HYDROGEOCHEMICAL CHARACTERIZATION OF GROUNDWATERS AND POREWATERS BENEATH THE BRUCE NUCLEAR SITE: EVIDENCE FOR DIFFUSION-DOMINATED TRANSPORT IN THE ORDOVICIAN

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ABSTRACT

Investigations of the controls on solute transport in porewater and groundwater below the Bruce nuclear site involved laboratory-scale diffusion measurements, as well as measurements of natural tracer ($\delta^{18}O$, $\delta^{2}H$, $^{87}Sr/^{86}Sr$, Cl and Br) distributions and isotopic compositions of CH_4, CO_2 and helium ($^{3}He/^{4}He$) in the porewaters and groundwaters. The analyses were performed on samples collected from drilled boreholes, DGR-1 through DGR-6, during site characterization activities and the results are summarized below.

With the exception of just a few samples from the Upper Silurian, the effective diffusion coefficient ($D_{e)}$ values measured from DGR cores are all less than 10^{-11} m^2/s, which is approximately one order of magnitude lower than measured D_e values from international programs in sedimentary rock. The majority of the data are in the range $10^{-13} < D_e < 10^{-11}$ m^2/s, with Lower Silurian and Upper Ordovician shale samples representing the higher end of this range because of their relatively high porosity (7 to 9%). The low porosity of the Middle Ordovician limestone (< 2%) results in low D_e values, clustering in the range $10^{-13} < D_e < 10^{-12}$ m^2/s.

The $\delta^{18}O$, Cl, and Br profiles in the Middle Ordovician carbonates define trends of decreasing $\delta^{18}O$ values and tracer concentrations with depth, and are interpreted to result from an extremely long period of diffusion-dominated transport (~300 Ma). Near the base of the Middle Ordovician carbonates the $\delta^{2}H$ data display a slight enrichment, which could represent upward diffusion of deuterium-enriched water originating in the underlying Precambrian shield. A Precambrian shield influence on the Ordovician porewater chemistry is inferred from the measured $^{87}Sr/^{86}Sr$ ratios in the Middle Ordovician carbonates, which are elevated above values expected for porewater in equilibrium with carbonate rock.

The CH_4 isotope data indicate the presence of biogenic gas in the Cobourg Formation and in the overlying Ordovician shales, while gas of thermogenic origin is present in the Middle Ordovician carbonates below. The fact that methane of differing origins has not mixed by diffusion across the Cobourg limestone suggests that there is an effective barrier to vertical transport near the base of the formation. The presence of a vertical transport barrier at this depth is also supported by the persistence of large gradients in the isotopic composition of helium.

The Cambrian groundwater chemistry displays a distinct reversal in the natural tracer profiles relative to the overlying Ordovician carbonates. The reversal in the profiles is abrupt compared to the gradual decline in concentrations and isotopic compositions observed with depth through the Ordovician carbonates. Irrespective of the mechanism(s) responsible for the Cambrian fluid chemistry beneath the Bruce nuclear site, however, the fundamental hypothesis that solute migration with the Ordovician sediments is diffusion dominated is well supported by the data.

1. INTRODUCTION

Hydrogeochemical studies seek to understand the nature and timing of physical and chemical processes that have operated to define the chemical characteristics of natural water. The term hydrogeochemistry refers to the chemistry of water as it is affected by a variety of chemical reactions with components of soil, sediment, rocks and minerals, and by various physical processes such as advection, evaporation and diffusion. Investigations of low-permeability geologic systems are limited by very low advection rates and solute velocities. Consequently, studies of porewater movement and solute transport in low-permeability geologic systems rely, in part, on hydrogeochemistry in order to elucidate 1) the age, or residence time, and origin of the porewater, 2) the processes responsible for observed spatial variations in porewater chemistry, and 3) the mechanisms controlling transport of solutes at long time frames.

Ontario Power Generation (OPG) is proposing the development of a Deep Geologic Repository (DGR) at the Bruce nuclear site, situated in the Municipality of Kincardine, Ontario, for the long-term management of Low and Intermediate Level Radioactive Waste (L&ILW). Extensive hydrogeochemical analyses have been conducted as part of a multi-disciplinary geoscientific site characterization related to the DGR project. The multi-disciplinary approach integrates regional- and site-scale data, including the stratigraphy and structural geology, physical hydrogeology, hydrogeochemistry, and paleohydrogeology of the region.

The data presented and discussed in this paper were obtained from laboratory analysis of continuous core extracted from four deep diamond-cored vertical boreholes, DGR-1, DGR-2, DGR-3 and DGR-4, and two deep inclined boreholes, DGR-5 and DGR-6. The hydrogeochemical data (including $^{87}Sr/^{86}Sr$, $\delta^{13}C$ and $\delta^{2}H$ in CH_4, $\delta^{13}C$ in CO_2, $\delta^{18}O$ and $\delta^{2}H$ in H_2O, $^{3}He/^{4}He$, Cl and Br) have been examined to develop an understanding of porewater origin and evolution. The specific objectives of this paper are:

- to assist in identifying the residence time and origin of the porewater and groundwater;
- to provide constraints on the processes and timing of solute transport related to the demonstration of DGR safety; and,
- to develop and test a site-specific natural analogue model using geochemical tracers.

2. BACKGROUND

The Bruce nuclear site, situated 225 km northwest of Toronto on the eastern shore of Lake Huron, is underlain by an 850 m thick sedimentary sequence of Cambrian to Devonian age. The sediments consist of near horizontally bedded and weakly deformed shales, carbonates and evaporites of the Michigan Basin. Within this sedimentary pile, the proposed DGR would be excavated within the low permeability argillaceous Middle Ordovician[1] limestone of the Cobourg Formation, at a depth of 680 m, and overlain by greater than 200 m of Upper Ordovician shale.

The work program for site characterization is outlined in the Geoscientific Site Characterization Plan (GSCP; [1],[2]), which describes the surface and sub-surface activities necessary to determine site suitability from both the geoscientific and engineering perspectives.

As a result of the site characterization activities, three hydrologic systems have been identified beneath the Bruce nuclear site: a shallow system, an intermediate system, and a deep system. The emphasis of this paper is the hydrogeochemical evolution of the Ordovician sediments within the deep hydrologic system, however, the three systems are described briefly below.

The shallow system (hydrostratigraphic units 1 and 2 in Figure 1) occurs from ground surface to a depth of approximately 169.3 m and contains fresh to brackish groundwater which flows upward and westward toward Lake Huron. The hydraulic conductivity (K_h), determined from in situ hydraulic straddle-packer testing, in the shallow system ranges from 10^{-10} m/s in the glacial till overburden to 10^{-4} m/s in the dolostone aquifer.

The intermediate system (hydrostratigraphic units 3 and 4 in Figure 1) extends from 169.3 to 447.7 m depth. The system has low permeability (K_h between 10^{-14} to 10^{-10} m/s) and groundwater flow predominantly occurs in two thin aquifers identified at intervals of 325.5-328.5 m and 374.5-378.6 m, in the upper Salina A1 Unit (K_h of 10^{-7} m/s) and in the Guelph Formation (K_h of 10^{-8} m/s), respectively. Flow direction in the upper Salina A1 Unit is toward Lake Huron, whereas flow is directed to the east, or inland, in the Guelph Formation.

The deep system occurs between 447.7 and 860.7 m depth and includes the Ordovician and Cambrian sediments (hydrostratigraphic units 5 through 8 in Figure 1). The Ordovician shales and the Trenton Group limestones are characterized as an aquiclude (K_h in the range of 10^{-15} to 10^{-14} m/s), the Black River Group is an aquitard (K_h of 10^{-12} m/s), and the Cambrian sandstone is an aquifer (K_h of 10^{-6} m/s). The low K_h values measured suggest that solute transport in the Ordovician sediments is dominated by diffusion. Further support for this interpretation is provided by the hydrogeochemical evidence presented herein.

3. METHODS

A variety of methods were utilized during the hydrogeochemical analyses to characterize the porewaters and groundwaters below the Bruce nuclear site as accurately as possible. The methods are summarized briefly below.

3.1. Sample Collection

All geoscientific activities associated with sample collection, handling, preservation and sealing, laboratory handling and technical report compilation were completed in accordance with the

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[1] A recently published update of the Paleozoic stratigraphy of southern Ontario includes minor modifications to the terminology of reference ages for the strata [3]. The Middle Silurian designation has been removed and now the Upper and Lower Silurian are separated at the top of the Eramosa Member of the Guelph Formation. In addition, the Black River and Trenton groups now comprise the lower portion of the Upper Ordovician Period. Acknowledging these recent re-interpretations, the descriptions here still follow the main sequence stratigraphic associations of [4] and [5].

