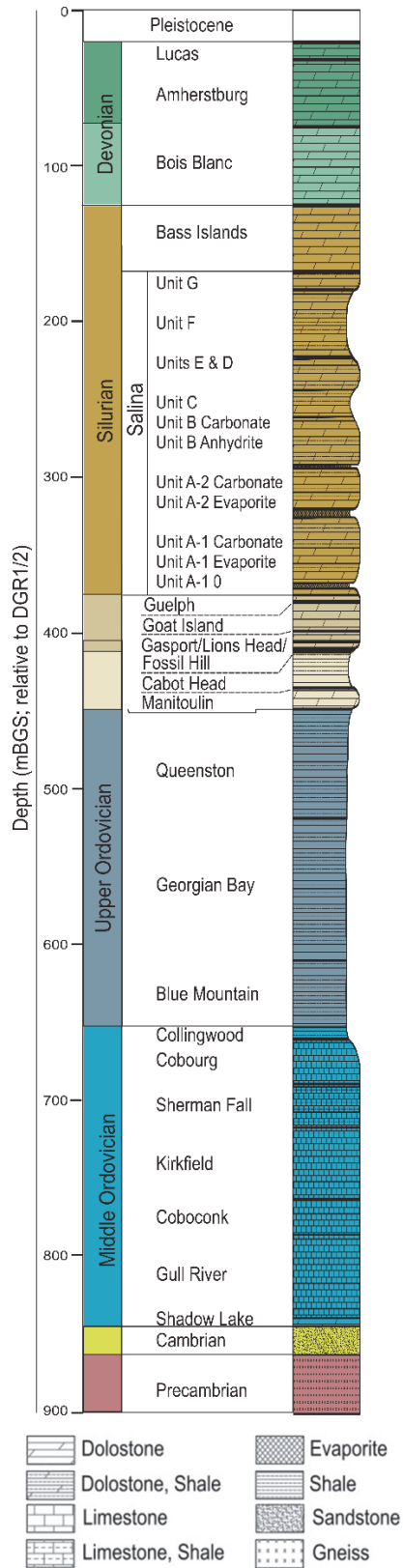


Figure 3: Lithostratigraphy of DGR-3 and DGR-4 Boreholes at the Bruce Nuclear Site (from Intera 2011)

3.3 MEASUREMENT OF STABLE ISOTOPES

The chemical composition and stable isotopes (^{18}O , ^2H , ^{37}Cl , and ^{81}Br) of the formation waters in Ontario were measured by earlier researchers (Dollar 1988; Cloutier 1994; Husain 1996; Weaver 1994; Weaver et al. 1995; Sherwood-Lollar and Frapé 1989; Shouakar-Stash 2008; Martini and Walter 1998). Analyses of major ions were completed at the University of Waterloo. Isotope Ratio Mass Spectrometry (IRMS) was used to analyze $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotopes (Shouakar-Stash 2008). The $\text{CO}_2\text{-H}_2\text{O}$ equilibration method by Epstein and Mayeda (1953) was used to measure the oxygen stable isotopes; afterward, Moser (1977) improved and put forward a new CO_2 method. In addition, Coleman et al. (1982) and Tanweer and Han (1996) described the Zn and Mn reduction method to measure hydrogen stable isotopes by analyzing the H_2 gas.

$\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ stable isotopes were analyzed in this study using the method described by Shouakar-Stash et al. (2005b). Many of the $\delta^{37}\text{Cl}$ measurements were completed, but had not been published prior to 2008 (Shouakar-Stash 2008). As part of this current research, samples from the data set of Shouakar-Stash (2008) were reanalyzed and were found to have very similar values. Methyl chloride (CH_3Cl) gas was utilized to analyze chlorine stable isotopes; this method is called continuous flow isotope ratio mass spectrometry (CF-IRMS) (Eggenkamp 1994; Shouakar-Stash et al. 2005b). All of the chlorine stable isotopes in southern Ontario (this study; Hobbs et al. 2011; Shouakar-Stash 2008) were measured using continuous flow isotope ratio mass spectrometry (CF-IRMS). Similarly, bromine stable isotopic analyses were conducted by CF-IRMS with isotopic measurement on the methyl bromide (CH_3Br) gas (Shouakar-Stash et al. 2005a). Based on these methods, the analytical precisions for the ^{18}O , ^2H , ^{37}Cl , and ^{81}Br isotopes are 0.2‰, 1.0‰, 0.1‰, and 0.1‰, respectively (Shouakar-Stash 2008).

4. RESULTS - GEOCHEMICAL COMPOSITION AND ISOTOPIC SIGNATURE

The geochemical and isotopic results for the formation waters from the Michigan Basin and southern Ontario are listed in Table A1 in the Appendix (Shouakar-Stash 2008; Hobbs et al. 2011).

According to the findings in southern Ontario and some parts of the Michigan Basin, the chlorine concentrations of the groundwater samples have a larger range of values compared to the bromine concentrations. The chlorine concentrations range from less than 1 mg/L to almost 300,000 mg/L, while the bromine concentrations range from less than 1 mg/L to near 8,500 mg/L (Shouakar-Stash et al. 2007). Meanwhile, the weight ratio between bromine and chlorine has a range between 0.0001 and 0.0389 (Shouakar-Stash et al. 2007). The oceanic Br/Cl ratio is approximately 0.0034, which can be compared to the brine water ratio and, in some cases, can be used to determine the extent of evaporation (Carpenter 1978; McCaffrey et al. 1987).

The chlorine isotopic values for groundwater samples in the Waterloo regional database have a range from -0.67‰ to +1.54‰ based on the isotope studies conducted by earlier researchers, and the bromine isotopic values have a range from -0.80‰ to +3.35‰ (Shouakar-Stash et al. 2007) (Table A1). For the regional Cl and Br isotopic data from Skuce et al. (2015), exclusive of the original WRHD, the $\delta^{37}\text{Cl}$ values ranged from -0.49‰ to +1.00‰ and $\delta^{81}\text{Br}$ values ranged from -1.29‰ to +2.21‰; very similar to the Shouakar-Stash data set.

The chlorine and bromine isotopic results of the formation waters measured as part of this study (DGR-3 and DGR-4 boreholes) are shown in Table 1 and fall within the ranges listed for formation waters in the combined regional data sets, shown in Table A1 and Table A2 in the Appendix.

Table 1: Geochemistry and Stable Water Isotopes of the Formation Waters in DGR-3 and DGR-4 from the Bruce Nuclear Site. Samples Were Collected from Three Stratigraphic Units (the Salina-A1 Unit, the Guelph Formation, and the Cambrian Formation)

Borehole	Depth	Stratigraphic Unit	TDS	Cl (mg/L)	Br (mg/L)	Sr (mg/L)	K (mg/L)	Na (mg/L)	Ca (mg/L)	Mg (mg/L)	SO ₄ (mg/L)	CO ₂ (mg/L)	δ ³⁷ Cl (SMOC)	Stdv	δ ⁸¹ Br (SMOB)	Stdv	δ ¹⁸ O (VSMOW)	δ ² H (VSMOW)	⁸⁷ Sr/ ⁸⁶ Sr
DGR-3	339.66m	Salina-A1 Unit	26.8	13745	16	17.5	125	7914	1014	586	2403	134.2	-0.03	0.10	-0.39	0.05	-14.40	-104.30	0.708694
DGR-3	389.99m	Guelph Formation	365.6	252239	2138	595.8	4375	103077	37918	9148	0	26.0	-0.32	0.06	-1.28	0.05	-2.30	-48.10	0.709096
DGR-3	860.53m	Cambrian Formation	224.5	157885	1731	876.2	993	35022	39156	6373	251	20.2	0.24	0.07	1.59	0.05	-4.80	-31.70	0.710228
DGR-4	327.08m	Salina-A1 Unit	30.5	16361	30	17.5	125	8595	1166	627	2556	227.9	-0.05	0.10	-0.37	0.12	-14.50	-102.70	0.708596
DGR-4	377.42m	Guelph Formation	375.5	275163	2055	490.7	4391	118855	15610	9467	169	19.8	-0.24	0.08	-1.10	0.10	-2.70	-50.00	0.709127
DGR-4	848.50m	Cambrian Formation	227.0	162512	1625	744.8	1017	34364	38896	6186	289	17.6	0.36	0.10	1.56	0.05	-5.20	-35.20	0.710247

Note: Geochemical, ¹⁸O and ²H analyses were from Heagle and Pinder (2010), and ⁸⁷Sr/⁸⁶Sr analyses were from Clark et al. (2010).

5. DISCUSSION

The geoscientific data presented and discussed below were obtained from groundwater samples taken from two deep boreholes, DGR-3 and DGR-4, at the Bruce nuclear site, Kincardine, Ontario (Figure 1) and a regional sedimentary formation fluid database from Hobbs et al. (2011), Shouakar-Stash (2008), and Skuce et al. (2015). The DGR samples are from three different stratigraphic units and the results are compared in a series of geochemical and isotopic plots against the combined regional databases ($\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ values), which include both the WRHD (Shouakar-Stash 2008; Hobbs et al. 2011) and the Skuce et al. (2015) database.

5.1 $\delta^{81}\text{Br}$ AND $\delta^{37}\text{Cl}$ ISOTOPIC COMPARISON

Salina A1 Unit Fluids

Figures 4a, b and c show the isotopic results for $\delta^{81}\text{Br}$ plotted against $\delta^{37}\text{Cl}$ for DGR-3, DGR-4 and combined regional hydrogeochemistry data set. Referring to the bedrock stratigraphic column for DGR-3 and DGR-4 (Figure 3), the bedrock of the Salina A1 Unit (Upper Silurian) is comprised of argillaceous dolostone and anhydritic dolostone. The DGR-3 (327.08 m) and DGR-4 (339.66 m) groundwater samples from the Salina A1 Unit fall in an area near the majority of Silurian samples and shallow Devonian samples from the combined regional databases (Figure 4b).

The Waterloo regional data set for sedimentary formation fluids in Ontario contains two fluid samples from the Salina A1 salt (SA1-1 and SA1-2), but these were only analyzed for $\delta^{37}\text{Cl}$ (both have values of -0.35‰). The $\delta^{37}\text{Cl}$ values of these two samples from Salina A1 salts are in the isotopic range (-0.40‰ to -0.20‰) for this geological unit as discussed in a recent study by Skuce et al. (2015). Eggenkamp et al. (1994) proposed that the first salt precipitated from the seawater has more enriched $\delta^{37}\text{Cl}$ isotope than the later precipitated salts. During the evaporative precipitation of salts, salts are more depleted in $\delta^{81}\text{Br}$ and more enriched in $\delta^{37}\text{Cl}$ than their corresponding residual fluids. Tan et al. (2009) concluded that the $\delta^{37}\text{Cl}$ value for early halite is more enriched than 0‰ , while the later halite has a value of between -0.50‰ and 0‰ . Therefore, the negative values of these two Salina A1 salts (SA1-1 and SA1-2) correspond to the $\delta^{37}\text{Cl}$ isotopic value of later halite precipitation. Therefore, there could be a halite dissolution origin for the Salina A1 Unit samples from the site. It is difficult to make comparisons on Figure 4b for the $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ isotopic signatures between the DGR samples and the Waterloo regional data set. However, the Salina A1 samples from the site are depleted for both isotopes and are consistent with the depleted nature of the Michigan Basin fluids, as noted in several earlier studies.

Based on a recent study by Skuce et al. (2015), the $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ isotopes for Salina A1 Unit waters range from -0.40‰ to -0.20‰ ($\delta^{37}\text{Cl}$) and -0.21‰ to $+0.13\text{‰}$ ($\delta^{81}\text{Br}$), respectively, in southern Ontario. The $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ isotopes of the Salina A1 samples at DGR-3 are -0.03‰ ($\delta^{37}\text{Cl}$) and -0.39‰ ($\delta^{81}\text{Br}$), respectively. The $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ isotopes of the Salina A1 samples at DGR-4 are -0.05‰ ($\delta^{37}\text{Cl}$) and -0.37‰ ($\delta^{81}\text{Br}$), respectively. The Bruce site samples from the Salina A1 Unit plot close to the A1 samples described by Skuce et al. (2015) in southern Ontario. Therefore, similar evolution and/or mixing/dilution processes appear to have occurred in the Salina A1 Unit across much of southern Ontario.

Guelph Formation Fluids

The DGR-3 (389.99 m) and DGR-4 (377.42 m) fluids from the Silurian Guelph Formation at the site plot near the Silurian Guelph Formation waters (SG-4, SG-7, SG-8, and SG-10) from the Waterloo regional data set and the equivalent Niagaran Formation waters from Ontario and Michigan (Figure 4b). Referring to the stratigraphic cross-section of the site (Figure 3), the bedrock of the Guelph Formation is comprised of dolostone and dolomitic limestone. The formation waters for the SG-4, SG-7, SG-8, and SG-10 wells were collected from strata of the dolomitic limestone, reef and inter-reef deposits across southwestern Ontario (Liberty and Bolton 1971; Dollar 1988).

The bromine isotopic signature for the DGR-3 (389.99 m, -1.28‰ SMOB) and DGR-4 (377.42 m, -1.10‰ SMOB) Guelph Formation waters are more depleted compared to the other Guelph Formation samples (614 m-749 m, -0.95‰ to -0.61‰ SMOB) from Ontario and Michigan that are presented in the database. Thus, the evolution and/or mixing/dilution processes for the samples from various depths may be different. Based on Shouakar-Stash (2008), the depleted $\delta^{81}\text{Br}$ values (Figure 4b) are similar and, therefore, most likely represent fluids with a source in the Michigan Basin.

Cambrian Formation Fluids

As shown in Figures 4a and 4c, Cambrian Formation fluids in DGR-3 (860.53 mbgs) and DGR-4 (848.50 mbgs) plot close to the deeper Ordovician Black River Group brines from the Toronto area Lakeview research borehole OHD-1. Sections of the OHD-1 boreholes (OHD-1 #2, OHD-1 #3, and OHD-1 #7) are near to the C-13 oil well, a Cambrian sample from the WRHD, as well as two Cambrian oil well samples from the Skuce et al. (2015) database.

The OHD-1 samples and Cambrian oil well samples are from the Niagara tectonic structural block, located on the north shores of Lake Ontario and Lake Erie, respectively (Figures 1, 2a, 2b). However, the OHD-1 samples were collected from relative shallow depths (from 300 m to 368 m below ground surface). The Cambrian C-13 sample is from 887 m below ground surface, similar to the depth of the Cambrian samples from the site.

