

Technical Report

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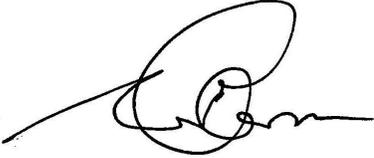
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DGR Site Characterization Document
Geofirma Engineering Project 08-200



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1 Introduction

Geofirma Engineering Ltd (formerly Intera Engineering Ltd.) has been contracted by the Nuclear Waste Management Organization (NWMO), on behalf of Ontario Power Generation, to implement the Geoscientific Site Characterization Plan (GSCP) for the Bruce nuclear site located near Tiverton, Ontario. The purpose of this site characterization work is to assess the suitability of the Bruce nuclear site to construct a Deep Geologic Repository (DGR) to store low-level and intermediate-level radioactive waste. The GSCP is described by Intera Engineering Ltd. (2006, 2008a).

As part of its NWMO contract, Geofirma Engineering Ltd. contracted the University of Ottawa for determination of radioisotope contents of groundwaters collected at the Bruce nuclear site and porewaters extracted from intact DGR borehole cores. This Technical Report presents the results and initial interpretation of radioisotope analyses of DGR groundwaters and porewaters completed as part of Phase 1 and 2 of the GSCP.

Work described in this Technical Report was completed in accordance with Test Plan TP-07-02 – Laboratory Testing of DGR-1 & DGR-2 Cores for Pore-Water Extraction and Analysis (Intera Engineering Ltd., 2007), TP-07-08 – Phase 1 Laboratory Testing of Opportunistic and Westbay Samples of Groundwater (Intera Engineering Ltd., 2008b), TP-08-05 – DGR-3 & DGR-4 Opportunistic Groundwater Sampling and Analysis (Intera Engineering Ltd., 2008c), TP-08-10 – Laboratory Testing of DGR-3 & DGR-4 Cores for Pore-Water Extraction and Analysis (Intera Engineering Ltd., 2008d), and TP-08-13 - Phase 2 Lab Testing of Opportunistic and Westbay Samples of Groundwater (Intera Engineering Ltd., 2008e),

Work described in this Technical Report was completed following the general requirements of the DGR Project Quality Plan (Intera Engineering Ltd., 2009).

2 Background

Among the presumed favourable characteristics of the DGR at the Bruce nuclear site, is the assumption that the deep groundwater system in the Ordovician shales and limestones is hypersaline and ancient. The very low measured permeability of the argillaceous sedimentary rocks (Geofirma Engineering Ltd., 2011) suggests diffusion is the controlling process in solute transport in these formations. An independent means of estimating the approximate age or residence time of the porewater or groundwater in the deep bedrock profile would corroborate and support the assumptions of an ancient groundwater system and of diffusion-controlled radionuclide migration. Given the potential geologic age of the groundwaters, radioisotope tracing provides an appropriate tool to estimate the age of the groundwater and porewater, and improve our understanding of solute transport at the Bruce nuclear site.

The radioisotopes considered for use are tritium, ^3H , with half-life $t_{1/2}$ of 12.32 years, carbon-14 or ^{14}C ($t_{1/2}=5730$ yr), chlorine-36 or ^{36}Cl ($t_{1/2}=301,000$ yr) and iodine-129 or ^{129}I ($t_{1/2}=1.6\times 10^7$ yr). These radioisotopes are chosen because of their long half lives, which may permit estimation of residence times of solutes in the groundwaters and porewaters of the DGR rocks at the Bruce nuclear site. Table 1 presents the mode of formation and applicable dating range for these radioisotopes. Table 2 presents a summary of the use of these radioisotopes to trace groundwater flow systems and porewaters.

Table 1 Radioisotopes Used in the DGR Program, with Half-life, Production and Useful Dating Range

<i>Element</i>	<i>Radioisotope</i>	<i>Half-life (yrs)</i>	<i>Production (in DGR context)</i>	<i>Dating Range (yrs)</i>
Hydrogen	Tritium, ^3H	12.32	Atmospheric ^{14}N (n,T) ^{12}C	50
Carbon	^{14}C	5730	Atmospheric ^{14}N (n,p) ^{14}C	30,000
Chlorine	^{36}Cl	301,000	Geogenic (U and Th) ^{35}Cl (n, γ) ^{36}Cl (Andrews et al., 1986)	1,000,000
Iodine	^{129}I	15,800,000	Geogenic (U) ^{238}U (spontaneous fission) ^{129}I (Fabryka-Martin, 1999)	80,000,000

The use of radioisotopes to date groundwaters relies on their time-dependant production and/or decay. As such, it is these solutes that are dated. In the case of tritium this allows dating of the water molecule itself. For ^{14}C , ^{36}Cl and ^{129}I , any age estimates relate to the solute. Reliable dating of the water then depends on understanding the origin and geochemical modification of the dissolved solute and its mobility in a closed system. For reasons pointed out by Phillips and Castro (2003), if diffusion of radioisotopes is a significant process affecting the migration of the isotopes over geologic time, as is clearly the case in the Ordovician rocks of the proposed DGR, then it is better to treat the radioisotopes as age tracers giving some indication of groundwater and porewater residence time but not of their age.