GSCP and established Test Plans in order to ensure consistency in methodology and data reporting.

Drill core samples were photographed, preserved by vacuum packaging (with prior nitrogen flushing) in the field, and then stored at temperatures below 8ºC before shipping. Cores were shipped to the University of Ottawa and the University of New Brunswick within a few days of drilling, in most cases, and stored at 4°C until analysis. Core samples were also shipped to the University of Bern, in Switzerland, where complementary geochemical and lithogeochemical analyses were performed.

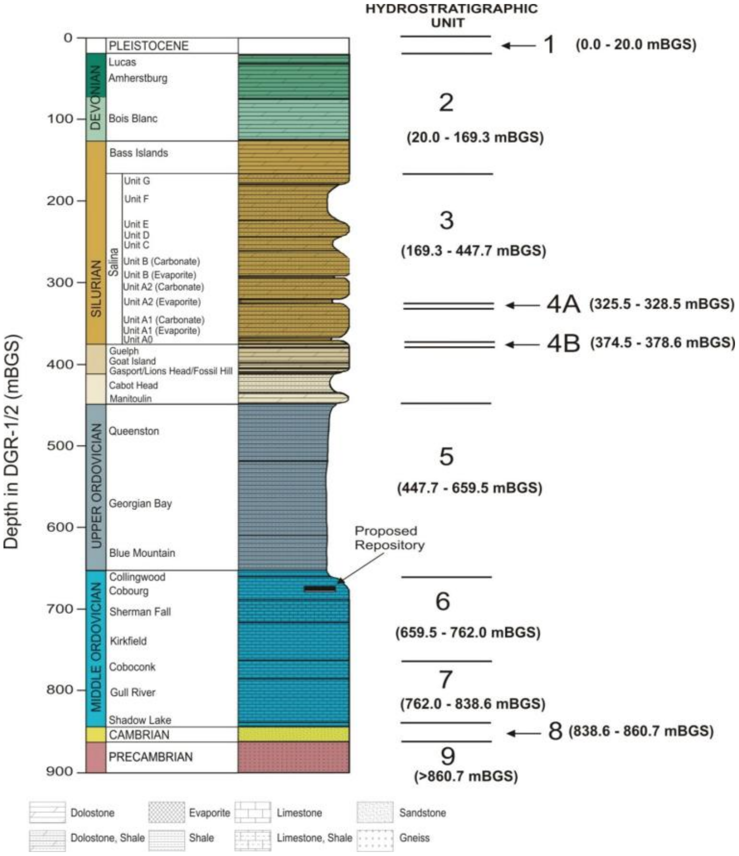


Figure 1. Stratigraphic column showing hydrostratigraphic units at the Bruce nuclear site.

3.2. Groundwater and Porewater Characterization

Stable isotopes of H_2O ($\delta^{18}O$ and $\delta^{2}H$) were measured at the University of Ottawa by isotope ratio mass spectrometry on water extracted from crushed core samples using vacuum distillation at 150°C for 6 hours [6],[7]. Verification testing was performed at the University of Ottawa using variable temperatures and extraction times to ensure that incomplete water yield and isotopic fraction effects were minimized in the vacuum distillation process [8].

The hydrogeochemical characteristics of groundwaters were obtained by direct sampling [9],[10]. In the case of porewaters, a leaching/extraction technique was used in which the dried rock samples remaining after vacuum distillation were leached with distilled water. The mass of solutes leached was normalized to the water content of the individual samples determined during distillation in order to determine concentrations [6],[7]. Cl and Br (DGR-2 only) were measured by ion chromatography; Br from DGR-3 and DGR-4 was measured by inductively coupled plasma mass spectrometry (ICP-MS).

The extraction of CO_2 also accompanied the vacuum distillation process. The CO_2 released from the rock during heating was trapped with water vapour at liquid N_2 temperature. Following vacuum distillation, samples were removed from the line and warmed to release the condensed CO_2, which was then analysed to determine both the concentration and the $\delta^{13}C$ composition using a Finnigan MAT Delta XL continuous flow mass spectrometer interfaced with a gas chromatograph (GC) to purify the gas.

Methane was extracted from rock cores by placing approximately 130 g of crushed core in a series of sealed jars and allowing the CH_4 to collect in the head space over a period of seven to eight weeks. The initial headspace was air at atmospheric pressure, and a mass balance correction was made for the 2 ppm of atmospheric CH_4 in air. The isotopic composition of the released methane was measured using a Finnigan MAT Delta XL continuous flow mass spectrometer interfaced with a GC to purify the gas.

Sr isotopes were measured in groundwater, porewater and rock core samples. For the porewater samples, paired leaches were analyzed in deionized water, including 1) a rapid leach (~1 hour) and 2) an extensive leach (~60 days) to compare potential contributions from the rock matrix. Following leaching, the rock samples were then rinsed extensively with deionized water and dried. The rock samples were then crushed to powder and leached with a mild acetic acid, which leached Sr only from the carbonate component of the rock. Sr was then removed from the leachate on ion exchange columns and re-eluted for preparation on filaments for analysis by thermal ionization mass spectrometry (TIMS) on a Triton instrument at Carleton University. Whole rock analyses were also undertaken on four Ordovician core samples to assess the potential contribution of ^{87}Sr from the aluminosilicate component of the rock. The samples were rinsed, crushed, and then dissolved in HCl. Remaining solids were dissolved in an HF/HNO_3 solution which was recombined with the HCl leachate before column extraction of Sr [11].

Helium isotopes were analyzed from subcore samples that were drilled in the laboratory using a Diamant® diamond-faced coring tool mounted on a benchtop drill press with water circulation system. The subcores were ~3 cm long and 0.6 cm diameter. The subcores were air dried with a hand blower, weighed, and transferred into copper or stainless steel tubes which were evacuated to a rough vacuum, < 1.33 Pa. Out-diffusion experiments on the samples allowed for the collection of helium gas within the extraction lines, which was then analyzed for helium isotopes using at MAPL 25-50 noble gas mass spectrometer at the University of Ottawa [12].

4. RESULTS AND DISCUSSION

The purpose of the following subsections is to highlight the usefulness of the hydrogeochemical data in assessing both 1) the origin and evolution of the sedimentary brines, and 2) the processes governing solute transport. The results and interpretation of the natural tracer analyses (Br, Cl, $\delta^{18}O$, $\delta^{2}H$, $^{87}Sr/^{86}Sr$ and the isotopes of CH_4 and He) are presented in the following subsections.

4.1. Origin of Sedimentary Brines

The brines in the Michigan Basin are considered to have formed from ancient seawater or evaporated ancient seawater [13],[14]. A comparison of regional data with the Cl and Br concentration data collected at the Bruce nuclear site suggests that the origin of the sedimentary brines at both the regional- and site-scales is the same, and that the fluids have been modified to varying degrees by mixing and water-rock interaction processes [15]. Figure 2 shows a comparison of the regional- [16] and site-scale data for Cl versus Br concentrations, illustrating the consistency between the two datasets.