According to the bedrock lithology described by Liberty (1969), the OHD-1 #2, #3, and #7 fluids from the Lakeview, Toronto, boreholes are from craton-derived clastic rocks and impure carbonate rocks. The Cambrian Formation waters in C-13 are found in sandstones and sandy dolostone strata (Trevail 1990).

C-13 is a petroleum producing well, similar to the boreholes from Skuce et al. (2015), and is located east of the Algonquin Arch, which is often described as a geological divide between the Appalachian Basin to the east and Michigan Basin to the west. The Cambrian in this part of southern Ontario has been observed to be more carbonate rich as one moves west and north within the Niagara tectonic structural block (McNutt et al. 1987). The Cambrian sourced fluids are enriched for both isotopes, similar to the Cambrian fluids from the site.

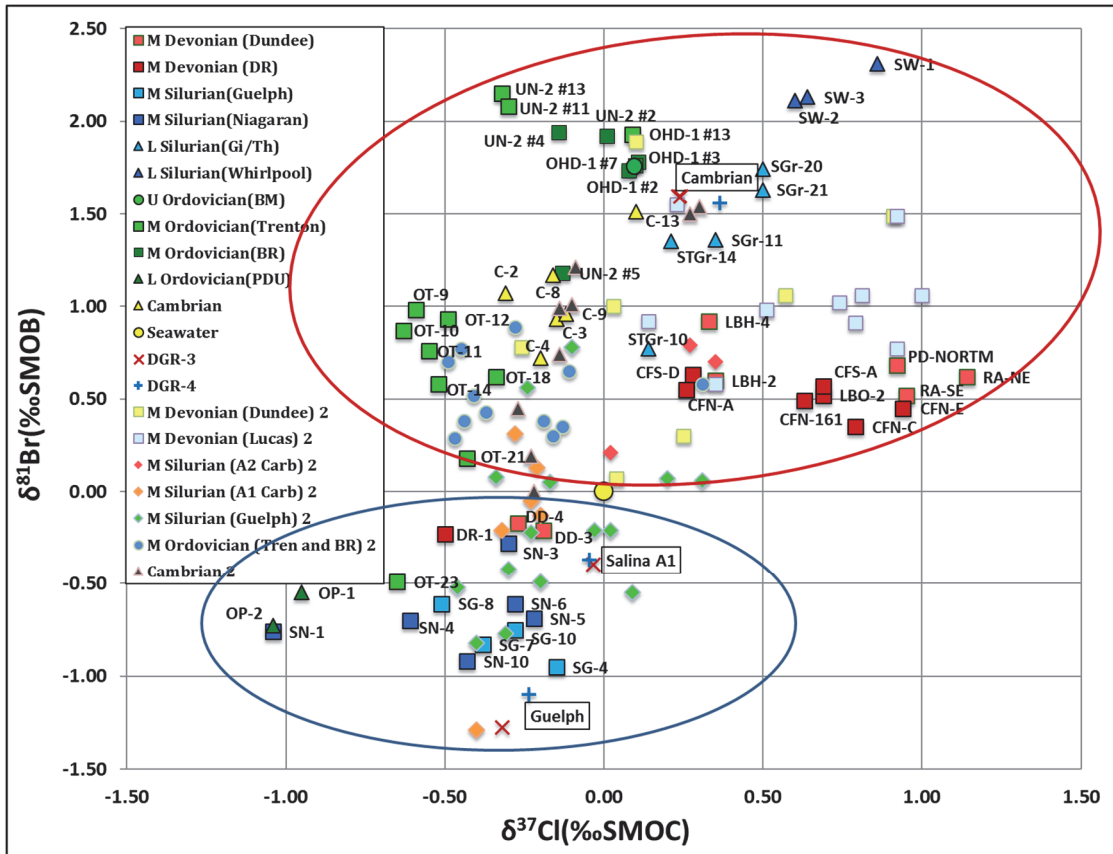


Figure 4a: $\delta^{81}\text{Br}$ versus $\delta^{37}\text{Cl}$ Isotopic Results for DGR-3, DGR-4 and Regional Data Set Groundwaters. The Number 2 behind Symbols in the Legend Refers to Data from the Skuce et al. (2015) Database. All Other Data Are from the WRHD. Data Set in Red Circle Is from Southeast of the Algonquin Arch, and Data Set in Blue Circle Is from Northwest of the Algonquin Arch

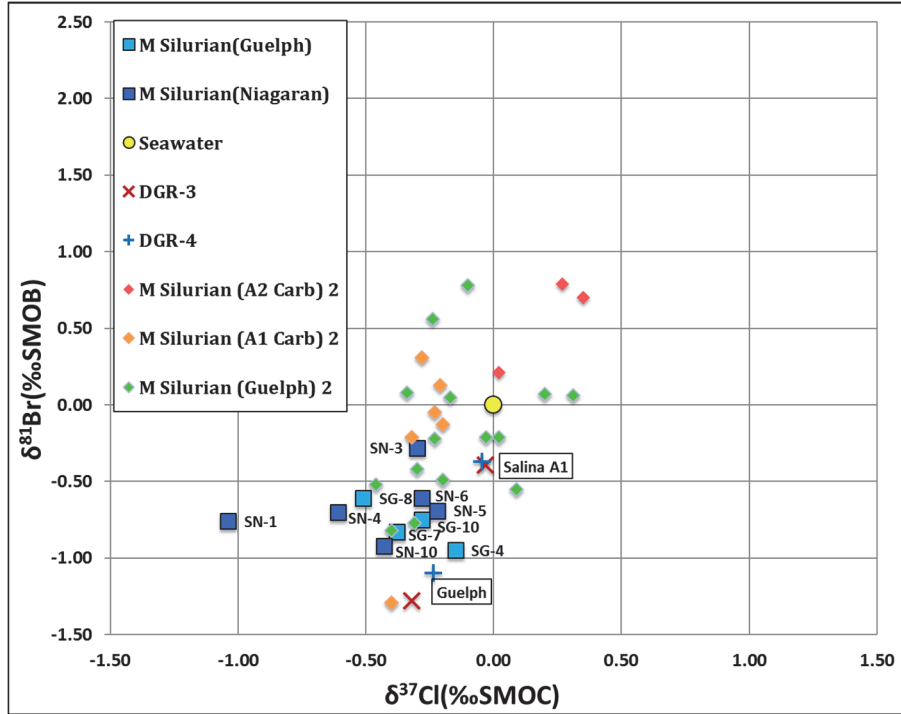


Figure 4b: Isotopic Results of $\delta^{81}\text{Br}$ versus $\delta^{37}\text{Cl}$ (Silurian). The Number 2 behind Symbols in the Legend Refers to Data from the Skuce et al. (2015) Database. All Other Data Are from the WRHD

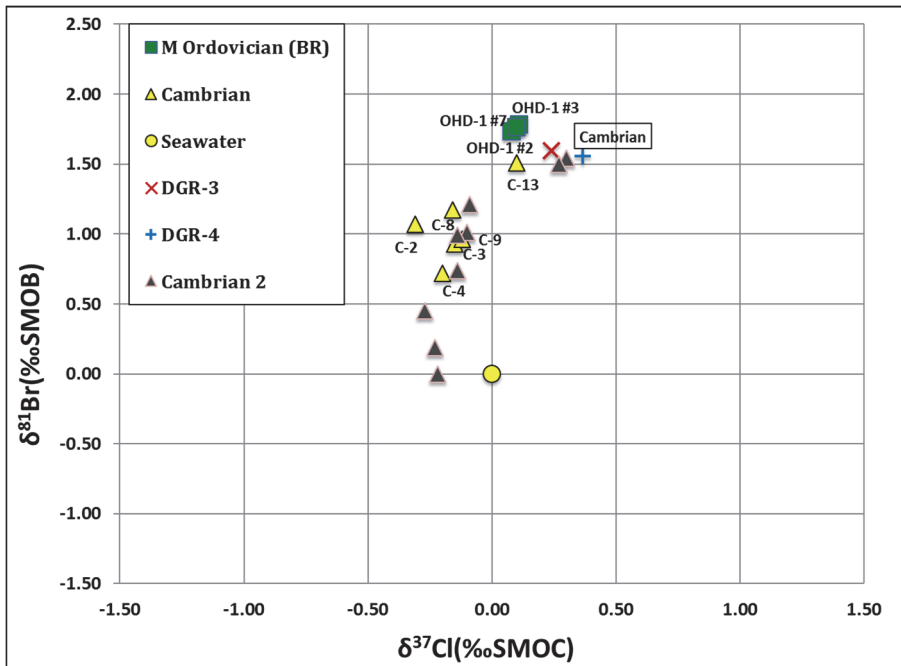


Figure 4c: Isotopic Results of $\delta^{81}\text{Br}$ versus $\delta^{37}\text{Cl}$ (Cambrian). Black Triangles on Plot Are Data from the Skuce et al. (2015) Database

Summary

To summarize, groundwaters within the Salina A1 Unit and the Guelph Formation are consistent with historical observations that Michigan Basin fluids have depleted in $\delta^{81}\text{Br}$ isotopic signatures (Figure 4b). Thus, the formation waters from the two Silurian aged zones at the site can be described as fluids sourced within the Michigan Basin. This is based on a comparison of numerous isotopic and geochemical parameters from the DGR samples and fluids from similar geological formations within the Michigan Basin.

The deeper Cambrian groundwater samples show enriched isotopic signatures (Figure 4c). All samples in the combined regional database from the Cambrian are also enriched in $\delta^{81}\text{Br}$ isotopes; however, the regional Cambrian data represents conditions east of the Algonquin Arch, nominally described as Appalachian Basin sourced fluids. The deeper Cambrian samples from the site could have a different basinal origin from the Silurian samples. The Cambrian samples from the DGR boreholes to the west of the Algonquin Arch may have the same origin as the Cambrian samples from the east of the Algonquin Arch. Several authors have invoked large-scale basinal fluid movements at various times in the geologic past that have resulted in dolomitization and the emplacement of hydrothermal ore/petroleum in southern Ontario (Frape et al. 1989; Budai et al. 1991; Ziegler and Longstaffe 2000a, 2000b; Bailey 2005). In addition, the dolomitized fluids are hypothesized to have migrated along faults and fracture systems in Ontario through the Cambrian sandstones underlying the Ordovician limestones of the Trenton and Black River groups (Frape et al. 1989; Budai et al. 1991; Ziegler and Longstaffe 2000a, 2000b; Bailey 2005).

5.2 $\delta^{81}\text{Br}$ ISOTOPIC RESULTS COMPARED TO BR CONCENTRATION

Figure 5 is a plot of the $\delta^{81}\text{Br}$ isotopic results versus Br concentrations for the six DGR groundwater samples (see Table 1) and the combined regional data sets. The data from the Guelph Formation waters at the site plot near the Waterloo regional data set for the Guelph and Niagaran Formation waters in Ontario and Michigan. The Salina A1 Unit samples from the site plot distinctly away from both the regional Silurian samples and the Guelph Formation waters from the site. The data from the Salina A1 Unit at the site have much lower Br concentration than the Waterloo regional data set for the Guelph and Niagaran Formation fluids in Ontario and Michigan. This may be the result of extreme dilution by glacial waters during the early Devonian period. The glacial waters, which are assumed to have no significant Br concentration, would have no influence on the $\delta^{81}\text{Br}$ isotopes of the DGR groundwater samples (see section 5.3 for detailed discussion). The observed $\delta^{81}\text{Br}$ isotopic values (-0.39‰ for DGR-3 and -0.37‰ for DGR-4) of the Salina A1 Units samples from the site are consistent with the $\delta^{81}\text{Br}$ isotopic values (-1.00‰ to 0.35‰ $\delta^{81}\text{Br}$) of the Silurian Formation waters based on the Waterloo regional data set. Analysis of the overlying Devonian groundwaters could provide an additional line of support for the proposed origin of the fluids.

Commonly, the dilution of formation waters at the margin of the Michigan Basin is higher than the central area of the Michigan Basin (McIntosh and Walter 2005, 2006). Halite dissolution, especially of the Salina salts in Ontario, has had a very small influence on the geochemical composition or concentration of chlorine and bromine (McIntosh and Walter 2005, 2006). The geochemical and isotopic data on Figure 5 illustrate that the bromine concentrations of the Salina A1 Unit waters at the site are similar to many of the shallow Devonian samples from boreholes near Sarnia, Ontario.

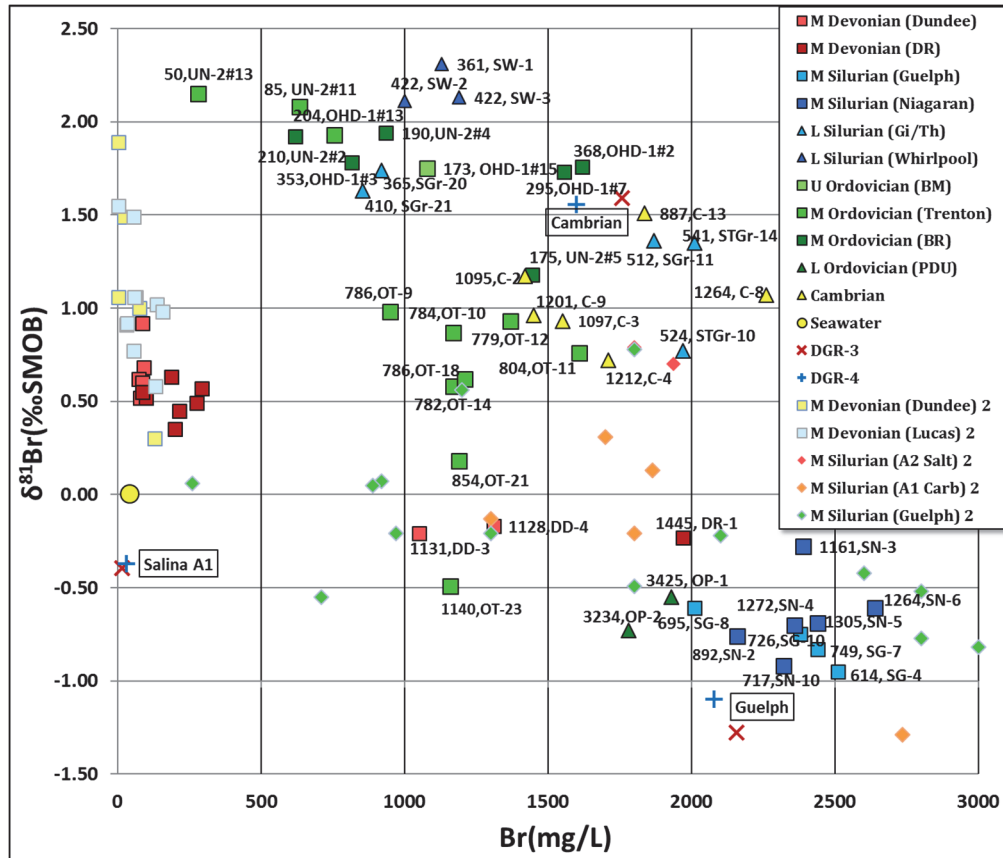


Figure 5: $\delta^{81}\text{Br}$ Isotopes versus Br Concentrations in Samples from the Bruce Nuclear Site and the Combined Regional Databases. The Number 2 behind Symbols in the Legend Refers to Data from the Skuce et al. (2015) Database. All Other Data Are from the WRHD