The use of these radioisotopes in geological systems generates questions of data reliability, in particular through contamination from on-site sources including drilling fluid contamination. These issues are addressed below, and specifically in Section 4.

In addition to the use of radioisotopes as dating and tracing tools, the accumulation of radiogenic helium (He) can be used as a constraint on age. The production of ^4He from alpha decay in the ^{238}U , ^{235}U and ^{232}Th decay series can be calculated from the concentrations of these elements in a rock horizon. In a closed system, the total concentration of ^4He then reflects the period of accumulation from the time of closure of the system to exchanges with external sources and sinks.

Table 2 Historical Use of Radioisotopes in Establishing Groundwater Ages

Radioisotope	Half Life (yrs)	Measured Phases	Example
³ H	12.4	GW	Lee et al. (1995) on shallow tritium in Devonian bedrock at Bruce nuclear Site
¹⁴ C	5730	GW	Plummer et al. (1990) on the use of ¹⁴ C to explain regional groundwater flow in the Madison aquifer up to 23 kyr [‡] b.p. [†]
³⁶ Cl	301,000	GW, PW	<p>Bentley et al. (1986) and Phillips et al. (1986) introduced ³⁶Cl into hydrogeology to extend the range of ¹⁴C ages in large regional groundwater flow systems in Alberta and Australia.</p> <p>AECL (Cornett et al., 1996) used ³⁶Cl to demonstrate that the residence time of dissolved Cl in the Cigar Lake (Saskatchewan) U deposit was of the order of 14 to 280 kyr.</p> <p>Hendry et al. (2000) employed ³⁶Cl to show that the residence time of dissolved Cl in a Cretaceous clay aquitard in Saskatchewan was between 0.75 and 1.9 Myr[‡] old.</p> <p>British Geological Survey geochemists (Metcalf et al., 2007) measured ³⁶Cl in order to demonstrate that the groundwater flow system beneath a proposed nuclear-waste site at Sellafield in England has been generally stable over the past 1.5 Myr despite the effects of glaciation and post-glacial rebound.</p>
¹²⁹ I	1.6 x 10 ⁷	GW, PW	<p>Moran et al. (1995) determined from ¹²⁹I analysis that formation waters in the US Gulf Coast oil-field brines were much older than the host rocks and were the result of “long-range vertical migration [of] the iodine, the brines and the associated hydrocarbons”.</p> <p>Moran (1996) later demonstrated that the iodine in the Anadarko basin of Oklahoma probably originated in organic-rich shale and was expelled from this shale during compaction between 2 and 90 Myr b.p.</p> <p>Fabryka-Martin (1999) summarized problems in ¹²⁹I dating of groundwaters and its successful application to the age of brine inclusions in Louisiana salt domes and to residence times in various groundwater flow systems.</p> <p>Bottomley et al. (2002) showed that residence times of deep marine brines sampled in the Con gold mine in Yellowknife, NWT were of the order of 80 Myr.</p> <p>Snyder et al. (2003) used ¹²⁹I and ³⁶Cl to conclude that a coalbed methane reservoir in the San Juan Basin of New Mexico contained formation waters with “minimum iodine ages” of 60 Myr.</p>
*GW: groundwater; PW: porewater; † b.p.: before present; ‡ kyr: 1,000 years, Myr: one million years			

3 Methodology

3.1 Methods of Sampling and Analysis

A limited number of groundwater samples were collected in the field under conditions designed to minimize atmospheric contamination from nearby nuclear reactors by ensuring that the pumped water was not exposed to air (Table 3). However, some drilling fluid may have added solute to the samples despite efforts to purge the permeable zones that were targeted for groundwater sampling.

Similarly, a somewhat larger number of porewater solutes were sampled by crush and leach extraction of solutes from cleaned core material (outer 1 cm removed) into distilled, de-ionized water. Samples were sent to both IsoTrace at the University of Toronto and Prime Lab at Purdue University for analysis by accelerator mass spectrometry (AMS). Table 3 shows the completed set of groundwater and porewater samples. The procedures used in the collection and preservation of the opportunistic groundwater samples are described in the following sections. The addition of drilling fluid to the intact core samples is considered to be negligible due to the low permeability of the formations sampled for radioisotopes. Comparison of porewater and groundwater isotope and solute concentrations from the same depths has shown no evidence of drill water influence (TR-07-21 Clark et al., 2010a).