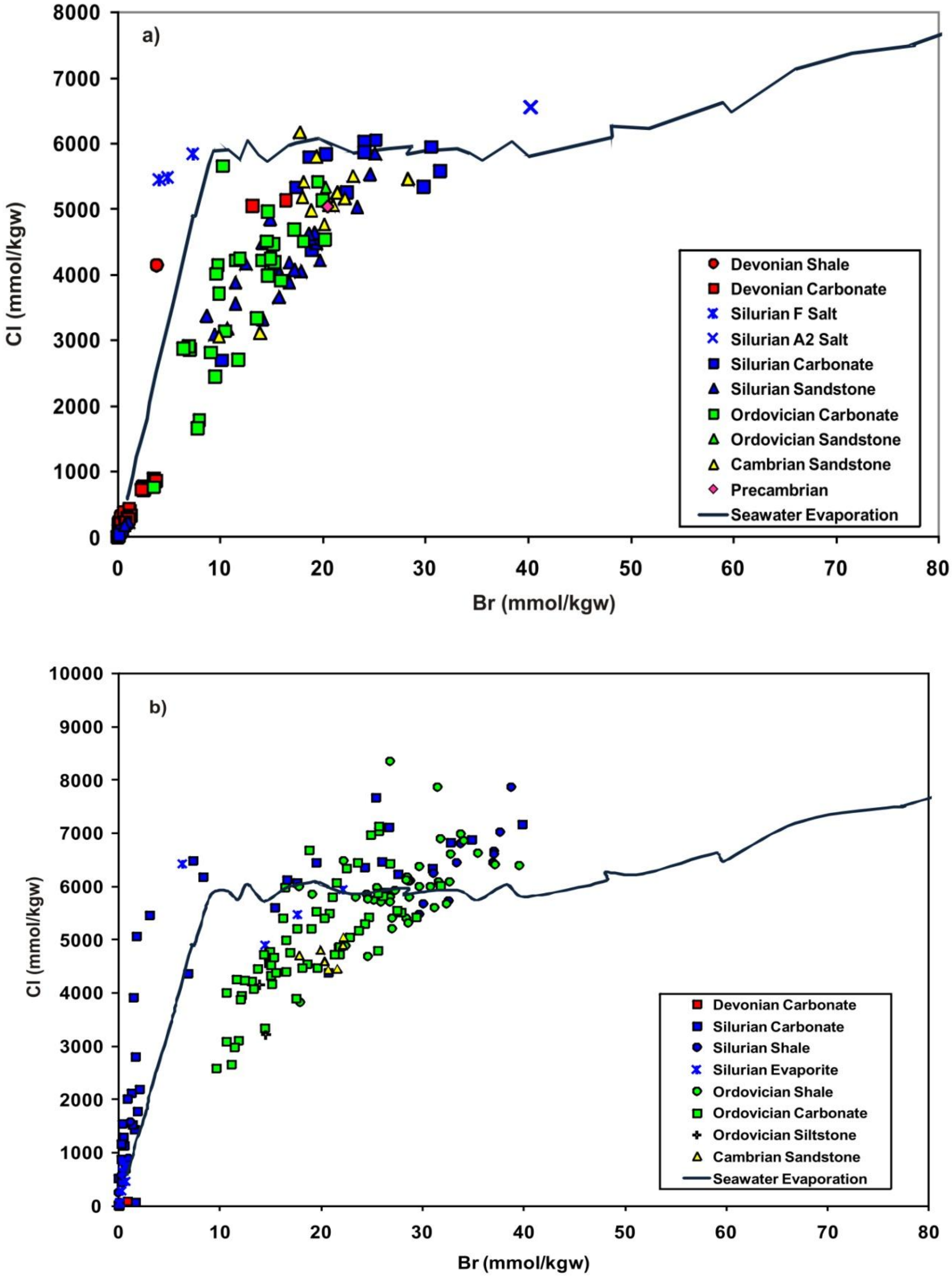


Figure 2. Cl versus Br concentrations from a) regional- and b) site-scale investigations.

4.2. Strontium Isotopes

Above the Guelph Formation aquifer, the $^{87}Sr/^{86}Sr$ ratios for Silurian porewater and groundwater at the Bruce nuclear site approach the values of the host rock and the seawater curve (Figure 3). The convergence demonstrates the dominance of the Silurian seawater $^{87}Sr/^{86}Sr$ signature in the evaporite minerals (anhydrite) and non-argillaceous limestones of the Salina units.

Consistent with the results for Sr isotopic analysis of oilfield groundwater from the Michigan and Appalachian basins [17], the $^{87}Sr/^{86}Sr$ ratios from Cambrian groundwaters and from the Ordovician and Lower Silurian porewaters at the Bruce nuclear site are more radiogenic than the Paleozoic seawater curve (Figure 3). With the exception of the Ordovician shale units, the $^{87}Sr/^{86}Sr$ signatures of the porewater are also more radiogenic than those of the host rocks. There are three possible explanations for the ^{87}Sr enrichment in the porewater:

- ingrowth of ^{87}Sr from ^{87}Rb decay since the Ordovician;
- leaching of ^{87}Sr from shield-derived siliciclastic material in the shale and the argillaceous component of the limestones; and,
- transport of Sr upward from an ^{87}Sr-enriched brine source in the underlying Precambrian shield.

Calculations suggest that the enriched $^{87}Sr/^{86}Sr$ ratios observed in the porewater of the Ordovician shales could be derived by ingrowth via ^{87}Rb decay, but only if all of the ^{87}Sr produced was released to the porewater, which is unlikely. Whole-rock analyses of the Ordovician shales indicate that they are highly enriched in radiogenic ^{87}Sr (Figure 3), suggesting that leaching of ^{87}Sr from old shield-derived silici-clastic material also contributes to ^{87}Sr enrichment in the porewater.

The Rb content of the argillaceous carbonates is too low to explain the ^{87}Sr enrichment in the Middle Ordovician porewater by ingrowth alone. A combination of ingrowth and leaching of ^{87}Sr from shield-derived silici-clastic material is possible, but the ^{87}Sr enrichment that would result might be expected to be proportional to the silici-clastic content of the enclosing rocks, and therefore the degree of enrichment in the argillaceous carbonate porewater should be lower than in the Upper Ordovician shale porewater. The ^{87}Sr enrichment in the porewater of the argillaceous carbonates is quite variable (Figure 3) but it is not significantly lower than the porewater ^{87}Sr enrichment in the shales. In fact, some of the limestone porewater samples from DGR-3 display the same degree of enrichment as the groundwater from the underlying Cambrian aquifer – some of the most enriched samples in the dataset. Highly radiogenic Sr signatures have been measured in Canadian Shield brines, and upward transport of ^{87}Sr from the underlying crystalline rock may have contributed to the observed enrichment in the Cambrian aquifer and in the porewater of the overlying Middle Ordovician carbonates.

The observed ^{87}Sr enrichment in the Ordovician likely resulted from some combination of the three processes described above, but the respective contributions cannot be resolved quantitatively. In any case, the presence of radiogenic Sr throughout the Ordovician indicates extremely long time periods for water-rock interaction and diffusion.

4.3. Methane, Carbon Dioxide and Helium

The presentation of CH_4, CO_2 and He data is limited to their respective isotopic compositions ($\delta^{13}C$ in CH_4 and CO_2, $\delta^{2}H$ in CH_4, and $^{3}He/^{4}He$) in porewaters from the Ordovician rocks because these data provide insight regarding the origin of the CH_4 and the solute transport processes acting on the gases.