The plot of $\delta^{81}\text{Br}$ isotopes versus Br/Cl weight ratios (Figure 6a) for the six DGR groundwater samples versus the combined regional database samples supports the ideas discussed above. The Br/Cl weight ratios of the Guelph and Cambrian formation waters are greater than seawater (Figure 6a). Thus, a residual, evaporated paleo-seawater could be the main end member of the Guelph and Cambrian Formation fluids at the site (Figure 6b). The Salina A1 Formation waters at DGR-3 and DGR-4 have a lower Br/Cl weight ratio than seawater (Figure 6a). Therefore, the Salina A1 Formation waters have different end member(s) than the other two formation fluids at the site. The Salina A1 samples from the site could be inferred as a non-marine water source and/or halite dissolution source based on processes and mixing scenarios shown on Figure 6b. The halite dissolution is more probable based on the low Br/Cl weight ratio (<0.002) of the samples. As halite is usually more deficient in Br relative to the fluid from which it precipitated, the dissolved halite would increase the Cl while Br decreases after dissolution. In addition, the Salina A1 Formation fluids show a depleted $\delta^{81}\text{Br}$ isotopic signature (-0.39‰ for DGR-3 and -0.37‰ for DGR-4). Halite salts usually have a depleted $\delta^{81}\text{Br}$ signature. Therefore, the depleted isotopic signature of the Silurian aged DGR fluids could be derived from the halite dissolution. Based on the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotopic data (Figure 7a), the depleted $\delta^{18}\text{O}$ isotopic signatures of the Salina A1 samples from the site are consistent with the $\delta^{18}\text{O}$ signature of the glacial waters. Therefore, these DGR fluids must be mixed with cold climate recharge waters to gain their depleted $\delta^{18}\text{O}$ isotopic signatures.

Based on the concentration trends of bromide versus chloride (Figure 6b), groundwaters from the Salina A1 Unit at the site plot just above the seawater evaporation line and have lower Br and Cl concentrations than seawater. Halite dissolution by a low concentration saline fluid and/or fresh water could have affected the Salina A1 Unit waters. On Figure 6b this would follow a line similar to the horizontal halite dissolution line (blue). In this case, the samples must have then been diluted by fresher, less saline water following the green mixing line on Figure 6b. The A1 samples plot close to the middle Devonian Formation waters with very low Cl and Br content (Figure 6b). It is likely that the Salina A1 Unit waters are comprised of three end members: a cold climate possibly glacial water (see also section 5.3), Devonian seawater and dissolved halite salt. In contrast, the Guelph and Cambrian formation fluids from the site plot close to the regional formation fluids from southern Ontario and Michigan (Figure 6b). For the samples from the site, the Cambrian Formation fluids plot just below the seawater evaporation line beyond the point of halite precipitation, while the Guelph Formation fluids are close to the evaporation line (Figure 6b). Therefore, the latter two formation fluids at the site went through extreme paleo-seawater evaporation, and there is no strong evidence of subsequent mixing or dilution. The close positions of the Guelph and Cambrian Formation fluids to the seawater evaporation line after the halite precipitation point indicate the existence of the evaporated paleo-seawater end-member for these two formation fluids at the site.

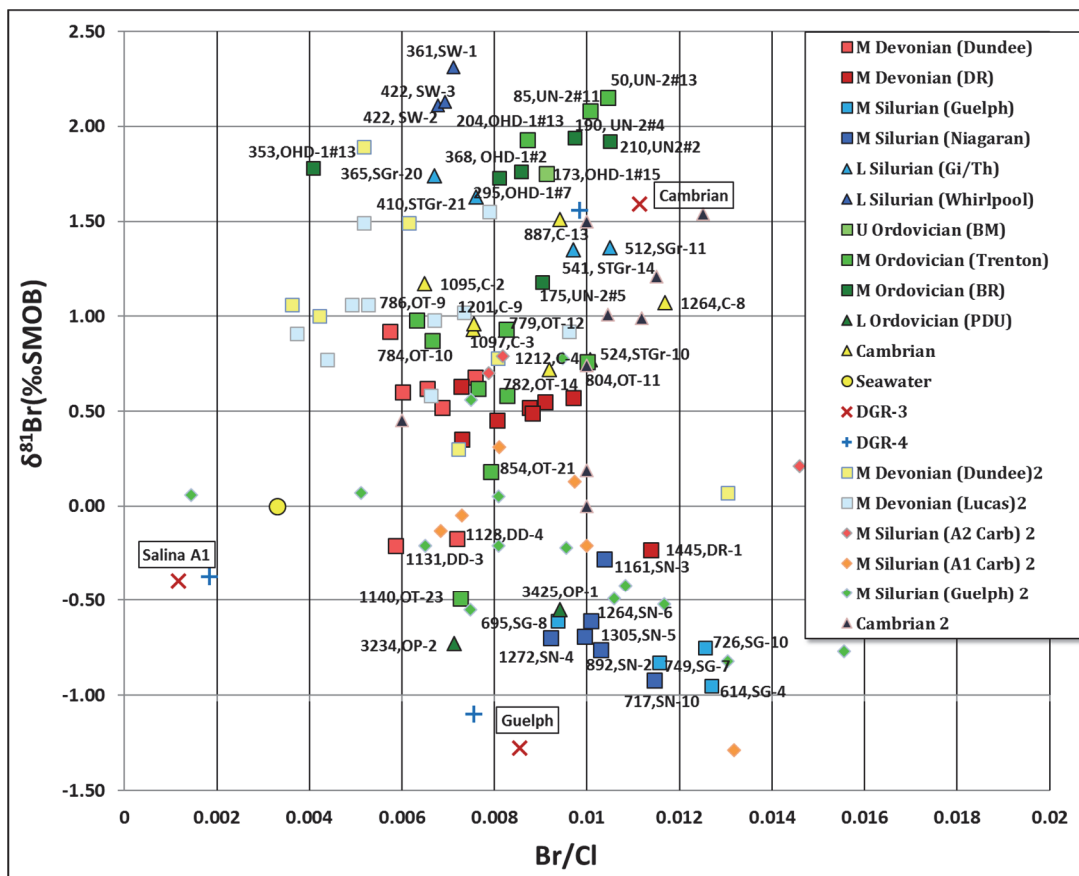


Figure 6a: $\delta^{81}\text{Br}$ Isotope versus Br/Cl Weight Ratio. The Number 2 behind Symbols in the Legend Refers to Data from the Skuce et al. (2015) Database. All Other Data Are from the WRHD

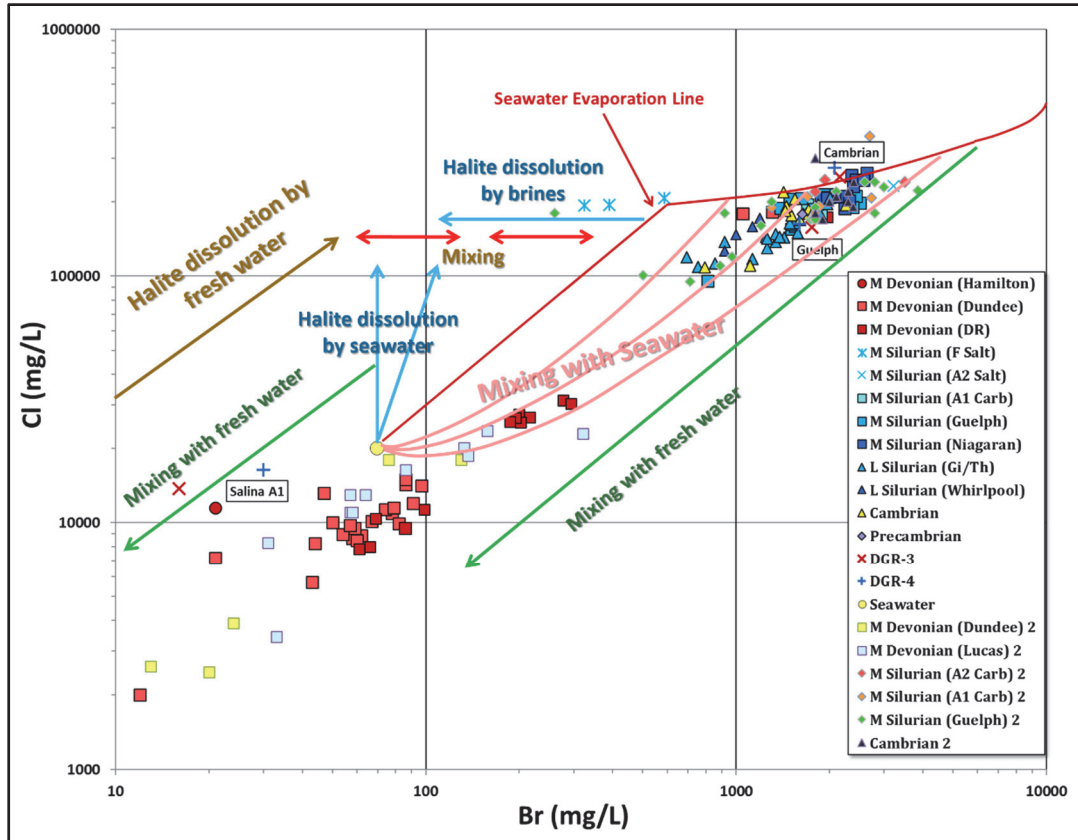


Figure 6b: Concentration Trends of Chloride versus Bromide during the Evaporation of Seawater. The Number 2 behind Symbols in the Legend Refers to Data from the Skuce et al. (2015) Database. All Other Data Are from the WRHD

5.3 $\delta^{18}\text{O}$ AND $\delta^2\text{H}$ ISOTOPE ANALYSIS

The ^{18}O - ^2H isotopic results for the groundwater samples from the Bruce nuclear site must also be discussed in the context of fluid origins – i.e., the concept of a sedimentary formation fluid origin versus a crystalline shield origin.

The $\delta^2\text{H}$ - $\delta^{18}\text{O}$ isotopic data for the DGR samples, obtained from NWMO (Intera 2011), is plotted with Holser's Curve (1979) on Figures 7a, b and c. The $\delta^2\text{H}$ - $\delta^{18}\text{O}$ isotopic data on Figures 7a and 7b show that the formation waters from the Salina A1 Unit at the site plot away from the other regional data for sedimentary formation fluids in Ontario and Michigan. The significantly depleted isotopic features of the DGR-3 (327.08 m) and DGR-4 (339.66 m) samples indicate mixing of the original saline formation water (evaporated paleo-seawater) with fresh water from a cooler time period and/or glacial melt water. The brines marked as Salina A1 Unit from the site could be diluted by glacial melt water during past glacial or interglacial periods (NWMO 2011; Intera 2011; Clark et al. 2013; Al et al. 2015). The glacial melt water shows significantly depleted isotopic signatures ($\delta^2\text{H}$ and $\delta^{18}\text{O}$), and this also results in lower chemical concentrations of chlorine and bromine than in the underlying, deeper formation waters. Several Devonian-sourced fluids from southwestern Ontario in the combined regional database have had their present isotopic signature attributed to a glacial fluid mixing history (Weaver et al.

1995; Dollar 1988; McNutt et al. 1987; NWMO 2011; Intera 2011). The samples from the Salina A1 Unit at the site have been described as having a potential mixing end member of glacial origin (NWMO 2011; Intera 2011; Clark et al. 2013; Al et al. 2015).

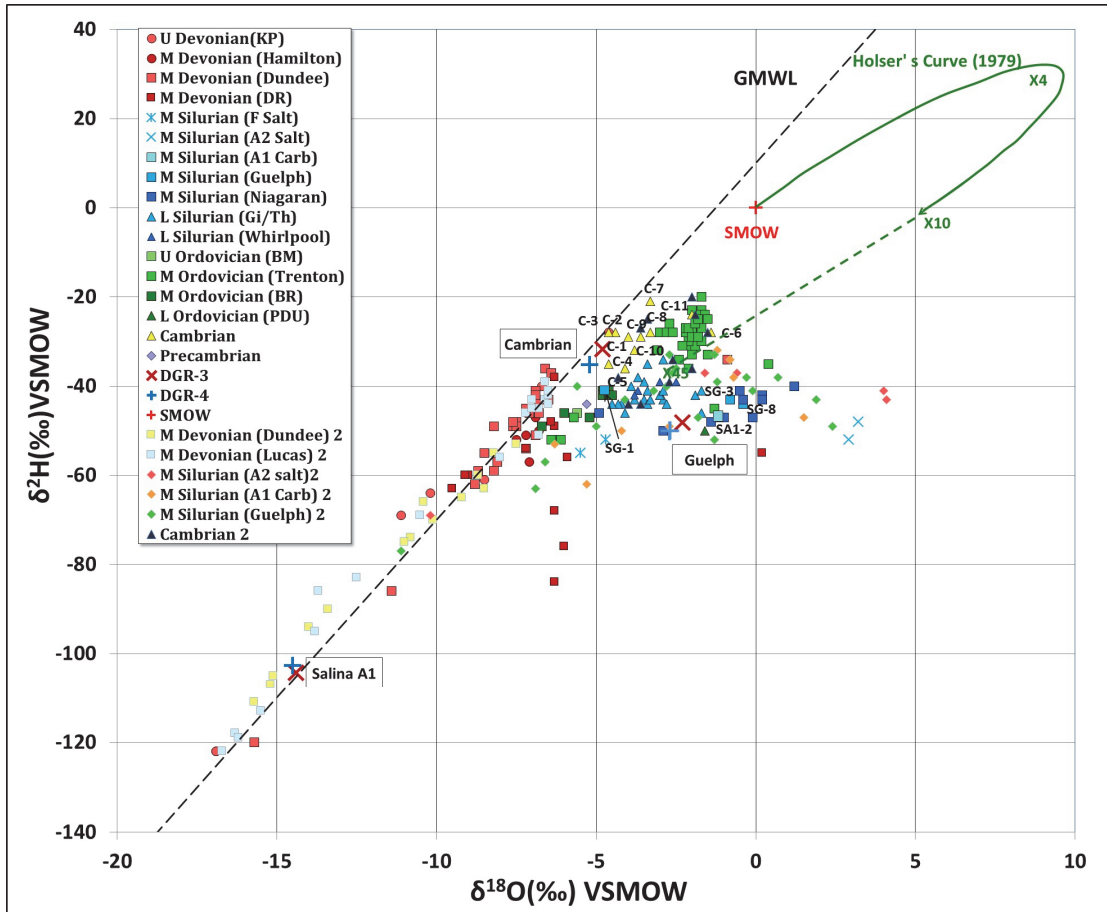


Figure 7a: Plot of Isotopic Results of $\delta^{18}\text{O}$ versus $\delta^2\text{H}$. The Number 2 behind Symbols in the Figure Legend Refers to Data from the Skuce et al. (2015) Database. All Other Data Are from the WRHD