Table 3 Summary of Radioisotope Analyses on DGR Groundwaters and Porewaters

<i>Formations</i>	<i>Sample</i>	<i>Radioisotopes</i>	<i>Number of Tests Per Radioisotope</i>
Devonian Dolostones	Groundwater from US-3 , US-7 & US-8	^3H , ^{14}C	7
Salina Upper A1Unit	Groundwater from DGR-3 & DGR-4	^3H , ^{14}C , ^{36}Cl and ^{129}I	2
Guelph Fm	Groundwater DGR-3 & DGR-4	^{36}Cl and ^{129}I	3
Upper Ordovician Shales	Porewater extraction from DGR-2 and DGR-4 cores	^{36}Cl and ^{129}I	3
Middle Ordovician Limestones	Porewater extraction from DGR-2 and DGR-4 cores	^{36}Cl and ^{129}I	6
Cambrian	Groundwater from DGR-2, DGR-3 & DGR-4	^{36}Cl and ^{129}I	4

Methods for He sampling and analysis are provided in TR-07-21 (Clark et al., 2010a) and TR-08-19 (Clark et al., 2010b), which describe new analytical methods in which 1/4" diameter microcores were taken from the centre of full cores and then encapsulated and evacuated. He and Ne that diffused out from the microcore were subsequently analyzed on a MAPL 215-50 noble gas mass spectrometer at the University of Ottawa.

3.1.1 Radiocarbon

The following procedures were used in the collection of opportunistic groundwater samples for radiocarbon. ^{14}C in dissolved inorganic carbon (DIC) was sampled by collection of one litre samples in glass bottles. Samples were collected with a minimum of contact with the open air, which was achieved by flushing the bottle headspace. An in-line filter was placed in the tubing connecting the pump to the surface and the tubing was placed at the bottom of a one-litre amber glass bottle with a cap that could be sealed. The bottle was allowed to overflow several times.

Two one-litre amber glass bottles were required for samples collected from the upper Devonian dolostones in US-3, US-7 and US-8 in order to obtain the necessary 10 mg DIC for analysis. Sufficient DIC was present in the groundwaters collected from the Bois Blanc and Bass Islands Formations (i.e., below 100 mBGS in US-8) and in the Salina Upper A1 Unit, that a one-litre sample was sufficient.

3.1.2 Procedure for ^{36}Cl and ^{129}I Measurements

^{36}Cl and ^{129}I in waters were collected in one-litre HDPE bottles. Minimum sample masses were 3 mg of each solute. No field filtering and no field preservation were required.

Eight rock core samples with high water content were chosen for ^{129}I measurements. The edges of cores were removed by chisel. To make powder, the core pieces were crushed using a mechanical crushing machine to a grain size of less than 2 mm. Each sample powder weighed about 1200 mg. The rock powder was put in a 2000 mL flask and then 500 mL deionised water (DIW) was added to each and left for 3 days. Approximately 250 mL of leachate was collected from each sample by decanting followed by centrifuging of the sediment. The leachate was then filtered using 0.45 μm filter discs and submitted for AMS analysis of both ^{36}Cl and ^{129}I .

Two facilities were used for analysis due to limited availability of accelerator time. Five leachate samples and three groundwater samples were analyzed at the IsoTrace Laboratory, University of Toronto, for ^{129}I , followed by three leachate samples and four groundwater samples at the PRIME Laboratory at Purdue University.

Difficulties with extraction of iodine from the high salinity Guelph Formation sample resulted in unacceptable analytical uncertainty, while the other three samples sent to the PRIME Laboratory had elevated analytical uncertainty. One blank sample of pure leach water (Ottawa River water) was submitted to PRIME Laboratory as a process blank. The resulting ^{129}I concentration (970,000 atoms ^{129}I per litre) was subtracted from the other samples. Measurements of stable ^{127}I were made by ICP-MS analysis in the Geochemistry Laboratory at the University of Ottawa.