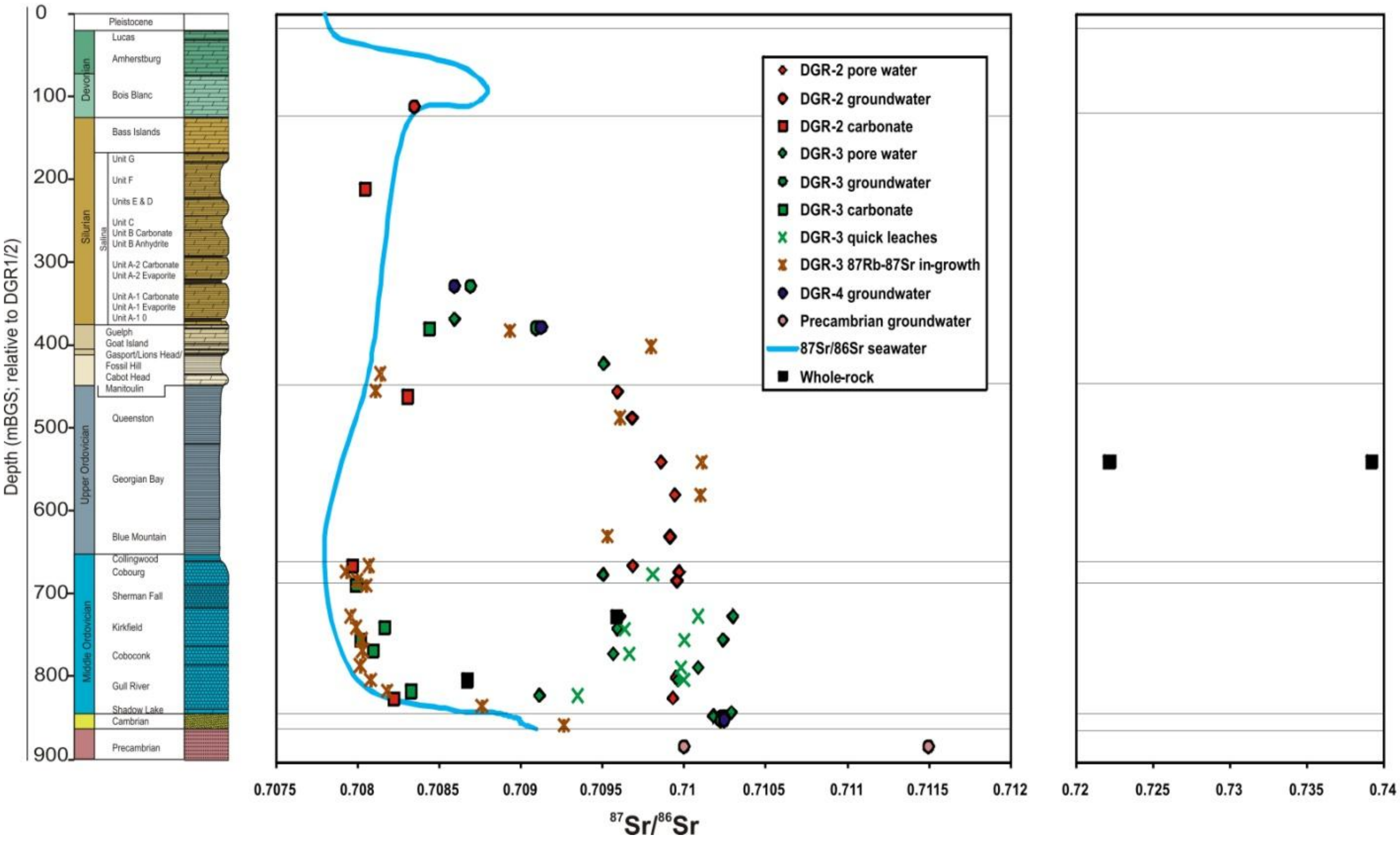
The $\delta^{13}C$ and δ^2H data for CH_4 display a clear separation above and below the Cobourg Formation (Figure 4). This type of systematic variation has been used to distinguish between biogenic and thermogenic origins for CH_4. The stable isotope data from CH_4 have been plotted on the variation diagram [18] and they define two fields (Figure 5): one field with strongly depleted values of $\delta^{13}C$ and δ^2H represents CH_4 of biogenic origin in the Upper Ordovician shales and the Cobourg Formation, and a second field represents CH_4 of thermogenic origin in the Middle Ordovician carbonates below the Cobourg Formation. These indications that CH_4 in the Upper Ordovician shales and Cobourg Formation is of biogenic origin are supported by the $\delta^{13}C$ data for CO_2 (Figure 4). The CO_2 residual in a system following biogenic CH_4 generation is expected to be enriched in $\delta^{13}C$, and the zone of enriched $\delta^{13}C$ in CO_2 observed in the Blue Mountain Formation shale corresponds closely to the zone of biogenic CH_4 formation that is inferred from the stable-isotope compositions of CH_4 (Figure 4).

The generation of thermogenic gas requires temperatures in excess of 70°C [19], and this condition has not prevailed since maximum burial in the Carboniferous, suggesting that the thermogenic gas is very old. The age of the biogenic CH_4 contained in the Ordovician rocks is unknown, but it is hypothesized that the biogenic CH_4 may also be ancient because the activity of a methanogenic archaea population may have been reduced in these rocks following consolidation during peak burial, which has resulted in median pore throat radii on the order of 5 nm. The evolution to high salinity and low water activity (0.6 to 0.7) porewater also may have contributed to diminished biogenic activity, although the influence of such high salinity on biogenic activity is not yet well established.

The separation of thermogenic gas below, from biogenic gas above, across a relatively short vertical distance (i.e., tens of meters), as defined by the steep gradient in the $\delta^{13}C$ and δ^2H isotope profiles, suggests that there has been very little vertical mixing. If the two types of CH_4 are of ancient origin, the fact that their vertical separation has persisted over the millennia indicates that there is an effective vertical barrier to advection and diffusion in the stratigraphy below the Cobourg Formation.

The $^3He/^4He$ data are presented as the isotope ratio in the sample (R_s) normalized to the isotope ratio in air (R_a) such that $xR_a = R_s/R_a$. The data are remarkably consistent among the three drill cores analyzed, and define two distinct regions of differing isotope ratio separated at the base of the Cobourg Formation, with xR_a of approximately 0.02 within and above the Cobourg Formation, and xR_a of approximately 0.035 below (Figure 4). Consistent with observations from the CH_4 and CO_2 isotope data, the clear separation between regions of differing He isotope composition indicates that there has been very little cross-formational mixing of He across the lower contact of the Cobourg Formation.

The steep gradients in the isotope profiles for the gases discussed above suggest that there is a discrete barrier to transport near the base of the Cobourg Formation where diffusion coefficients must be extremely low.



Notes: The seawater $^{87}Sr/^{86}Sr$ curve [20] is shown for reference.

Figure 3. Depth profiles for $^{87}Sr/^{86}Sr$ in groundwater, porewater and the host rocks at DGR-2, DGR-3 and DGR-4.

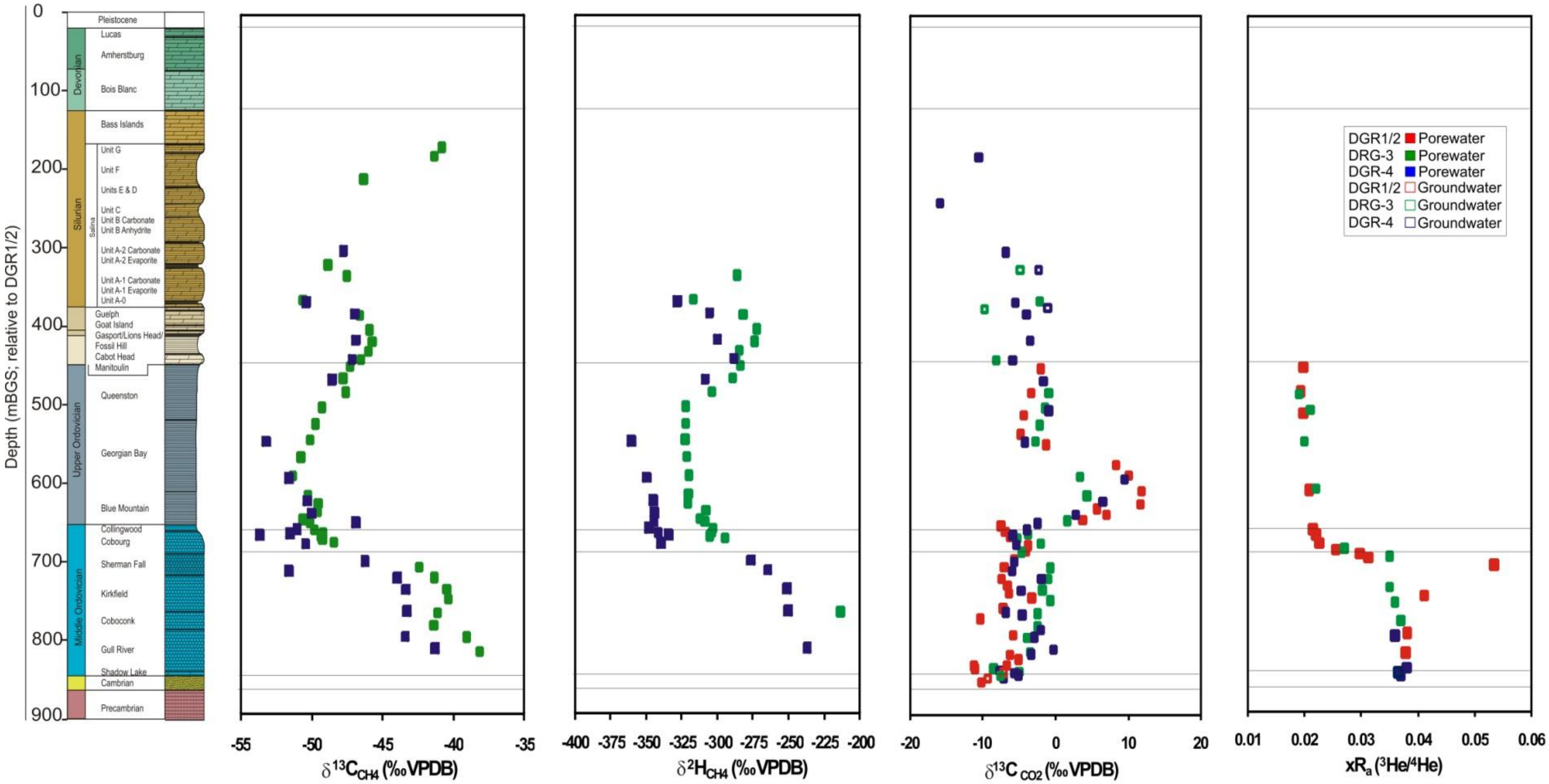
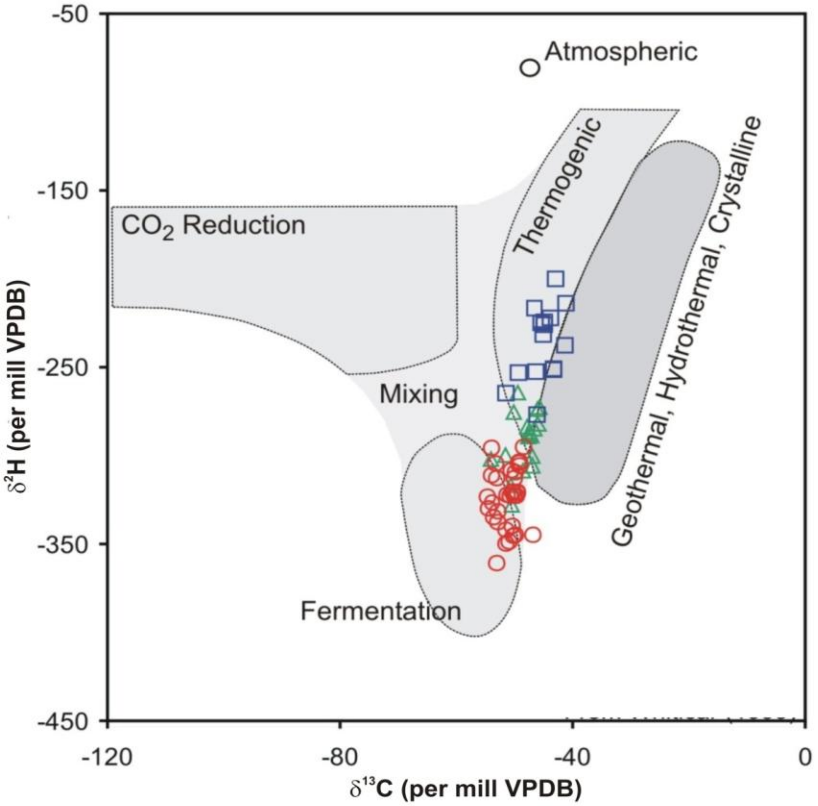