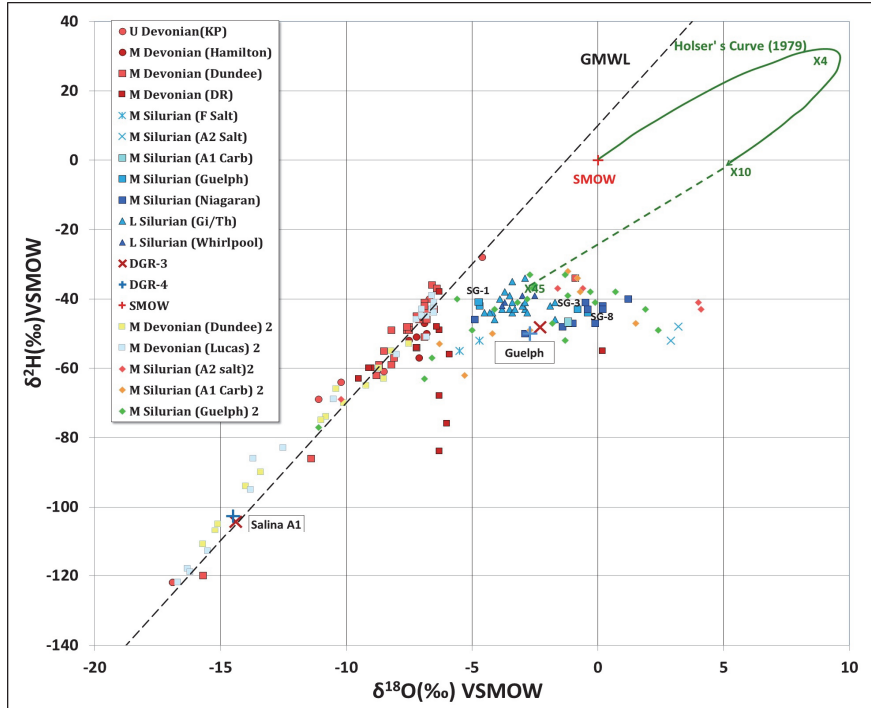


Figure 7b: Isotopic Results of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (Silurian and Devonian). The Number 2 behind Symbols in the Legend Refers to Data from the Skuce et al. (2015) Database. All Other Data Are from the WRHD

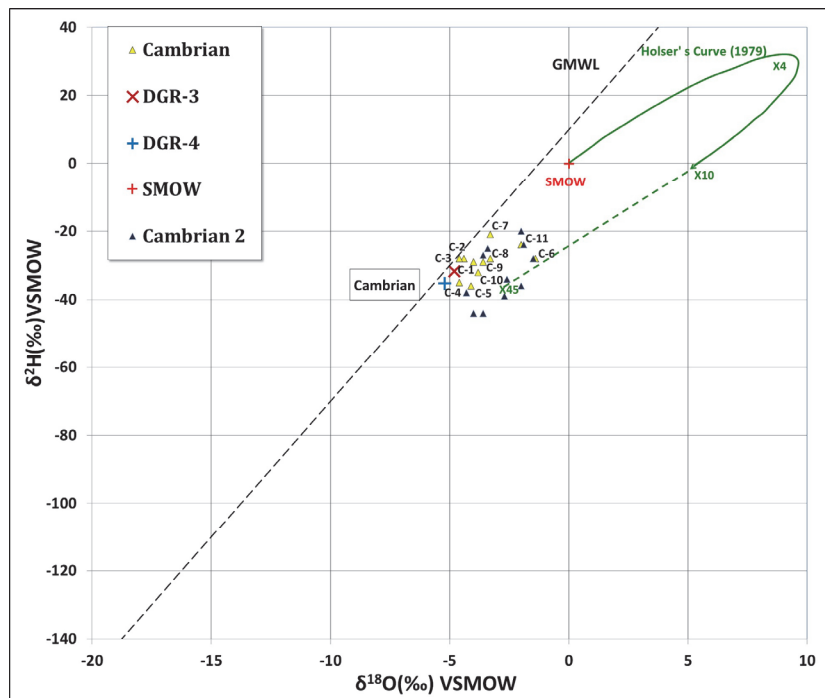


Figure 7c: Isotopic Results of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (Cambrian). Black Triangles on Plot Are Data from the Skuce et al. (2015) Database

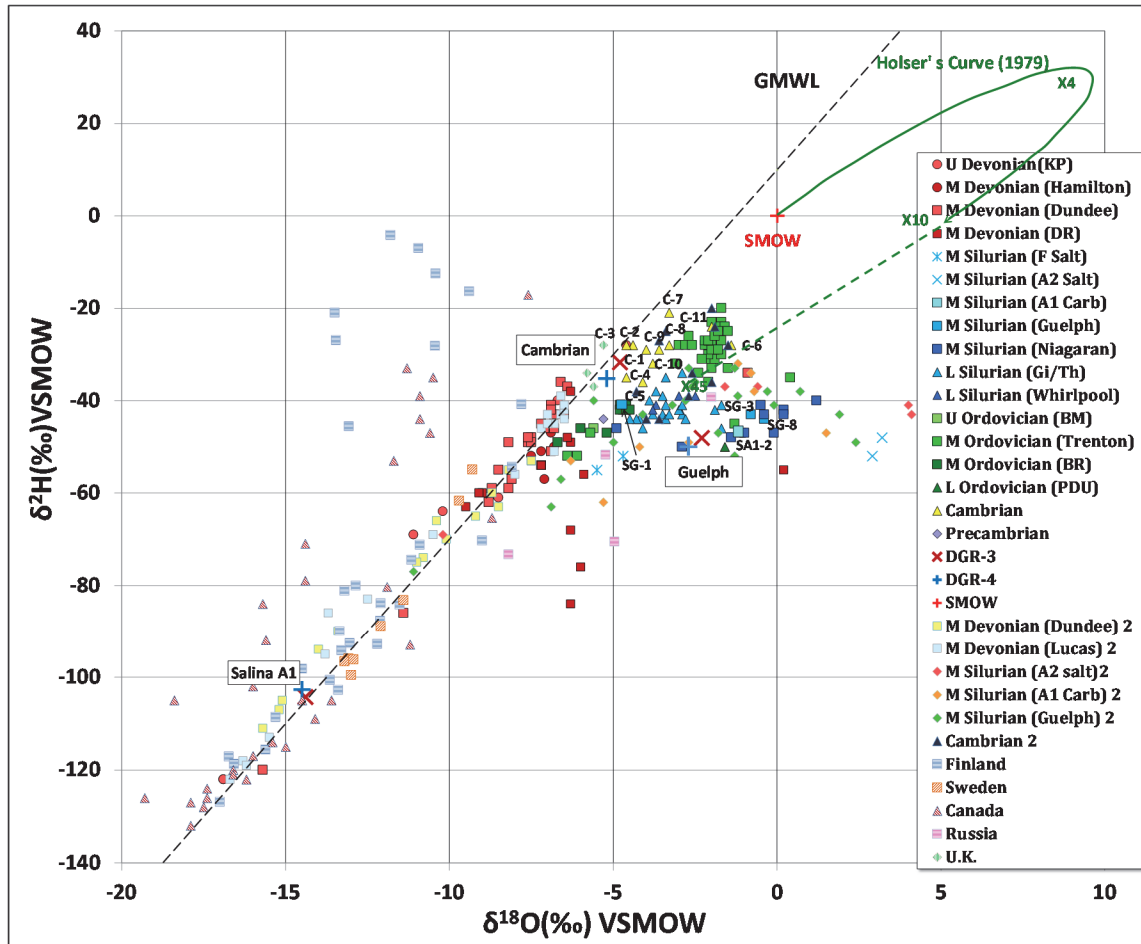


Figure 7d: Isotopic Signatures of Groundwater in Crystalline and Sedimentary Rocks. The Number 2 behind Symbols in the Legend Refers to Data from the Skuce et al. (2015) Database. All Other Sedimentary Data Are from the WRHD. Additional Data (Symbols Filled with Lines) Are from Crystalline Environments (Finland, Sweden, Canada, Russia and U.K.) from Frapet et al. (2014)

Similar to the regional Guelph Formation waters elsewhere in Ontario, the Guelph Formation samples from the site have very high bromine and chlorine concentrations and Ca-rich features. Thus, the origins of the Guelph Formation waters at both the site and regional scales are similar, based on the analysis of their geochemical and isotopic signatures.

Finally, the Cambrian samples at the site plot with the regional Cambrian samples in Ontario, and are located to the right and below the GMWL (Figure 7c). According to the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ results shown on Figure 7c, the DGR-3 (860.53 m) and DGR-4 (848.50 m) samples plot within the range of the combined regional data sets from Cambrian Formation fluids in Ontario and Michigan. Holser's curve (1979) indicates that the Cambrian Formation waters are derived from evaporated paleo-seawater. A comparison of the Cambrian data to crystalline shield brine data shows that samples with similar concentrations have very different ^{18}O - ^2H isotopic values

(Figure 7d). The shield samples plot above and to the left of the glacial meteoric waterline (Frape et al. 1987). Although shield brines also have enriched $\delta^{81}\text{B}$ values (e.g. Stotler et al. 2010), it is felt that the Cambrian isotopic signatures are predominantly due to a sedimentary origin based on their water (^{18}O - ^2H) isotopic signatures. The Bruce site samples from the Cambrian Formation plot close to the combined regional data sets from the same time units on the east of Algonquin Arch. Therefore, it is more probable that the Cambrian Formation fluids sampled from the site are derived from the same ancient sedimentary brines of Appalachian origin, before the Cambrian Formation units were eroded and became more isolated units in the two basins.

5.4 $\delta^{81}\text{BR}$ ISOTOPE AND $^{87}\text{SR}/^{86}\text{SR}$ ANALYSIS

Figure 8 shows the relationship between $\delta^{81}\text{Br}$ isotopes and the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios determined for samples from the site (Intera 2011) and for fluids from the combined regional data sets. The regional formation fluids and the formation fluids from the site are divided into two groups. The deepest fluids from the site are surrounded by most of the regional Ordovician, Lower Silurian and Cambrian formation fluids, while the relative shallow fluids from the site lie within the regional samples from Upper Silurian and Devonian formation fluids. The Guelph Formation fluids have similar strontium isotopic ratios to the regional Guelph Formation fluids. The Cambrian fluids from DGR are slightly more radiogenic for ^{87}Sr than regional Cambrian samples from the Niagara block; in particular samples such as C-13 discussed earlier. The authors do not feel this is a significant difference. This similarity supports the hypothesis of the source (Michigan Basin origin) and evolutionary history (paleo-seawater evaporation) of the Guelph Formation fluids. Samples of the A1 Salina at the site have very similar Sr isotopic values to regional Silurian A1 samples reported by Skuce et al. (2015). In many additional plots of chemical parameters and isotopic parameters (not shown), this similarity between fluids from the three depths at the Bruce nuclear site and those from the combined regional databases by Hobbs et al. (2011) and Skuce et al. (2015) is observed.

values appear to be influenced by dilution with an ^{18}O - ^2H depleted fluids (most likely glacial in origin). Therefore, the Salina A1 Unit samples from the site were derived from halite dissolution most likely by cold climate recharge, having a depleted $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotopic value.

Fluids from the Guelph Formation sampled at the site are isotopically depleted in $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$, similar to regional fluids from the Guelph/Niagaran petroleum producing wells in the Michigan Basin. The $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ isotopic compositions and the Cl/Br ratios determined for groundwaters from two relative shallow zones in both DGR boreholes from the Silurian Salina A1 Unit and the Guelph Formation are consistent with previous theories that the Michigan Basin fluids are depleted in $\delta^{81}\text{Br}$ isotopic signatures (Figure 4b). Thus, the formation waters from the two Silurian aged zones at the site can be described as fluids sourced within the Michigan Basin.

The halide isotopic similarity for the Cambrian fluids from the site and the combined regional databases suggests a similar origin for the fluids. Both $\delta^{81}\text{Br}$ and $\delta^{37}\text{Cl}$ are enriched, similar to Appalachian Basinal fluids to the east and south. This suggests that Cambrian samples from the site, located to the west of the Algonquin Arch, may have the same origin as the Cambrian samples from the east of the Algonquin Arch. This would suggest that this fluid found within the Cambrian may be very old and have maintained their isotopic signatures since they were emplaced by a regional basinal fluid event at a time when Cambrian sediments were continuous in the area before erosional events created the present stratigraphic boundaries.

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APPENDIX A: BR-CL ISOTOPIC ANALYSIS METHODS AND REGIONAL GEOCHEMICAL AND ISOTOPIC DATA

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A.1 BR-CL ISOTOPIC ANALYSIS METHODS

Continuous flow Isotope Ratio Mass Spectrometry (CF-IRMS) method with gas chromatography (GC) was used to analyze the $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ isotopes from the Bruce Nuclear Site at the University of Waterloo (Shouakar-Stash et al. 2005a, b).

a) Brief procedure for Bromine isotope analysis

1) Bromide Separation

- Solution is operated in the special distillation apparatus to isolate Bromine from impure solution, which depends on the differences of oxidation-reduction behaviour of different halogens (Figure 1A). Separation technique is described in the CF-IRMS paper by Shouakar-Stash et al. (2005a).