3.2 Data Interpretation

^{14}C allows estimation of groundwater residence times up to 30 kyr, which is only applicable for examining solute migration in relatively short time periods. It may, however, provide estimates of the rate of circulation of the shallow (<200 m) groundwaters in the Devonian and Upper Silurian strata. Water-rock interaction causes the dilution of ^{14}C by 'dead carbon' dissolved from ^{14}C -free calcite, dolomite and ankerite minerals within the formation sampled. This phenomenon is corrected by consideration of the $\delta^{13}\text{C}$ of the dead carbonate minerals and of the DIC, as well as the sample geochemistry. Also, gypsum dissolution in the Devonian and Silurian rocks may cause de-dolomitization of the formations sampled such that dead carbon is added to the total DIC causing the uncorrected ^{14}C ages to appear older than is the case. Further complications arise from diffusion of ^{14}C into the low-permeability rocks adjacent to fractures and from methanogenesis.

Computational methods for correcting ^{14}C measurements in these circumstances are summarized in Clark and Fritz (1997). The low salinity groundwaters in the Devonian and Upper Silurian strata are suitable for radiocarbon dating given the evidence for local recharge (Lee et al., 1995). It is anticipated that the measured percent modern carbon (pMC) can be corrected by an exercise of geochemical and isotopic modelling.

The use of both ^{36}Cl and ^{129}I as groundwater and porewater tracing tools is based on interpretations of:

- (i) their decay from atmospherically-derived initial concentrations;
- (ii) their in-growth towards secular equilibrium activities during subsurface production (^{129}I from spontaneous fission of ^{238}U , and ^{36}Cl from the in-situ neutron activation of ^{35}Cl by a secondary

- neutron flux generated by alpha particles released in the ^{238}U , ^{235}U and ^{232}Th decay schemes), and
- (iii) advective or diffusive mixing (allochthonous sources) of ^{36}Cl and ^{129}I .

In the Bruce DGR geological setting, the residual activities for atmospherically-derived ^{36}Cl and ^{129}I in the Ordovician shales and limestones would be zero due to the great time since sedimentary rock formation relative to their half lives. However, matrix U would contribute to a build-up of these radionuclides to a level of secular equilibrium, where the rate of decay equals the rate of production, generally equal to about 5 to 7 half-lives of the nuclide. In the case of ^{129}I , this means a period of ~80 million years, while in the case of ^{36}Cl it suggests a period of 1.5 million years. This activity can be calculated for each sample interval in DGR-3 and DGR-4 based on measured U concentrations in the rock formations. Within the DGR section, two zones of high production potential for radio-halides are the Ordovician shales, in particular the Blue Mountain Formation shale, and the Precambrian, due to their enrichments in U.

Measured activities of ^{129}I and ^{36}Cl will provide one of three possible results for each horizon analysed. Any given measurement will be:

- (i) less than secular equilibrium activity;
- (ii) equal to secular equilibrium activity; or
- (iii) greater than secular equilibrium activity.

Interpretation of such results must then take into account the variations in these radio-halide activities and the potential for movement through the bedrock profile. In the case that activities of ^{129}I and/or ^{36}Cl are below secular equilibrium values in the section, the pore waters are presumed younger than the period of time required for secular equilibrium. This then constrains their age within the formation. Calculated pore water ages with associated uncertainties can then be calculated, provided initial specific activities of these nuclides can be estimated.

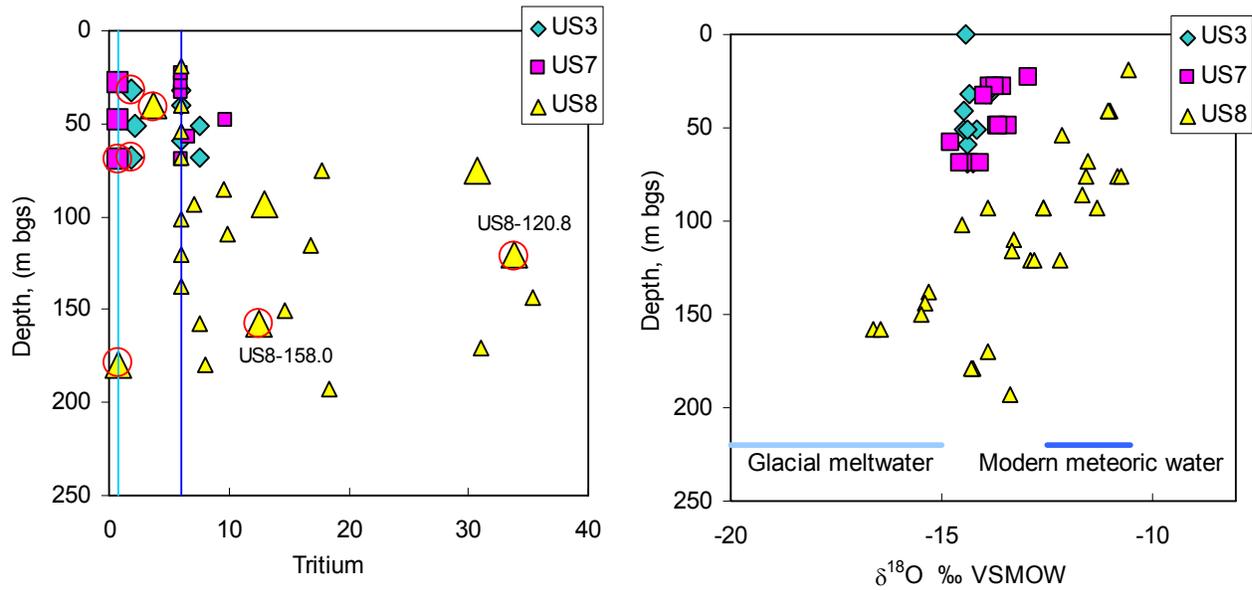
In the case that radioisotope concentrations are found to be equal to their secular equilibrium value (derived from the local U and Th concentrations), the estimate provides a greater-than age for the pore waters. However, solute migration from high production zones must be considered as well. For example, high values in the Precambrian (~3 ppm U) would contrast with lower anticipated levels in the overlying Gull River Formation (0.6 ppm U). In addition, the potential to find high concentrations of ^{36}Cl and ^{129}I in the over-pressured Cambrian allows testing whether upward migration from the Precambrian basement has occurred.