Figure 4. Depth profiles for δ^{13}C and δ^{2}H in CH_4, δ^{13}C in CO_2 and ^{3}He/^{4}He from DGR-2, DGR-3 and DGR-4.



Notes: Green triangles represent data from the Queenston Formation and above, red circles from the Cobourg, Blue Mountain and Georgian Bay formations, and the blue squares from below the Cobourg Formation.

Figure 5. Discrimination diagram indicating fields for CH_4 of biogenic (CO_2 reduction and fermentation) and thermogenic origin.

4.4. Natural Tracers

In order to evaluate the influence of solute transport processes over geologic time, the hydrogeochemical investigations included the determination of aqueous species (e.g., δ^{18}O, δ^2H, Cl, Br) that could be expected to behave as natural tracers and thereby provide a basis for quantifying rates and mechanisms of solute transport in a manner similar to international studies ([21],[22],[23]).

Trends in the measured porewater and groundwater data (Figure 6) should be considered in terms of deviations from some initial baseline condition. For these ionic and isotopic tracers, the initial condition would be their respective concentrations in the porewater of the Michigan Basin rocks around the time when they were first deposited (see Section 4.1). Taking into account the knowledge that normal marine conditions were thought to exist during the Cambrian and most of the Ordovician, followed by restricted marine (evaporative) conditions in the Silurian and Devonian, an initial Cl concentration near halite saturation (approximately 6000 to 7000 mmol/kgw) is proposed for the Silurian and Devonian fluids to represent evaporated seawater, and an initial Cl concentration of 600 mmol/kgw is suggested for the Ordovician and Cambrian formation fluids. On a plot of δ^2H versus δ^{18}O, it is commonly observed that the isotopic composition of ancient sedimentary basin water plots to the right of and below the global meteoric water line. This feature has been observed for water in the Michigan Basin, and a review of available data ([24],[25],[13] and [14]) suggests that an initial δ^{18}O value of approximately -2‰ should be representative.

The following features are observed in the tracer data.

- Devonian and Upper Silurian: tracer values are relatively low in the Devonian and Upper Silurian formations and show an overall increasing trend with depth toward the Guelph Formation.
- Lower Silurian and Upper Ordovician: from the Guelph Formation downward through the Upper Ordovician shales, the porewater has very high salinity and relatively enriched δ^{18}O and δ^{2}H values – all characteristic of evaporated seawater.
- Middle Ordovician: there is a downward trend toward depleted ^{18}O, reduced Cl and Br concentrations, and a very minor enrichment in ^{2}H.
- Cambrian: the trends in the Middle Ordovician are interrupted at the Cambrian where there is an abrupt increase in the tracer values.

Devonian and Upper Silurian: The δ^{18}O and δ^{2}H profiles in the Silurian and Devonian stratigraphic units provide evidence for infiltration of some combination of glacial melt water and warmer climate water during glacial and interglacial periods, presumably during the Pleistocene. The occurrence of ^{18}O- and ^{2}H-depleted water (-14.5‰ and -110‰, respectively) in a thin aquifer at 325.5-328.5 m depth in the Silurian Salina A1 carbonate unit (Figure 6) is indicative of the presence of glacial melt water and represents the maximum depth of glacial melt water infiltration observed at the Bruce nuclear site. These results are consistent with those for the northern margins of the Michigan Basin [26]. The cyclic nature of glacial-interglacial periods in the past 1 to 2 Ma [27] could have resulted in repeated infiltration events in the Devonian (and possibly Silurian) stratigraphy of southern Ontario. Subsequent diffusive equilibration between saline formation waters in the low-permeability sediments and relatively fresh glacial and meteoric water in the more permeable units would have occurred during interglacial periods.

Lower Silurian and Upper Ordovician: The tracer values in this interval (4880 to 7868 mmol Cl/kgw; 27 to 49 mmol Br/kgw; δ^{18}O from -3.9 to -1.9‰ and δ^{2}H from -55.9 to -40.9‰) are consistent with the initial condition inferred above for the Silurian and Devonian – evaporated seawater with very high salinity, and δ^{18}O and δ^{2}H values that plot to the right of the global meteoric water line. Porewater that originated as evaporated seawater is expected in the Silurian and Devonian rocks because of the restricted marine conditions that existed in the basin at that time. The present-day salinity in the Upper Ordovician shales (average Cl concentration of 5800 mmol/kgw) is much higher than the initial normal marine conditions of deposition. The deposition of Upper Silurian evaporites while the basin was restricted would have created a steep salinity gradient across the Upper Silurian-Middle Silurian boundary. This condition would have resulted in the downward diffusion of solutes from the Upper Silurian. Over millions of years, downward diffusive transport of solutes from the Silurian, could explain the present-day occurrence of high salinity porewater in the Upper Ordovician.