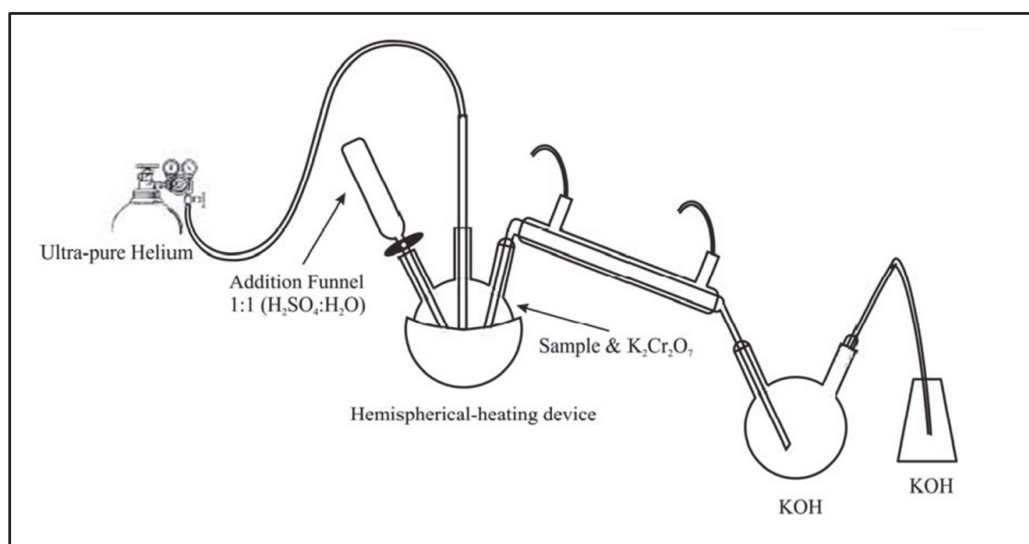


Figure A1: Bromine Distillation Apparatus (from Shouakar-Stash 2005a)

2) Silver Bromide Preparation

- The solution is first acidified to pH ~ 2 by adding ultra-pure concentrated nitric acid (HNO₃).
- 18 g of potassium nitrate (KNO₃) is added to the solution to increase the ionic strength.
- 2 mL of silver nitrate (AgNO₃) solution (0.2 M) is added to precipitate AgBr.
- Stored in a dark environment (24 hours) during AgBr settling.
- Then rinsed twice with 5% HNO₃.
- Placed into an oven at 80°C overnight to dry.

3) Methyl Bromide Preparation

- 0.5 mg AgBr samples are moved into 20 mL amber crimp vials to react with methyl iodide (CH₃I) completely. The whole process is conducted in a glove bag under helium flow.

- CH₃Br (100 µL) is added to the samples, and then vials (4-6) are sealed.
- Place vials in an oven for 56 ± 5 hours at 80°C for the reaction to complete.

4) Isotope analysis

- The first step is sample injection, which is done automatically via an autosampler (CombiPAL).
- The second step is gas separation via the gas chromatograph (GC).
- The third step is the analysis of the CH₃Br by mass spectrometer.

The internal precision using pure methyl bromide gas is less than 0.03‰ (STDV), while the external precision using seawater standard could be 0.06‰ (STDV) for n = 12 or less (Shouakar-Stash et al., 2005a).

b) Brief procedure for Chlorine isotope analysis

1) Silver Chloride Preparation

- Adding ultra-pure water or evaporate the solution to get desired concentration.
- Solution is acidified to PH~2 with ultra-pure nitric acid (HNO₃) and heated at 80°C for a few minutes to drive off CO₂.
- Then, 0.4 M potassium nitrate (KNO₃) solution is added to reach a high ionic strength.
- Anhydrous sodium phosphate dibasic (Na₂HPO₄) and citric acid monohydrate (HOC(CH₂CO₂H)₂CO₂H.H₂O) (0.0004 and 0.0098 mol, respectively) are added to buffer pH at ~2 and to remove small amounts of sulfide, phosphate and carbonate from the precipitate.
- 1 mL silver nitrate (AgNO₃) solution (0.2 M) is added to the residual solution to separate the AgCl from solution.
- 24 hours' storage in a dark cabinet for AgCl settling, and then placement into an oven at 80°C overnight to dry.

2) Methyl Chloride Preparation

- 0.2 mg AgCl samples are moved into 20 mL amber crimp vials to react with methyl iodide (CH₃I) completely. The whole process is conducted in a glove bag under helium flow.
- CH₃I (100 mL) is added to the samples and then vials (3-4) are sealed.
- Place vials in an oven for 48 hours at 80°C for the reaction to complete.

3) Isotope analysis

- Sample analysis is conducted under three protocols including CombiPAL (sample injection), the Agilent 6890 GC setup (gas separation), and the mass spectrometry method (chlorine isotope analysis).

The internal precision using pure CH_3Cl gas is less than 0.04‰ (STDV), while the external precision using seawater standard could be 0.07‰ (STDV) for $n = 12$ or less (Shouakar-Stash et al. 2005b).

A.2 GEOCHEMICAL AND ISOTOPIC DATA FROM SOUTHERN ONTARIO AND MICHIGAN

Table A1: Geochemical Data and Stable Water Isotopes of the Formation Waters from Southern Ontario and Michigan (from the PhD Thesis of Shouakar-Stash, 2008). The samples and data presented in this table were compiled from various authors: [1] Dollar 1988; [2] Walter, Pers. Comm.; [3] Cloutier 1994; [4] Husain 1996; [5] Weaver 1994; [6] Sherwood-Lollar and Frappe 1989

Author	Sample Name	Rock Type	Water Type	Depth m	Ca mg/L	Na mg/L	Mg mg/L	K mg/L	Sr mg/L	Cl mg/L	Br mg/L	SO ₄ mg/L	HCO ₃ mg/L	F mg/L	Br/Cl	$\delta^{18}\text{O}$ (VSMOW) (‰)	$\delta^2\text{H}$ (VSMOW) (‰)	³ H TU	$\delta^{37}\text{Cl}$ (SMOC) (‰)	$\delta^{81}\text{Br}$ (SMOB) (‰)	⁸⁷ Sr/ ⁸⁶ Sr	TDS mg/L
Late Devonian (Kettle Point Antrim)																						
[3]	LD-90-3-5	Shale	Na-Cl	52	127	5410	120	31	5	8600	7	1	1210		0.000814	-11.1	-69		1.82			15511
[3]	DOW-90-3-4	Shale	Na-Cl	44	8.41	189	0.1	11	0.5	164	0.7	42	164		0.004268	-8.5	-61					641
[4]	BRP-143	Shale	Na-Cl	44	39.6	278	14	5	0.8	393	0.4	10	194		0.001018	-16.9	-122		0.01			934
[4]	BRP-151	Shale	Na-Cl	46	26.5	338	12	9	0.5	390	0.3	6	202		0.000769	-16.9	-122		0.24			984
[2]	SP A2-32	Shale	Na-Cl		6770	82600	3590	667	323	147000	307	<5	5		0.002088	-4.6	-28		-0.39	0.71000		241262
[2]	WSMC2-10	Shale	Na-Cl		7700	63700	4690	487	424	128200	454		16		0.003541	-6.7	-40		-1.11			205671
[2]	HGR D4-6	Shale	Na-Cl		3280	42400	2140	370	221	74300	179		24		0.002409	-10.2	-64		-0.35			122914
Late Devonian (Hamilton)																						
[3]	LD-90-3-4	Shale	Na-Cl	68	122	3K40	68	29	3	5800	5	349	200		0.000862	-7.5	-52		0.89			10415
[3]	LD-90-3-3	Shale	Na-Cl	89	104	2590	59	47	4	3530	5	783	376		0.001416	-7.2	-51		0.67			7499
[3]	LD-90-3-2	Shale	Na-Cl	131	200	4230	137	41	14	7260	0	324	724		0.000000	-6.9	-47		0.18			12930
[3]	DOW-90-3-3	Shale	Na-Cl	77	164	3760	75	47	3	6080	6	379	214		0.000987	-7.1	-57		0.00			10728
[3]	DOW-90-3-2	Shale	Na-Cl	106	367	5940	208	67	8	11500	21	572	404		0.001826	-6.8	-50		0.03			19086
Middle Devonian (Dundee)																						
[3]	DOW-90-3-1	Carbonate	Na-Cl	142	127	2920	70	48	3	3880	9	819	504		0.002320	-6.9	-51		-0.72			8380
[3]	LD-90-3-1	Carbonate	Na-SO ₄ -Cl	142	92	1510	28.9	136	2	793	4	1830	470		0.005044	-7.2	-54					4866
[1]	DD-1	Carbonate	Na-Cl	108	660	3690	632	85	29	10000	50	795	293		0.005000	-11.4	-86		0.05		0.70852	15940
[1]	DD-2	Carbonate	Ca-Na-Cl	97	623	414	83	19	12	2000	12	98	<7		0.006000	-15.7	-120				0.70949	3260
[1]	DD-3	Carbonate	Na-Ca-Cl	1131	31500	70600	5410	3030	750	179000	1050	166	<7	17	0.005866				-0.19	-0.21	0.70816	291500
[1]	DD-4	Carbonate	Na-Ca-Cl	1128	40300	56600	6990	3370	1120	182200	1310	150	90	10	0.007190	-0.9	-34		-0.27	-0.17	0.70823	292000
[5]	PD-COCH	Carbonate	Na-Ca-Mg-Cl		1180	3470	715	91	23	8650	58	1700	264		0.006705	-7.5	-48				0.70822	16155
[5]	PD-NORTH	Carbonate	Na-Ca-Cl		15K0	4830	898	115	29	12000	91	2200	325		0.007583	-6.9	-41		0.92	0.68		22073
[5]	PD-RAL	Carbonate	Na-Ca-Mg-Cl		1580	4390	908	117	30	10900	78	2000	158		0.007156	-6.8	-43	2.4			0.70820	20166
[5]	PD-WEST	Carbonate	Na-Ca-Mg-Cl		1400	3870	793	105	26	9920	82	1940	258		0.008266	-7.1	-46					18399
[5]	RA-N	Carbonate	Na-Ca-Mg-Cl		1140	3420	675	85	24	8870	62	1380	348		0.006990	-7.6	-49	7.1				16008
[5]	RA-NE	Carbonate	Na-Ca-Cl		1410	4360	808	105	28	11300	74	1810	499		0.006549	-6.8	-46		1.14	0.62	0.70820	20145
[5]	RA-SE	Carbonate	Na-Ca-Cl		1490	4530	858	111	28	11500	79	1920	320		0.006870	-7.2	-45		0.95	0.52		20540
[5]	RA-SW	Carbonate	Na-Ca-Cl		1320	3970	758	100	25	10100	67	1690	308		0.006634	-7.5	-49					18342
[5]	LAI-1	Carbonate	Na-Mg-Ca-Cl		1270	3670	818	103	25	9500	59	1790	589		0.006211	-6.6	-36					17828

Author Sample Name		Rock Type	Water Type	Depth m	Ca mg/L	Na mg/L	Mg mg/L	K mg/L	Sr mg/L	Cl mg/L	Br mg/L	SO ₄ mg/L	HCO ₃ mg/L	F mg/L	Br/Cl	δ ¹⁸ O (VSMOW) (‰)	δ ² H (VSMOW) (‰)	³ H TU	δ ³⁷ Cl (SMOC) (‰)	δ ⁸¹ Br (SMOB) (‰)	⁸⁷ Sr/ ⁸⁶ Sr	TDS mg/L	
Middle Devonian (Dundee)																							
[5]	LAI-2	Carbonate	Na-Mg-Ca-Cl		1300	3520	803	102	26	8980	54	2010	548		0.006013	-6.5	-43		1.02		0.70821	17346	
[5]	LAI-3	Carbonate	Na-Mg-Ca-Cl		1220	3430	773	107	23	8240	44	2110	561		0.005340	-6.4	-37	0.8				16512	
[5]	WB-11	Carbonate	Na-Mg-Ca-Cl		736	2100	450	62	51	5700	43	751	572		0.007544	-8.5	-55		1.16		0.70813	10470	
[5]	WB-2	Carbonate	Na-Mg-Ca-Cl		918	2620	593	76	21	7190	21	787	599		0.002921	-8.2	-49	7.2				12829	
[5]	WB-7	Carbonate	Na-Mg-Ca-Cl		1100	3090	6XK	85	22	8450	60	1320	512		0.007101	-7.6	-48		1.25			15334	
[5]	WB-8	Carbonate	Na-Mg-Ca-Cl		1240	3590	843	III	27	9750	57	1230	536		0.005846	-6.9	-42				0.70820	17388	
[5]	LBH-1	Carbonate	Na-Mg-Ca-Cl		1700	4450	1170	152	32	13200	47	1400	157		0.003561	-8.7	-59					22314	
[5]	LBH-2	Carbonate	Na-Mg-Ca-Cl		2000	4950	1320	156	34	14300	86	2340	5		0.006014	-8.8	-62		0.35	0.60		25194	
[5]	LBH-3	Carbonate	Na-Mg-Ca-Cl		1940	4900	1340	169	36	14100	97	2140	5		0.006879	-8.2	-59	0.8			0.70827	24731	
[5]	LBH-4	Carbonate	Na-Mg-Ca-Cl		1760	5150	1300	171	36	15000	86	1220	112		0.005733	-8.1	-57		0.33	0.92		24839	
Middle Devonian (Detroit River)																							
[5]	LBO-2	Carbonate	Na-Mg-Ca-Cl		1530	4030	940	131	34	11300	99	448	40		0.008761	-7.5	-53		0.69	0.52		18556	
[5]	LBO-3	Carbonate	Na-Ca-Mg-Cl		1640	3130	920	125	35	10400	69	630	113		0.006635	-7.2	-54					17066	
[5]	CFN-14	Carbonate	Na-Ca-Mg-Cl		1310	2390	608	85	29	7990	66	796	219		0.008260	-9.5	-63		0.50		0.70833	13500	
[5]	CFN-A	Carbonate	Na-Ca-Mg-Cl		1570	3170	830	123	35	9460	86	916	171		0.009091	-9.0	-60		0.26	0.55		16365	
[5]	CFN-B	Carbonate	Na-Ca-Mg-Cl		1190	2590	673	98	27	7810	61	398	297		0.007810	-9.1	-60	37.7				13148	
[5]	CFN-161	Carbonate	Na-Ca-Mg-Cl		5990	10900	2750	445	100	31400	277	1240	328		0.008822	-6.3	-84	1.1	0.63	0.49	0.70825	53400	
[5]	CFN-C	Carbonate	Na-Mg-Ca-Cl		3830	8690	2430	307	70	27400	200	760	221		0.007299	-6.3	-38	0.8	0.79	0.35	0.70827	43912	
[5]	CFN-E	Carbonate	Na-Ca-Mg-Cl		4020	8090	2270	288	67	26800	216	1220	328		0.008060	-5.9	-56		0.94	0.45	0.70826	43304	
[5]	CFS-A	Carbonate	Na-Ca-Mg-Cl		4320	9330	2330	311	70	30300	294	1390	345		0.009703	-6.0	-76		0.69	0.57		48694	
[5]	CFS-B	Carbonate	Na-Ca-Mg-Cl		4240	9700	2270	325	67	25500	202	1350	148		0.007922	-6.3	-49	0.8	0.49			43805	
[5]	CFS-C	Carbonate	Na-Ca-Mg-Cl		3800	8910	2160	309	67	26600	195	941	206		0.007331	-6.4	-48		0.72			43192	
[5]	CFS-D	Carbonate	Na-Mg-Ca-Cl		3500	8320	2150	299	67	25700	187	808	421		0.007276	-6.3	-68		0.28	0.63		41456	
[1]	DR-1	Carbonate	Ca-Na-Cl	1445	64900	23400	7960	8320	2060	173100	1970	205	258	14	0.011381	0.2	-55		-0.50	-0.23	0.70913	281900	
Middle Silurian (F Salt)																							
[1]	SF-1	Salt	Na-Cl	150	8200	100000	2850	2600	214	207000	587	750			0.002836	-5.5	-55		-0.20		0.70866	322200	
[1]	SF-2	Salt	Na-Cl	150	10300	94500	3100	2780	197	194100	390	510	73		0.002009							305900	
[1]	SF-3	Salt	Na-Cl	150	9630	94400	3370	2600	158	192900	325	595	76		0.001685	-4.7	-52					304000	
Middle Silurian (A2 Salt)																							
[1]	SA2-1	Salt	Ca-Na-Mg-Cl	250	48400	33400	16600	5000	1620	232000	3220	110			0.013879	2.9	-52				0.70853	340400	
[1]	SA2-2	Sail	Ca-Na-Mg-Cl	250	46800	33600	16200	6400	1620	232000	3214	106			0.013853	3.2	-48				0.70866	340000	
Middle Silurian (A1 Carbonate)																							
[1]	SA1-1	Carbonate	Ca-Na-Cl	645	52000	37700	11400	4520	740	176000	1880	167	76		0.010682				-0.35			284400	
[1]	SA1-2	Carbonate	Ca-Na-Cl	649	54700	37900	10900	4760	969	195300	1700	193	18		0.008705	-1.1	-47		-0.35		0.70849	306400	
Middle Silurian (Guelph)																							
[1]	SG-1	Carbonate	Na-Ca-Cl	354	15000	41200	3780	1430	263	95500	810	810	127	164	0.008482	-4.7	-42				0.71029	158800	
[1]	SG-2	Carbonate	Na-Ca-Cl	448	31300	65500	7770	1880	436	189100	1390	250	69	8	0.007351						0.70931	297600	
[1]	SG-3	Carbonate	Na-Ca-Cl	553	44500	61300	9000	2740	599	206900	1620	127	43		0.007830	-0.8	-43		-0.40			326800	
[1]	SG-4	Carbonate	Ca-Na-Cl	614	60300	46600	8250	3040	1220	197800	2510	119	<7		0.012690				-0.15	-0.95	0.70915	319800	

Author Sample Name	Rock Type	Water Type	Depth m	Ca mg/L	Na mg/L	Mg mg/L	K mg/L	Sr mg/L	Cl mg/L	Br mg/L	SO ₄ mg/L	HCO ₃ mg/L	F mg/L	Br/Cl	δ ¹⁸ O (VSMOW) (‰)	δ ² H (VSMOW) (‰)	³ H TU	δ ³⁷ Cl (SMOC) (‰)	δ ⁸¹ Br (SMOB) (‰)	⁸⁷ Sr/ ⁸⁶ Sr	TDS mg/L	
Middle Silurian (Guelph)																						
[1]	SG-5	Carbonate	Na-Ca-Cl	571	29000	70000	8200	2040	449	189100	1390	259	84	8	0.007351						0.70934	300400
[1]	SG-6	Carbonate	Ca-Na-Cl	646	53700	42100	9520	3240	744	186300	1780	227	<7	8	0.009554						0.70889	297600
[1]	SG-7	Carbonate	Ca-Na-Cl	749	66000	42300	8440	3270	1120	210900	2440	239	<7	8	0.011569				-0.38	-0.83	0.70946	334700
[1]	SG-8	Carbonate	Ca-Na-Cl	695	61500	46000	10600	3400	997	214600	2010	61	<7		0.009366	-0.4	-44		-0.51	-0.61	0.70908	339200
[1]	SG-9	Carbonate	Ca-Na-Cl	770	53100	42900	13300	2150	580	205500	1490	203	<7	8	0.007251						0.70929	319200
[1]	SG-10	Carbonate	Ca-Na-Cl	726	57200	39400	8670	3340	1220	189500	2380	172	<7		0.012559				-0.28	-0.75	0.70902	301900
[1]	SG-11	Carbonate	Ca-Na-Cl	518	52600	49900	9500	4840	702	213700	1920	170	245		0.008985						0.70893	333300
[1]	SG-12	Carbonate	Na-Ca-Cl	597	34700	53200	7080	2390	572	155200	1510	300	<7	27	0.009729						0.70931	255000
[1]	SG-13	Carbonate	Ca-Na-Cl	670	50200	54800	8230	2810	684	208200	1920	170	77	8	0.009222						0.70907	327000
Middle Silurian (Niagaran)																						
[1]	SN-1	Carbonate	Ca-Na-Cl	892	62000	40800	8680	6080	1270	209700	2160	79	<7	319	0.010300	0.2	-42		-1.04	-0.76	0.70833	330800
[1]	SN-2	Carbonate	Ca-Na-Cl	895	61300	40300	8530	5920	1270	208500	1880	79	<7	295	0.009017	-1.4	-48					327800
[1]	SN-3	Carbonate	Ca-Cl	1161	73800	24800	17900	8560	2040	230400	2390	59	<7		0.010373	-2.9	-50		-0.30	-0.28		359900
[1]	SN-4	Carbonate	Ca-Cl	1272	78500	25300	17900	9280	2170	256200	2360	38	<7		0.009212	-4.9	-46		-0.61	-0.70	0.70861	391700
[1]	SN-5	Carbonate	Ca-Na-Cl	1305	77300	31000	11900	10300	2040	245300	2440	42	<7		0.009947	1.2	-40		-0.22	-0.69		380300
[1]	SN-6	Carbonate	Ca-Cl	1264	79500	25200	15500	9820	2500	261800	2640	49	<7		0.010084	-1.0	-47		-0.28	-0.61	0.70848	397000
[1]	SN-7	Carbonate	Ca-Na-Cl	1010	62900	45300	8550	4320	1160	210700	2270	94	<7	8	0.010774	0.2	-43		-0.30		0.70935	335300
[1]	SN-8	Carbonate	Ca-Na-Cl	1001	61900	45100	8080	3900	1190	187800	2240	105	<7	11	0.011928	-0.5	-41		-0.30		0.70939	310300
[1]	SN-9	Carbonate	Ca-Na-Cl	713	54900	46000	9600	3560	919	207100	1970	89	<7		0.009512	-0.4	-43				0.70909	324100
[1]	SN-10	Carbonate	Ca-Na-Cl	717	62600	42600	8530	3370	1060	202500	2320	89	<7	8	0.011457	-0.1	-47		-0.43	-0.92	0.70929	323100
[2]	Cold Springs WHI-29	Carbonate	Ca-Cl		88643	26275	10176	18285	3661	244975	2570	36			0.010491				-0.39			394620
Early Silurian (Grimsby/Thorhold)																						
[1]	STGr-1	Sandstone	Na-Ca-Cl	431	29000	48100	5980	1000	464	137600	1340	385	<7		0.009738	-3.5	-43					223900
[1]	STGr-2	Sandstone	Na-Ca-Cl	380	36700	51900	7030	1410	611	158500	1550	259	<7		0.009779	-2.9	-34				0.70977	258000
[1]	STGr-3	Sandstone	Na-Ca-Cl	374	27400	42200	6620	899	463	129400	1260	447	<7		0.009737	-4.2	-44					208700
[1]	STGr-4	Sandstone	Na-Ca-Cl	414	34700	49400	6100	981	536	149200	1580	320	<7		0.010590	-2.9	-43					242800
[1]	ST-5	Sandstone	Na-Ca-Cl	292	30500	44500	5830	1010	490	148100	1340	413	<7		0.009048	-4.1	-46		0.78		0.71014	232200
[1]	ST-6	Sandstone	Na-Ca-Cl	408	33700	45200	6210	1040	544	143400	1430	339	<7		0.009972	-3.4	-44					231900
[1]	SGr-7	Sandstone	Na-Ca-Cl	424	33600	50600	5880	1010	530	160800	1510	332	<7		0.009391	-3.3	-43					254300
[1]	SGr-8	Sandstone	Na-Ca-Cl	426	34200	49500	5840	1130	522	164300	1540	345	<7		0.009373	-3.0	-42					257400
[1]	STGr-9	Sandstone	Na-Ca-Cl	522	42100	49700	7500	1260	697	179000	1650	272	<7		0.009218	-2.8	-44					282200
[1]	STGr-10	Sandstone	Na-Ca-Cl	524	45700	58000	8000	1390	784	195800	1970	164	<7		0.010061	-1.9	-42		0.14	0.77		311800
[1]	SGr-11	Sandstone	Na-Ca-Cl	512	44600	58700	7700	1450	745	178300	1870	174	<7		0.010488	-1.7	-41		0.35	1.36		293500
[1]	SGr-12	Sandstone	Na-Ca-Cl	524	26900	38900	5310	878	456	117500	1130	657	<7		0.009617	-3.9	-40					191700
[1]	STGr-13	Sandstone	Na-Ca-Cl	547	31400	45100	5630	877	509	144300	1380	423	<7		0.009563	-3.4	-41		0.35			229600
[1]	STGr-14	Sandstone	Na-Ca-Cl	541	47700	58600	8230	1400	883	207000	2010	123	<7		0.009710	-1.7	-46		0.21	1.35	0.71018	325900
[1]	SGr-15	Sandstone	Na-Ca-Cl	554	34600	46900	6280	930	564	163600	1490	404	<7		0.009108	-3.5	-39					254800
[1]	SGr-16	Sandstone	Na-Ca-Cl	572	28100	45800	4870	911	452	144200	1250	530	<7		0.008669	-3.4	-35				0.71076	226100
[1]	STGr-17	Sandstone	Na-Ca-Cl	544	29100	43300	5070	846	483	142200	1260	450	<7		0.008861	-2.9	-41		0.13			222700
[1]	SGr-18	Sandstone	Ca-Na-Cl	289	39700	22800	6780	664	347	109200	755	560	<7		0.006914	-4.3	-44					180800
[1]	SGr-19	Sandstone	Ca-Na-Cl	335	39800	20900	3540	637	358	119400	694	235	<7		0.005812	-4.5	-44		0.37		0.71092	185600
[1]	SGr-20	Sandstone	Ca-Na-Cl	365	42700	30300	5470	822	481	137400	920	405	<7		0.006696	-3.7	-38		0.50	1.74	0.71036	218500
[1]	SGr-21	Sandstone	Ca-Na-Cl	410	42000	26400	3930	713	426	112600	855	329	<7		0.007593	-3.8	-43		0.50	1.63		187300

Author Sample Name	Rock Type	Water Type	Depth m	Ca mg/L	Na mg/L	Mg mg/L	K mg/L	Sr mg/L	Cl mg/L	Br mg/L	SO ₄ mg/L	HCO ₃ mg/L	F mg/L	Br/Cl	$\delta^{18}\text{O}$ (VSMOW) (‰)	$\delta^2\text{H}$ (VSMOW) (‰)	³ H TU	$\delta^{37}\text{Cl}$ (SMOC) (‰)	$\delta^{81}\text{Br}$ (SMOB) (‰)	⁸⁷ Sr/ ⁸⁶ Sr	TDS mg/L
Early Silurian (Whirlpool)																					
[1]	SW-1	Sandstone																			
[1]	SW-2	Sandstone	361	50400	32400	4250	782	489	158800	1130	320	47	8	0.007116	-3.0	-39		0.86	2.31	0.71103	248600
[1]	SW-2	Sandstone	422	47300	29900	3710	763	452	147500	1000	376	60		0.006780	-3.7	-41		0.60	2.11	0.71107	231000
[1]	SW-3	Sandstone	422	51100	36400	5500	870	507	171600	1190	375	<7		0.006935	-2.5	-39		0.64	2.13		267500
[1]	SW-4	Sandstone	459	43400	28200	4460	770	420	126100	920	433	<7		0.007296	-3.8	-42				0.71112	204700
Late Ordovician (Blue Mountain)																					
[6]	OHD-1 #15	Carbonate	173	38600	21800	4520	404	702	118300	1080	120	44		0.009129	-5.6	-46		0.09	1.75		185570
Middle Ordovician (Trenton)																					
[1]	OT-1	Carbonate	647	15600	35700	3680	1600	529	98700	578	453	<7	4	0.005856	-2.1	-31				0.70978	156900
[1]	OT-2	Carbonate	657	16000	35300	3510	1600	540	99800	725	742	34		0.007265	-1.7	-23		0.00		0.70980	158200
[1]	OT-3	Carbonate	645	15800	35800	3500	1630	467	101100	563	575	<7	5	0.005569	-1.9	-31		0.30		0.70976	159400
[1]	OT-4	Carbonate	738	23300	39800	5480	1970	402	111300	832	630	<7	6	0.007475	-1.7	-30				0.70996	183700
[1]	OT-5	Carbonate	743	23500	41400	6130	2120	739	131800	856	152	<7	6	0.006495	-1.9	-29		-0.60		0.70973	206700
[1]	OT-6	Carbonate	771	17400	36900	4280	1690	574	103200	550	410	58	4	0.005329	-2.2	-28		-0.30		0.70982	165000
[1]	OT-7	Carbonate	790	35200	43600	7410	2310	606	149500	920	263	17		0.006154							239800
[1]	OT-8	Carbonate	775	32600	46800	6520	2410	525	148100	1190	353	33		0.008035	-2.1	-30				0.71041	238500
[1]	OT-9	Carbonate	786	36500	48800	7410	2270	612	150500	950	263	<7		0.006312	-2.1	-27		-0.59	0.98	0.70900	247300
[1]	OT-10	Carbonate	784	36700	48700	7930	2330	633	175900	1170	260			0.006652	-2.3	-31		-0.63	0.87	0.71029	273600
[1]	OT-11	Carbonate	804	36730	45700	7270	2320	733	160900	1610	271			0.010006	-1.9	-26		-0.55	0.76	0.71030	255500
[1]	OT-12	Carbonate	779	39200	45300	6910	2120	729	166100	1370	321			0.008248	-2.0	-29		-0.49	0.93	0.71030	262100
[1]	OT-13	Carbonate	791	32600	55200	7300	2390	578	161200	1150	320	32		0.007134	-2.1	-27		-0.50		0.71007	260700
[1]	OT-14	Carbonate	782	33000	48700	6750	2390	548	141400	1170	358	<7	8	0.008274	-2.0	-33		-0.52	0.58	0.71036	234300
[1]	OT-15	Carbonate	787	31300	46100	6530	2300	527	149500	1120	380	60	8	0.007492	-2.2	-27		-0.40		0.71023	237800
[1]	OT-16	Carbonate	778	32800	46100	6600	2680	529	148600	1220	347	49	13	0.008210	-2.1	-36		-0.55		0.71034	238900
[1]	OT-17	Carbonate	781	29700	43200	5960	2150	568	138600	1270	366	<7		0.009163						0.71036	221800
[1]	OT-18	Carbonate	786	34100	45400	6700	2310	658	158300	1210	348			0.007644				-0.34	0.62	0.71036	249000
[1]	OT-19	Carbonate	844	31100	42000	5440	2190	518	147000	780	393	12		0.005306	-1.8	-24		-0.70			229400
[1]	OT-20	Carbonate		27200	46500	5170	2080	467	142300	765	485	45		0.005376	-2.0	-23					225000
[1]	OT-21	Carbonate	854	32500	49700	5960	2070	619	150300	1190	335	<7	246	0.007917	-3.1	-32		-0.43	0.18	0.71045	242700
[1]	OT-22	Carbonate	1225	21700	41900	4470	3230	493	122700	625	620	49		0.005094						0.70962	195700
[1]	OT-23	Carbonate	1140	31000	48000	5450	3390	595	159800	1160	327	86		0.007259	-1.3	-45		-0.65	-0.49	0.70887	249700
[1]	OT-24	Carbonate	1247	21800	42300	4270	3130	494	122000	925	402	66	168	0.007582	-1.7	-27		-1.13		0.70958	195300
[1]	OT-25	Carbonate	1238	18300	40300	3790	3060	447	117600	797	538	90	160	0.006777	-2.0	-27				0.71000	184800
[1]	OT-26	Carbonate	1203	19200	41300	4360	3330	490	118500	857	256	81	171	0.007232	-2.1	-27				0.70991	188300
[1]	OT-27	Carbonate	1287	20500	42500	4620	3490	505	123200	917	312	69	184	0.007443	-1.9	-26				0.70977	196000
[1]	OT-28	Carbonate	1299	19800	42000	4320	3460	489	119400	650	622	48	8	0.005444						0.70980	190700
[1]	OT-29	Carbonate	1278	21400	41200	4670	3490	512	117600	917	418	66	191	0.007798	-1.6	-24				0.70985	190200
[1]	OT-30	Carbonate	1280	54900	53200	7790	5250	1060	222000	1780	129	95	10	0.008018	0.4	-35		-0.31		0.70827	346100
[1]	OT-31	Carbonate	1279	23800	46200	5070	3960	564	137300	909	411	73	10	0.006621	-1.7	-20		-1.31		0.70992	218200
[1]	OT-32	Carbonate	1259	23800	45900	5170	3770	546	134100	890	400	61	708	0.006637	-1.5	-25					214600
[1]	OT-33	Carbonate	1289	21600	41900	4110	3890	518	117500	725	460	57	7	0.006170							190700
[1]	OT-34	Carbonate	1290	22200	44100	4280	3990	550	133000	911	474	71	6	0.006850	-1.8	-29				0.71027	209500