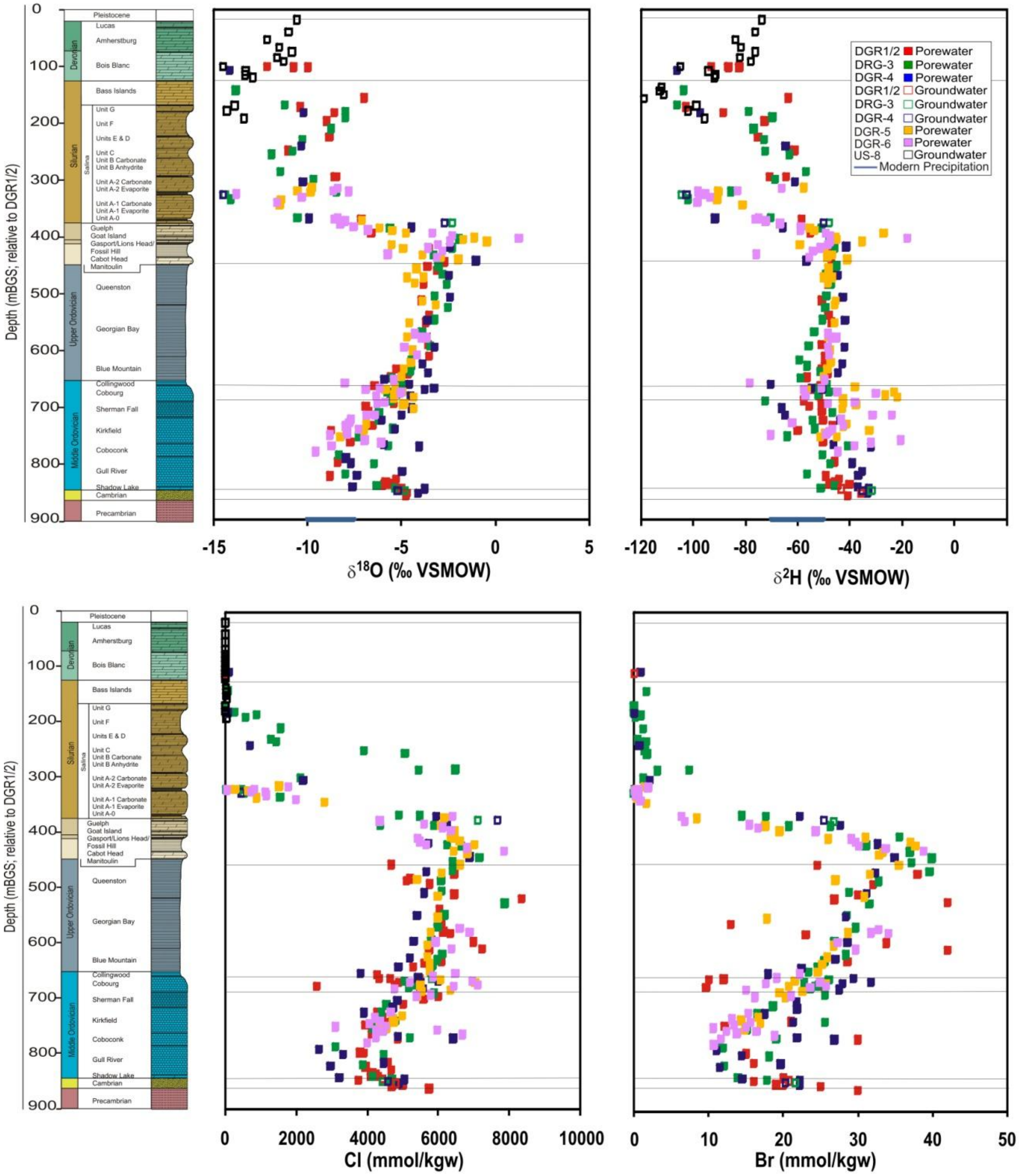


Figure 6. Vertical depth profiles for natural tracers.

Middle Ordovician: Similar to the data from the Upper Ordovician, present day tracer values in the Middle Ordovician are significantly evolved from that of the normal marine conditions present during deposition. The porewater Cl and Br concentrations, ranging respectively from 3100 to 7536 mmol Cl/kgw, and from 11.1 to 32.5 mmol Br/kgw, exceed normal marine concentrations (approximately 600 mmol Cl/kgw and 0.84 mmol Br/kgw), and the δ^{18}O values, ranging from -8.78 to -2.4‰, are depleted with respect to sedimentary basin brines. With increasing depth, the trend in the Middle Ordovician is toward a gradual decrease in Cl, Br and $\delta^{18}O$, but there is a slight increase in $\delta^{2}H$ observed within the Black River Group carbonates (Figure 6). The smooth nature of the trends suggests that diffusion is the dominant transport mechanism.

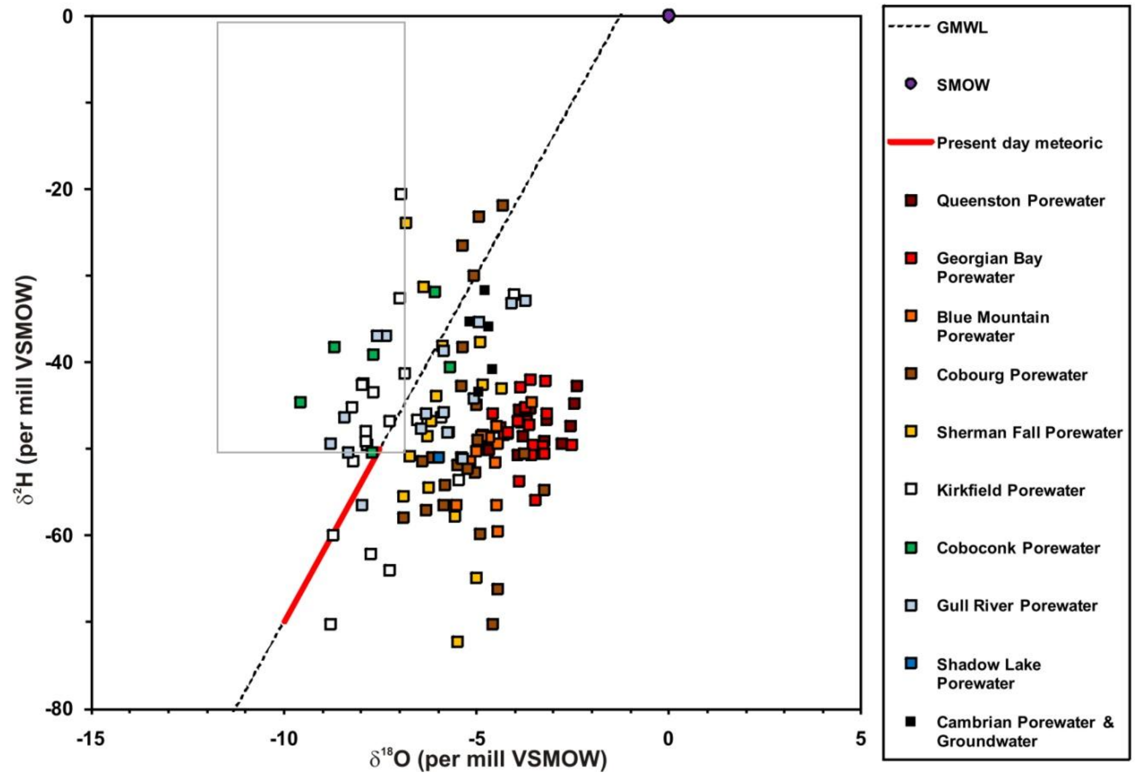
Consistent with the model for the Upper Ordovician, the high Cl and Br concentrations and the trend with depth toward lower concentrations could be explained by diffusion downward from the Upper Silurian. Similarly, the trends in the $\delta^{18}O$ and $\delta^{2}H$ tracer profiles could result from diffusive mixing with water at depth that is relatively depleted in ^{18}O and enriched in ^{2}H. This end member could not be the brine that is currently contained in the Cambrian sandstone because it has a higher salinity and more enriched isotopic composition than the porewater in the Middle Ordovician carbonates (Figure 6). However, as discussed below, the high permeability of the Cambrian sandstone could have allowed for exchange of groundwater in the aquifer in the geologic past. The question then arises as to when the high salinity groundwater moved into the aquifer, and if the precursor groundwater in the aquifer and the underlying shield could have provided a suitable end member to generate the observed trends.

The composition of brine in the Precambrian below the Michigan Basin is not known, but there has been considerable effort extended to develop an understanding of Precambrian shield groundwater elsewhere in Canada and around the world, which may be relevant ([28],[29],[30],[31],[32],[33],[34],[35] and [36]). It should be expected that the water present in the Michigan Basin during the Cambrian and Ordovician (normal marine seawater) would have invaded the underlying shield to some extent, so it is likely that the shield groundwater composition has been influenced by fluids in the basin.

Reasonable inferences can be made to constrain the isotopic composition of Precambrian groundwater or porewater below the Michigan Basin. Previous research on present-day shield brines provides knowledge of geochemical modifications to the stable isotope composition of groundwater that result from diagenetic reactions in shield settings ([28],[29],[30],[31],[32],[37],[33],[35] and [36]). Over very long periods of time, under conditions of low water to rock ratios, mineral hydration reactions in shield settings cause the isotopic composition of groundwater to evolve toward $\delta^{18}O$ depletion and $\delta^{2}H$ enrichment, leading to characteristic signatures that plot to the left of the GMWL (Figure 7). On this basis, various researchers ([28],[29],[31] and [32]) have proposed $\delta^{18}O$ values ranging from -13 to -7‰ for a hypothetical shield groundwater end member. The stable isotopic data from the Ordovician porewater display a trend toward $\delta^{18}O$ depletion and $\delta^{2}H$ enrichment along a trajectory toward the hypothetical shield brine end member (Figure 7), suggesting that diffusion between Middle Ordovician porewater and shield groundwater could explain the observed trends in the Middle Ordovician.