Author Sample Name	Rock Type	Water Type	Depth m	Ca mg/L	Na mg/L	Mg mg/L	K mg/L	Sr mg/L	Cl mg/L	Br mg/L	SO ₄ mg/L	HCO ₃ mg/L	F mg/L	Br/Cl	δ ¹⁸ O (VSMOW) (‰)	δ ² H (VSMOW) (‰)	³ H TU	δ ³⁷ Cl (SMOC) (‰)	δ ⁸¹ Br (SMOB) (‰)	⁸⁷ Sr/ ⁸⁶ Sr	TDS mg/L
Middle Ordovician (Trenton)																					
[1] OT-35	Carbonate	Na-Ca-Cl	1292	20700	42500	4090	3650	507	126400	872	535	96	8	0.006899	-1.8	-25				0.71010	199300
[1] OT-36	Carbonate	Na-Ca-Cl	1292	21400	42500	3960	3770	478	126100	650	505	48	8	0.005155							199400
[1] OT-37	Carbonate	Na-Ca-CT	1288	20900	43000	4130	3760	508	125700	877	491	75	7	0.006977	-1.5	-33				0.71003	199400
[1] OT-38	Carbonate	Na-Ca-Cl	1293	25300	41800	4720	3300	477	131800	789	507	<7	7	0.005986	-2.4	-34				0.70994	208700
[1] OT-39	Carbonate	Na-Ca-Cl	637	13100	38800	3670	2010	473	101900	510	415	61		0.005005	-2.7	-26				0.70958	160900
[1] OT-40	Carbonate	Na-Ca-Cl	308	9850	36400	3720	1840	524	86600	460	66	66		0.005312	-3.0	-28			-1.09	0.70929	139500
[1] OT-41	Carbonate	Na-Ca-Cl	310	10800	36400	3850	1850	496	87000	440	66	137		0.005057	-2.8	-28			-0.60	0.70938	140900
[1] OT-42	Carbonate	Na-Ca-Cl	614	10500	37500	3670	1880	567	87500	460	<15	76		0.005257	-2.6	-28				0.70929	142100
[6] UN-2 #13	Carbonate	Na-Ca-Cl	50	6250	8120	1840	141	277	26975	282	175	53		0.010454	-6.4	-52	69.0	-0.32	2.15	0.71057	44113
[6] OHD-1 #13	Carbonate	Ca-Na-Cl	204	26600	18400	3280	321	515	86700	755	125	41		0.008708	-6.1	-52	22.0	0.09	1.93	0.70993	136737
[6] UN-2 #11	Carbonate	Na-Ca-Cl	85	15100	17900	4080	271	705	63050	635	210	32		0.010071	-5.7	-47	50.0	-0.30	2.08	0.71060	101983
Middle Ordovician (Black River)																					
[6] OHD-1 #7	Carbonate	Ca-Na-Cl	295	58000	37100	7080	636	1210	192045	1555	140	<7		0.008097	-4.8	-41	<6	0.08	1.73	0.70981	297766
[6] UN-2 #5	Carbonate	Ca-Na-Mg-Cl	175	36000	40800	11200	709	1130	159900	1445	165	26		0.009037	-6.0	-46	<6	-0.13	1.18	0.71042	251375
[6] OHD-1 #5A	Carbonate	Ca-Na-Cl	326	57800	35700	7100	641	1200	186000	1620	145	29		0.008710	-4.8	-42	<6				290235
[6] OHD-1 #5B	Carbonate	Ca-Na-Cl	326	59000	38500	7230	651	1220	182000	1595	155	<7		0.008764	-4.6	-42	<6	0.32			290351
[6] OHD-1 #3	Carbonate	Ca-Na-Cl	353	58500	35100	7150	649	1220	200500	817	150	<7		0.004075	-4.6	-41	<6	0.11	1.78	0.70979	304086
[6] UN-2 #2	Carbonate	Na-Ca-Cl	210	15000	17400	4090	322	335	59000	619	575	44		0.010492	-6.7	-49	32.0	0.01	1.92	0.71027	97385
[6] UN-2 #4	Carbonate	Ca-Na-Mg-Cl	190	23400	24900	7230	469	488	96000	935	520	45		0.009740	-5.2	-47	25.0	-0.14	1.94	0.71038	153987
[6] OHD-1 #2	Sandstone	Ca-Na-Cl	368	58300	37600	7200	657	1220	189000	1620	155	<7		0.008571	-4.5	-42	<6	0.10	1.76	0.70981	295752
Early Ordovician (Prairie du Chien)																					
[1] OP-1	Sandstone	Ca-Na-Cl	3425	68000	26700	7200	14200	2350	205000	1930	63	<7		0.009415	-1.6	-50		-0.95	-0.55	0.70930	325400
[2] LAHAR 1-7	Sandstone	Ca-Cl		89200	30120	7560	12720	3632	245673	1719	83			0.006997				-0.26			390707
[2] FOSTER 1-21	Sandstone	Ca-Na-Cl		65250	43500	5568	9483	2906	215081	2311	43			0.010745				-0.18			344142
[2] PRASS 1-12	Sandstone	Ca-Cl		67600	22702	5744	10600	2848	179576	2229	91			0.012413				-0.34			291389
[1] OP-2	Sandstone	CaCl	3234	87500	22600	8700	18400	2850	249700	1780	<30	<7		0.007129				-1.04	-0.73	0.70923	391500
Cambrian																					
[1] C-1	Sandstone	Ca-Na-Cl	1217	47900	41000	6750	1410	1210	179000	1680	277	<7		0.009385	-4.0	-29		-0.24		0.71028	279200
[1] C-2	Sandstone	Ca-Na-Cl	1095	60000	47700	6710	1340	1640	218700	1420	52	21		0.006493	-4.4	-28		-0.16	1.17	0.71002	337600
[1] C-3	Sandstone	Ca-Na-Cl	1097	60200	48500	6680	1330	1690	205600	1550	47	19		0.007539	-4.6	-28		-0.15	0.93		325600
[1] C-4	Sandstone	Ca-Na-Cl	1212	57800	49900	7710	1480	1170	186100	1710	96	<7	11	0.009189	-4.6	-35		-0.20	0.72	0.70990	306000
[1] C-5	Sandstone	Ca-Na-Cl	1070	32100	24900	3240	645	1010	110100	1110	980	<7		0.010082	-4.1	-36		0.19		0.70957	174100
[1] C-6	Sandstone	Na-Ca-Cl	1011	22400	40100	4380	2060	418	108400	792	645	<7	11	0.007306	-1.4	-28		-0.50		0.71007	179200
[1] C-7	Sandstone	Ca-Na-Cl	1209	46500	43400	5860	1380	1210	176500	1510	247	<7		0.008555	-3.3	-21				0.70986	276600
[1] C-8	Sandstone	Ca-Na-Cl	1264	51200	50800	6510	1810	1320	193400	2260	134	<7		0.011686	-3.3	-28		-0.31	1.07	0.70990	307400
[1] C-9	Sandstone	Ca-Na-Cl	1201	52800	45000	7060	1560	1290	191800	1450	131	17		0.007560	-3.6	-29		-0.12	0.96	0.70980	301100
[1] C-10	Sandstone	Ca-Na-Cl	1203	50500	43600	6900	1550	1210	183800	1440	169	17		0.007835	-3.8	-32		-0.06			289200
[1] C-11	Sandstone	Ca-Na-Cl	1149	43600	47700	5340	1570	1130	168700	1610	210	<7		0.009544	-2.0	-24		-0.40		0.71029	269900
[1] C-12	Sandstone	Ca-Na-Cl	1087	53500	42100	5670	1150	1230	183000	1770	138	<7		0.009672							288600
[1] C-13	Sandstone	Ca-Na-Cl	887	54800	44200	7180	937	1210	194900	1835	146	<1		0.009415				0.10	1.51	0.70951	305200
Precambrian																					
[6] OHD-1 #1	Granitic	Ca-Na-Cl	380	68500	32200	5030	499	1400	178400	1635	143	<1		0.009165	-5.3	-44	8.0	0.30			287807

Table A2: Geochemical Data and Stable Isotopes of the Formation Waters in Southern Ontario (from Skuce et al. 2015)

Sample ID	Formation of Origin	Ca mg/L	Na mg/L	Mg mg/L	K mg/L	Sr mg/L	Cl mg/L	Br mg/L	SO ₄ mg/L	HCO ₃ mg/L	Br/Cl	δ ¹⁸ O (VSMOW) (‰)	δ ² H (VSMOW) (‰)	δ ³⁷ Cl (SMOC) (‰)	δ ⁸¹ Br (SMOB) (‰)	⁸⁷ Sr/ ⁸⁶ Sr	TDS mg/L
Port Dover Quarry	Dundee (subcrop)	190	227	26	7.5	2.3	230	<3	42	168	0.0130	-7.5	-53	0.04	0.07	0.70894	901
T012149 (D)	Dundee (subcrop)	487	846	155	33.1	30.3	2478	20	370.8	145	0.0081	-10.8	-74	-0.26	0.78	0.70863	4678
T012101	Dundee	149	627	99	20.3	–	1128	8	16	–	0.0071	-15.7	-111				2518
T011050	Dundee	140	587	51	55.8	2.7	910	3.3	79.5	522	0.0036	-10.4	-66	0.57	1.06	0.70858	2356
T012150 (D)	Dundee	834	1160	23	101	28.8	3900	24	180	146	0.0062	-13.4	-90	0.91	1.49	0.70833	6385
T009537	Dundee	2050	6850	1460	216	46.3	18000	130	2100	351	0.0072	-8.5	-63	0.25	0.30	0.70829	31260
T008979	Dundee	1110	4830	943	129	29.3	18000	76	540	276	0.0042	-9.2	-65	0.03	1.00	0.70842	25952
F013661	Dundee	255	290	59	10.8	6.8	450	<3	27	365	0.0067	-11	-75			0.70851	1453
F005427	Dundee	649	202	49	8.5	4.5	580	3	320	141	0.0052	-15.1	-105				1963
T012111	Dundee	155	676	82	29	12.9	993	ND	18.9	–	–	-14	-94			0.70866	1976
T012111 (3)	Dundee	144	755	118	28.4	9.7	2600	13	260	3	0.0050	-10.1	-70	0.10	1.89	0.70862	3945
TAQA North battery	Columbus	183	830	149	22.5	23.5	1900	13	13	379	0.0068	-15.7	-115	0.21	0.72	0.70826	3542
T009308	Columbus	388	2410	381	62.3	36.5	5600	33	17	646	0.0059	-14.2	-104	0.15	1.37	0.70812	9618
T007578	Columbus	212	833	150	16.7	16.2	1500	9.8	39	339	0.0065	-15.8	-118	0.22	0.97	0.7083	3133
T012124(L)	Lucas	895	424	0.5	91.1	–	963	5.6	77	–	0.0058	-13.7	-86				2592
T012145 (L1)	Lucas	3060	8312	1540	454	67.1	20077	133	1352.1	159	0.0066	-6.6	-43	0.35	0.58	0.70842	35688
T012145 (L2)	Lucas	1585	7530	1185	136	100	16378	86	1323.6	255	0.0053	-6.6	-39			0.70813	29278
T012146	Lucas	641	3350	459	91.7	60.5	8300	31	640	101	0.0037	-6.8	-51	0.79	0.91	0.70809	13696
Oil Springs 2	Lucas	2854	6474	1674	252	69.3	18680	137	937.2	217	0.0073	-7.2	-46	0.74	1.02	0.70826	32142
Oil Springs 3	Lucas	3473	8316	2071	308	83.3	23556	158	994.9	201	0.0067	-6.5	-44	0.51	0.98	0.70823	40156
Oil Springs 4	Lucas	3248	7811	1890	334	81.6	22938	321	948	210	0.0140	-6.8	-45			0.70818	38663
T012152 (L)	Lucas	743	1247	142	78	18.7	3434	33	56.7	160	0.0096	-15.5	-113	0.14	0.92	0.70921	5944
T009650	Lucas	1880	5080	916	198	30.3	13000	57	1900	241	0.0044	-7	-43	0.92	0.77	0.70827	23328
T005511	Lucas	1440	5770	928	135	30.1	13000	64	1900	308	0.0049	-7	-45	0.81	1.06	0.70824	23601
LAI front battery	Lucas	1490	4630	876	155	25.1	11000	57	1800	250	0.0052	-6.5	-42	0.92	1.49	0.70825	20339
T011323	Lucas	1310	4290	852	122	31.5	11000	58	1900	344	0.0053	-6.5	-41	1.00	1.06	0.70823	19929
T012149 (L)	Lucas	556	301	198	11	14.6	355	1.6	2000	270	0.0045	-13.8	-95			0.70815	4343
McGregor Quarry 1	Lucas	467	204	225	16.6	12.6	380	<3	1690.1	125	0.0079	-16.3	-118	0.23	1.55	0.70836	3769
McGregor Quarry 2-1a	Lucas	350	94	169	6.2	12.8	170	<3	1319.9	242	0.0176	-16.2	-119			0.70844	2792
McGregor Quarry 2-1b	Lucas	353	253	175	–	13.8	301	–	1401	–	–	-16.7	-122				2497
St. Mary's Quarry	Lucas	146	64	32	2.5	16	22	<3	210	85	0.1364	-10.5	-69			0.70815	580
Goderich harbour well	Lucas	519	102	114	1.9	14.9	230	3	1300	183	0.0130	-12.5	-83			0.70807	2474
T012135	Amherstberg	15500	36100	3890	1240	226	80000	658	366	5	0.0082	-6.7	-53	-0.15	0.45	0.70928	138066
T012152 (DR)	Amherstberg	2520	2680	1.1	260	73.3	9700	85	13	50	0.0088	-8.6	-63	-0.04	0.53	0.70925	15342
T012177	Basslands	629	370	20	10.6	12.2	870	<3	1300	27	0.0034	-11.2	-74			0.70817	3241
T012177 (2)	Basslands	543	836	45	33.8	16.3	1600	<3	1300	21	0.0019	-10.5	-77			0.70823	4382
T002484	Salina E-unit (subcrop)	799	1320	149	80.7	17	3500	33	56	160	0.0094	-9	-62	0.40	1.69	0.70868	6208
Sulphur Springs C. A.	Salina E-unit (subcrop)	567	7	52	2.1	12.6	8.6	3	1200	212	0.3488	-11.7	-81			0.7085	2070