Cambrian: The tracer profiles in the Cambrian sandstone depart from the trends observed in the Middle Ordovician and display an abrupt shift back toward high salinity and more enriched $\delta^{18}O$ values (Figure 6). The similarity between the present-day brine in the Cambrian below the Bruce nuclear site and the Cambrian and deep Ordovician brines elsewhere in the Appalachian and Michigan basins ([38],[17],[24],[25]), respectively, suggests that the Cambrian fluid underlying the Bruce nuclear site originated at depth within the Michigan Basin.

Based on the conceptual model proposed above for the evolution of the Upper and Middle Ordovician porewaters, this feature in the Cambrian profiles is presumed to represent a recent exchange of groundwater in the permeable Cambrian formation, which disrupted the diffusion-controlled mixing relationship that had developed between basin and shield end members. Based on the evolutionary history of the Michigan Basin, the possible drivers for long-distance fluid migration in the recent geologic past are limited and the conceptual model asserts that fluid migration occurred in response to differential uplift of the basin due to repeated isostatic adjustments associated with glaciation and deglaciation.



Notes: The red to black transition in porewater symbols represents increasing depth. The grey box represents the proposed range of composition for a hypothetical shield end member.

Figure 7. Plot of δ^{18}O versus δ^2H for Ordovician and Cambrian porewater from DGR-2, DGR-3 and DGR-4.

5. NUMERICAL MODELLING

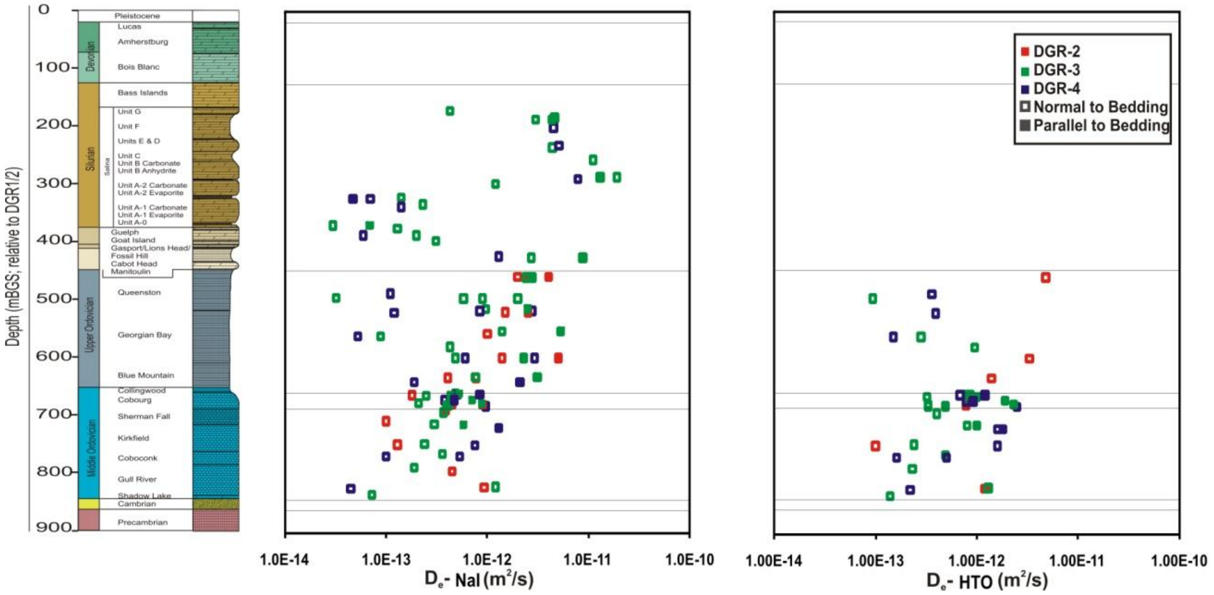
Numerical simulations of diffusive transport were conducted in 1-D, using MIN3P, with the intention of assessing the feasibility of the interpretation, or conceptual model, presented above, and if possible, to place time constraints on the development of the observed features in the natural tracer profiles in a diffusion-dominated system. MIN3P is a general purpose flow and reactive transport code for variably saturated media [39]. In the simulations discussed, reaction processes were not included and the model was used to simulate conservative solute transport by diffusion only. Justification of the modelling parameters used is provided in subsections 5.1 and 5.2, followed by a presentation of the modelling results.

5.1. Diffusion Coefficients

Effective diffusion coefficients (D_e) were measured at the University of New Brunswick using steady-state through-diffusion and X-ray radiography testing techniques. Testing was completed on preserved cores collected from Silurian and Ordovician formations in boreholes DGR-2, DGR-3 and DGR-4. Measurements were conducted in both normal and parallel to bedding orientations. The detailed methods are described in [40].

With the exception of just a few samples from the Upper Silurian, the D_e values measured from DGR drill cores are all less than 10^{-11} m^2/s (Figure 8). The majority of the data are in the range $10^{-13} < D_e < 10^{-11}$ m^2/s, with Lower Silurian and Upper Ordovician shale samples representing the higher end of this range because of their relatively high porosity (7 to 9%). The low porosity of the Middle Ordovician limestone (< 2%) results in low D_e values, which cluster in the range $10^{-13} < D_e < 10^{-12}$ m^2/s, with only a few samples displaying values slightly greater than 10^{-12} m^2/s.

There are systematic differences in D_e values as a function of the orientation of the measurements with respect to bedding direction. With only two exceptions in the Upper Silurian, the D_e values from paired samples are greatest for diffusion in the orientation parallel to bedding. The anisotropy ratio (D_e parallel/D_e normal) ranges from 1 to 4 for measurements made with the iodide tracer, and from 1 to 7 for measurements made with tritiated water, HTO [41].



Notes: The D_e values were determined by radiography using NaI tracer and/or through-diffusion using NaI or HTO tracer.

Figure 8. Plots of effective diffusion coefficients (D_e) versus depth.

The distribution of D_e values is shown in Figure 8. In Table 1, D_e is presented as a function of the free-water diffusion coefficient (D_0), the porosity (φ) and the tortuosity factor (τ_f):

(1)

Based on the isotopic evidence indicating limited diffusion of CH_4 and He across the Cobourg and Blue Mountain formations, simulations were conducted using diffusion coefficients for this interval that were reduced by an order of magnitude to simulate the presence of an in situ barrier (e.g., occlusion of porosity due to partial saturation and/or secondary mineral infilling) (see

Table 1). The diffusion parameters for the Precambrian listed in Table 1 are not constrained by site-specific measurements but are considered to be reasonable estimates [42].

5.2. Modelling Parameters and Boundary Conditions

Simulations of diffusive transport for the natural tracers in the Ordovician sediments were conducted in a single stage lasting 300 million years (Ma). Transport in all stratigraphic units was by diffusion only. Chloride diffusion was simulated to represent the evolution of salinity between the normal marine condition in the Cambrian and Ordovician, and the evaporated seawater brine in the Silurian and Devonian. Diffusion of ^{18}O was simulated to represent the evolution of the isotope profile in response to mineral hydration reactions occurring in the underlying shield.

The simulations are supported by stratigraphic and hydrostratigraphic information from DGR drilling (Figure 1), measured data for porewater $\delta^{18}O$ and Cl concentrations (Figure 6), an estimate of the Precambrian groundwater $\delta^{18}O$ composition (-10 ± 3‰ based on Precambrian shield literature; Figure 7), and the initial $\delta^{18}O$ composition of the Michigan Basin brines (-2‰) estimated from available data sources ([24],[25],[13],[14]). The laboratory-determined diffusion coefficients (Figure 8; Table 1) were used to assign the diffusion properties throughout the domain.

Table 1. Distribution of Diffusion Parameters Used in Diffusion Simulations

Depth (m)	Stratigraphy	Porosity	Tortuosity[1]	D_e (m^2/s)
0 to 120	Devonian	0.1	0.188	5.0×10^{-11}
120 to 180	Silurian: Bass Islands	0.017	0.023	1.0×10^{-12}
180 to 220	Silurian: Salina Units F and G	0.11	0.038	1.1×10^{-11}
220 to 300	Silurian: Salina Units B to E	0.18	0.038	1.8×10^{-11}
300 to 450	Silurian: Manitoulin to Salina Unit A	0.059	0.0038	6.0×10^{-13}
450 to 610	Upper Ordovician Shale – Saturated	0.084	0.016	3.6×10^{-12}
610 to 660	Upper Ordovician Shale	0.084 (0.01)[2]	0.016	4.3×10^{-13}
660 to 700	Middle Ordovician Limestone	0.013 (0.002)[2]	0.02	1.1×10^{-13}
700 to 840	Middle Ordovician Limestone	0.013	0.02	6.9×10^{-13}
840 to 860	Cambrian Sandstone	0.14	0.2	7.4×10^{-11}
860 to 1160	Shallow Precambrian	0.005[3]	0.2[3]	2.7×10^{-12}
1160 to 1610	Deep Precambrian	0.0025[3]	0.2[3]	1.3×10^{-12}

Notes: [1] Calculated from D_0 and laboratory measurements of D_e and porosity. [2] Reduction of porosity by a factor of approximately 10 to simulate the natural barrier to solute transport near the base of the Cobourg. [3] Assumed values.

An initial concentration of 7000 mmol Cl/kgw (evaporated seawater brine) was assigned throughout the Silurian and Devonian, and an initial concentration of 600 mmol/kgw for Cl was assigned in the Ordovician and below to represent normal marine seawater. For Cl simulations, free exit boundary conditions were applied at the top and bottom of the domain. A free exit boundary condition was applied at the top of the domain, and a constant concentration ($\delta^{18}O$ = -12‰) boundary condition was assigned at the bottom of the domain to represent mineral hydration reactions operating in the crystalline bedrock [31]. The bottom of the domain was established 750 m below the Precambrian-Paleozoic unconformity (1610 mBGS).

5.3. Modelling Results

The dashed yellow lines in Figures 9a and 9b represent results of the simulation conducted with D_e values as measured. The dashed blue lines represent results of simulations in which D_e has been reduced by a factor of ten in the Blue Mountain and Cobourg formations (see Table 1). Porewater measurements from boreholes DGR-2 through DGR-4 are also shown for comparison.

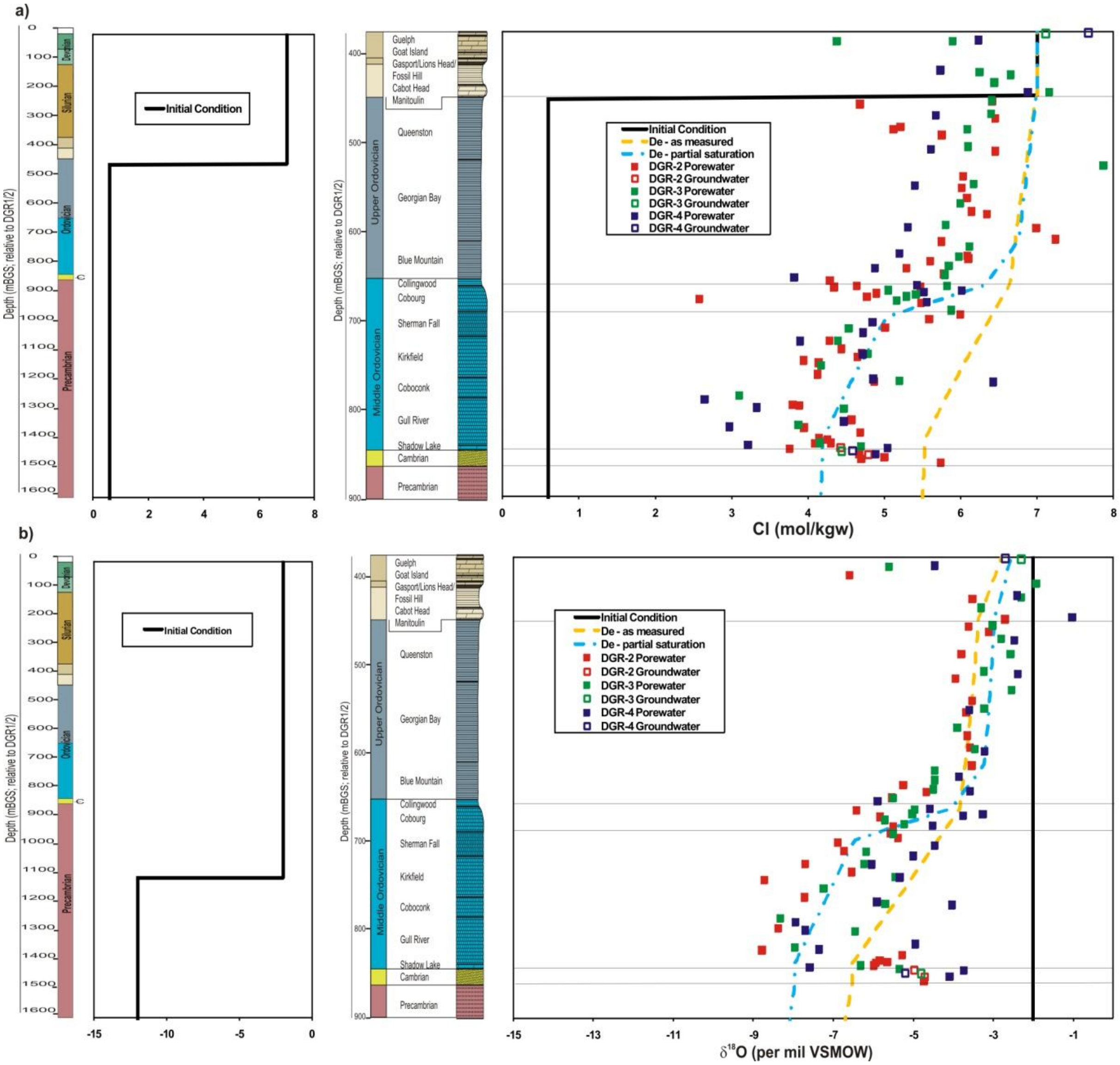


Figure 9. Results of the 1-D diffusion modelling.

The results for salinity and $\delta^{18}O$ diffusion simulations over a period of 300 Ma do not match well with the measured tracer profiles (Figure 9a,b) when D_e values are not adjusted (yellow lines) to represent a transport barrier near the Blue Mountain and Cobourg formations.

In the case where a transport barrier is included in the form of reduced D_e values (blue lines) in the Blue Mountain and Cobourg formations, the simulations provide a good fit to the measured porewater data (Figure 9a,b). The salinity (Cl) tracer profile develops as a result of salt diffusion downward from the Silurian and the $\delta^{18}O$ profile results from diffusive mixing with a shield brine at the base of the profile, suggesting that the conceptual model may be a reasonable explanation for the trends observed in the tracer profiles and supports the hypothesis that solute transport in the Ordovician sediments is diffusion-dominated.

The principal controls on the shape of the simulated profiles are the boundary conditions, the contrast in D_e between the Upper and Middle Ordovician, and the inclusion or exclusion of a transport barrier (lowering of the D_e values) near the base of the Cobourg Formation.

6. CONCLUSIONS

The data from the Bruce nuclear site indicate that the deep sedimentary brines underlying the Bruce nuclear site are of similar composition to those described more broadly from the Michigan Basin, suggesting that the brines are of seawater, or evaporated seawater, origin and have been modified over many millions of years by various mixing and water-rock interaction processes.

Concentrations of Cl and Br increase with depth from the surface toward the top of the Guelph Formation, and $\delta^{18}O$ and $\delta^{2}H$ range from relatively depleted values near surface to more enriched values toward the top of the Guelph Formation. Below the Guelph Formation, concentrated brines occur at all depths down to the top of the Precambrian and there is no evidence for glacial or meteoric water infiltration.

Radiogenic $^{87}Sr/^{86}Sr$ ratios in the Middle and Upper Ordovician porewater are interpreted to result from a combination of ^{87}Sr leaching from shield-derived detrital minerals, in situ ^{87}Rb decay, and diffusion of ^{87}Sr upward from an enriched end member in the shield. All of these mechanisms indicate long porewater residence time.

Separation between biogenic CH_4 in the Upper Ordovician shales and thermogenic CH_4 in the Middle Ordovician carbonates indicates that advective mixing has not occurred since the gases have been resident in the system and that diffusive transport is extremely slow. Similarly, separation between He with different $^{3}He/^{4}He$ ratios in the same interval suggests that diffusion is extremely slow and that there is a barrier to vertical solute migration near the base of the Cobourg Formation.

A conceptual model has been developed to explain the evolution of the natural tracer profiles and has been tested using 1-D numerical simulations. The simulation results provide a reasonable fit to the measured tracer data and suggest that the time frame required for the development of the natural tracer profiles within the Ordovician sediments is on the order of hundreds of millions of years. The simulation results, in addition to hydrogeochemical data presented in the paper ($^{87}Sr/^{86}Sr$; the isotopes of CH_4, CO_2 and helium; chloride, bromide, $\delta^{18}O$ and $\delta^{2}H$; D_e), provide multiple lines of evidence in support of the hypothesis that solute transport in the Ordovician sediments is dominated by diffusion.

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