Sample ID	Formation of Origin	Ca mg/L	Na mg/L	Mg mg/L	K mg/L	Sr mg/L	Cl mg/L	Br mg/L	SO ₄ mg/L	HCO ₃ mg/L	Br/Cl	δ ¹⁸ O (VSMOW) (‰)	δ ² H (VSMOW) (‰)	δ ³⁷ Cl (SMOC) (‰)	δ ⁸¹ Br (SMOB) (‰)	⁸⁷ Sr/ ⁸⁶ Sr	TDS mg/L
Brantford spring	Salina A-2 (subcrop)	567	61	28	2.3	0.3	500	0.3	38	284	0.0006	-10.2	-69			0.70881	1488
Goderich salt mine N	Salina A-2 carbonate	84085	31007	15177	7431	1470	240000	3502	89	22	0.0146	4	-41	0.02	0.21	0.70886	383732
T007498	Salina A-2 carbonate	38900	91900	6050	5690	747	245695	1936	200	38	0.0079	-1.6	-37	0.35	0.70	0.70887	391550
T008641	Salina A-2 carbonate	57700	79300	8940	5600	1070	220000	1800	230	5	0.0082	-0.6	-37	0.27	0.79	0.70856	374770
T008633	Salina A-1 carbonate	35982	62939	7680	2660	708	191512	1863	244	<2	0.0097	-1.2	-32	-0.21	0.13	0.70946	303892
T007583	Salina A-1 carbonate	54222	52336	8269	3654	924	207443	2734	150	<2	0.0132	-0.7	-38	-0.40	-1.29	0.70848	330281
T001539	Salina A-1 carbonate	74600	48300	14100	7330	1240	370000	2700	110	<2	0.0073	1.5	-47	-0.23	-0.05	0.7085	518533
T011888	Salina A-1 carbonate	42100	46100	8300	6910	839	180000	1800	250	84	0.0100	-2.7	-49	-0.32	-0.21	0.70879	286440
T008596	Salina A-1 carbonate	39900	79200	9270	4880	946	190000	1300	360	16	0.0068	-4.2	-50	-0.20	-0.13	0.70839	325930
T003536	Salina A-1 carbonate	35600	99600	13500	4130	780	210000	1700	250	5	0.0081	-0.8	-34	-0.28	0.31	0.70928	365643
T008657-1	Guelph	11886	36917	2617	697	185	100904	501	624	-	0.0050	-4.1	-43				154554
T008657-2	Guelph	26665	85500	5874	1623	408	180000	920	330	2	0.0051	-3.2	-41	0.20	0.07	0.70877	301858
T002235-1	Guelph	6780	112000	987	600	143	180000	260	1200	4	0.0014	-11.1	-77	0.31	0.06	0.70888	302015
T002235-2	Guelph	6800	143300	1100	605	161	160000	280	1400	4	0.0018	-2.6	-37				313207
T012124 (G) - A	Guelph	36432	47580	7862	2121	-	169944	1741	203	-	0.0102	-2.5	-36				265883
T012124 (G) - B	Guelph	35863	46874	7707	2033	-	170591	1769	201	-	0.0104	-2.7	-33	-0.24	0.56	0.7092	265039
T012150 (G)	Guelph	20100	98000	4850	2790	403	160000	1200	660	93	0.0075	-1.2	-39	-0.20	-0.49	0.70928	288158
North Seckerton battery	Guelph	43200	56100	6850	3540	1140	170000	1800	340	16	0.0106	-1.3	-33	-0.23	-0.22	0.70928	283048
Corunna battery	Guelph	44700	76600	6700	4100	943	220000	2100	250	<2	0.0095	-0.1	-41	-0.31	-0.77	0.70927	355477
Seckerton battery	Guelph	69600	52700	8210	4810	1210	180000	2800	130	13	0.0156	0.7	-38	-0.30	-0.42	0.70911	319540
Ladysmith battery	Guelph	70300	54896	10620	5550	1310	240000	2600	130	<2	0.0108	2.4	-49	-0.46	-0.52	0.7092	385484
Moore Brine Facility	Guelph	102000	72600	16800	5420	1420	240000	2800	120	3	0.0117	1.9	-43	-0.40	-0.82	0.70937	441259
Den-Mar Brine Facility	Guelph	99500	61700	13700	6020	1550	230000	3000	130	26	0.0130	-0.3	-38	-0.10	0.78	0.71049	415714
T004912	Guelph	91900	71000	5660	1570	2030	190000	1800	100	<2	0.0095	-5.6	-40	0.09	-0.55	0.70917	364171
T004678	Guelph	13800	38000	3120	1190	294	95000	710	1000	70	0.0075	-2.8	-40	-0.03	-0.21	0.7089	153210
T005442	Guelph	30700	106000	5740	3430	817	200000	1300	360	31	0.0065	-6.6	-57	-0.17	0.05	0.70915	348436
Lowrie Dawn battery	Guelph	18700	52000	4360	1730	423	110000	890	140	5	0.0081	-1.3	-52	-0.34	0.08	0.70888	188314
T010097	Guelph	80825	31308	13753	3696	1306	222203	3853	95	<2	0.0173	-6.9	-63	0.02	-0.21	0.70854	358146
T001521	Guelph	21400	83400	4950	2670	415	120000	970	740	<2	0.0081	-3	-36				234622
T008932	Clinton-Cataract	37804	50782	6599	1207	-	152763	1566	421	-	0.0103	-3.2	-47				251142
T008812	Clinton-Cataract	31237	47267	5679	1086	-	135938	1324	458	-	0.0097	-4.1	-38			0.71033	222989
T011830	Clinton-Cataract	29300	48200	5510	765	543	150000	1100	560	<2	0.0073	-4	-39				236120
T010691	Clinton-Cataract	27307	40097	6138	978	-	122542	1133	519	-	0.0092	-3.1	-48				198714
T011549	Clinton-Cataract	30052	45848	6326	1070	-	145041	1408	475	-	0.0097	-2.9	-36				230220
T005741	Clinton-Cataract	33932	48770	5631	1024	-	150503	1511	340	-	0.0100	-3.5	-54				241711
T004185	Clinton-Cataract	35462	50741	6416	1177	-	153560	1562	297	-	0.0102	-0.9	-39	0.29	1.59	0.71045	249215
T003188	Clinton-Cataract	58000	59300	10800	1670	1220	250000	2400	180	<2	0.0096	-1.9	-42	0.25	1.50	0.71036	383666
T011814	Clinton-Cataract	53000	59500	9920	1700	1130	280000	1900	260	<2	0.0068	-1.2	-20	-0.13	0.35	0.71035	407661

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T009153	Trenton-BlackRiver	27300	57400	5610	3340	768	180000	1100	330	<2	0.0061	-1.5	-22	-0.45	0.77	0.7103	275902
T010019	Trenton-BlackRiver	27800	79000	6220	3120	871	150000	1200	360	<2	0.0080	-1.6	-20	-0.37	0.43	0.71055	268628
T007330	Trenton-BlackRiver	28500	57500	5710	3120	631	170000	1200	350	<2	0.0071	-1.7	-24	0.31	0.58	0.71042	267071
T007636	Trenton-BlackRiver	28950	62900	5730	3070	634	160000	1300	380	<2	0.0081	-1.5	-22	-0.28	0.89	0.7104	263024
T008358	Trenton-BlackRiver	30100	75700	6620	3200	758	170000	1200	400	20	0.0071	-1.4	-23	-0.41	0.52	0.71038	288050
T009605	Trenton-BlackRiver	32500	89400	7360	3730	965	150000	1200	300	<2	0.0080	-1.4	-21	-0.47	0.29	0.71032	285523
T007954	Trenton-BlackRiver	27400	58100	6067	3100	806	170000	1200	210	3	0.0071	-1.6	-18	-0.44	0.38	0.71034	266940
T008313	Trenton-BlackRiver	27900	61100	6200	3090	686	160000	1200	360	8	0.0075	-0.9	-31	-0.11	0.65	0.71031	260593
T008057	Trenton-BlackRiver	70900	85900	9180	3940	1220	230000	1600	300	<2	0.0070	-1.8	-27	-0.49	0.70	0.71033	403179
T009859	Trenton-BlackRiver	38900	63100	8080	3600	843	190000	1600	250	<2	0.0084	-1.2	-25	-0.16	0.30	0.71011	306446
T007240	Trenton-BlackRiver	42700	71900	7620	2890	1070	230000	2000	200	<2	0.0087	-1.5	-24	-0.19	0.38	0.71008	358453
T006658A	Trenton-BlackRiver	41335	65700	7090	2800	956	182278	1935	197	<2	0.0106	-2.6	-11			0.70991	302689
T007793	Trenton-BlackRiver	1360	1830	321	46	10.1	4143	22	7.2	<2	0.0053	-2	-36	-0.14	0.74	0.70988	7934
T005912	Cambrian	85000	86500	8440	2490	1510	210000	2100	140	3	0.0100	-1.5	-28	-0.22	0.00	0.70951	396232
T001591	Cambrian	37300	90100	8220	4000	766	200000	2000	220	8	0.0100	-3.4	-25	-0.09	1.21	0.7098	342669
T001303	Cambrian	48800	62000	6760	2200	1420	200000	2300	220	<2	0.0115	-2.6	-34	-0.10	1.01	0.70979	323747
T011362	Cambrian	94200	72200	8540	2780	1750	220000	2300	160	<2	0.0105	-2.7	-39				402027
T001343	Cambrian	37600	50400	6240	1950	889	170000	1900	470	<2	0.0112	-3.6	-27	-0.14	0.99	0.70983	269504
T008532	Cambrian	56634	49690	6740	1232	1385	191086	2390	120	<2	0.0125	-4.3	-38	0.30	1.54	0.7093	309954
T008532 (2)	Cambrian	78200	47400	9590	1760	1910	240000	2400	120	<2	0.0100	-3.6	-44	0.27	1.50	0.7093	381499
T007369	Cambrian	47535	50228	5768	1615	1131	180000	1800	200	<2	0.0100	-2	-20	-0.23	0.19	0.71033	288769
T007369 (2)	Cambrian	46700	64300	6250	2390	1170	300000	1800	240	<2	0.0060	-1.9	-24	-0.27	0.45	0.71027	422936
F014364	uncertain shallow aquifer	17	80	9	3.2	0.6	20	<3	22	259	0.1500	-10.2	-70			0.70919	419
F020066 / T012165	uncertain shallow aquifer	615	330	182	18.2	12	760	8.7	1800	81	0.0114	-10.7	-73	-0.01	1.90	0.70895	3814
T012116	uncertain shallow aquifer	637	30	37	3.9	8.1	80	0.7	640	163	0.0088	-10.3	-70			0.70843	1602
Hemlock Creek 1	uncertain shallow aquifer	70	36	27	5.7	1.2	63	0.3	120	166	0.0048	-9.8	-68			0.70894	493
Ancaster sulphur spring	uncertain shallow aquifer	750	1450	182	59	34.3	4000	43	420	181	0.0108	-10.6	-69	-0.11	2.21	0.70995	7130
Church Road Spring	uncertain shallow aquifer	710	461	227	42.3	12.8	960	11	1800	160	0.0115	-12.1	-90			0.70881	4391
Twelve Mile Creek	uncertain shallow aquifer	114	37	39	3.1	1	68	0.5	72	383	0.0074	-10.5	-78			0.71072	724
TAQA North flood water	drift aquifer	77	197	38	4.5	3.6	620	3	2	249	0.0048	-16.5	-121			0.70876	1209
T0121355	probably Dundee/Lucas	192	1320	178	30.3	11.1	1500	11	110	281	0.0073	-14.2	-98			0.70871	3673

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