4 Results

4.1 Tritium and Carbon-14

The tritium contents of US series wells collected in the fall of 2008 are given in Figure 1 together with a chart of $\delta^{18}\text{O}$ with depth; note that all depths are relative to DGR-1. US-3 samples have low but measurable tritium suggesting that they incorporate a minor component of modern groundwater, or residual drilling fluid. With the exception of one measurement, all US-7 groundwaters are below the analytical detection limit. All US-3 and US-7 samples are from the upper 75 m zone, yet are greater than about 50 years. By contrast, many of the US-8 samples, which are mostly from depths from 75 to 200 m below surface, contain tritium. This anomalous distribution of tritium in these deeper groundwaters could be due to the presence of residual drilling fluid, or due to the presence of karst features at depth, allowing selective penetration of modern meteoric water to these depths. The distribution of ^{18}O in the US-8 series depth profile (Figure 1) suggests that samples down to a depth of 100 m are dominated by modern meteoric water which may be tritium-bearing. However, below this depth, glacial meltwater is present and suggests that deep circulation of modern meteoric waters here is unlikely. Therefore, the presence of residual drilling fluid may be responsible for the measured tritium in these US-8

samples.



Note: Tritium detection limits are shown by vertical grid lines (light blue for enriched - <0.8 TU; dark blue for direct counting - <6 TU). Samples measured for radiocarbon (below) are identified on the tritium-depth plot, showing that US8-120.8 and US8-158.0 have elevated tritium and therefore will have incorporated anthropogenic ¹⁴C.

Figure 1 Tritium in US Series Wells with Depth (left hand chart; larger symbols indicate enriched tritium measurements) and δ¹⁸O with Depth (right hand chart)

Measurements of ¹⁴C for select groundwaters from the US-8 series boreholes and from the Salina Upper A1 Unit in the DGR-3 and DGR-4 boreholes are given in Table 4, together with apparent or uncorrected ages.

The ¹⁴C method of dating groundwater has inherent uncertainties due to geochemical reactions following recharge that can alter the inorganic carbon content, and thus the ¹⁴C of groundwaters. To account for ¹⁴C dilution through carbonate dissolution in the subsurface, a correction was applied to the apparent ¹⁴C ages using the ¹³C mixing model (Pearson and Hanshaw, 1970; Clark and Fritz, 1997).

The ¹³C mixing model provides a measure of the ¹⁴C dilution caused by carbonate dissolution in the groundwater system, as any process that alters the DIC pool will affect both carbon-13 and carbon-14. As ¹³C is stable, it retains a measure of the associated ¹⁴C dilution. The δ¹³C mixing model is summarized by the following equations:

$$q = \frac{\delta^{13}C_{DIC} - \delta^{13}C_{carb}}{\delta^{13}C_{rech} - \delta^{13}C_{carb}} \quad (1)$$

Where

- δ¹³C_{DIC} = measured ¹³C in groundwater
- δ¹³C_{rech} = estimated ¹³C for DIC in the infiltrating groundwaters
- δ¹³C_{carb} = estimated ¹³C for the calcite being dissolved

Table 4 Percent Modern Carbon (pMC), Apparent (uncorrected) and Corrected Radiocarbon Ages of Groundwater Samples; Radiocarbon Ages Corrected Using the $\delta^{13}\text{C}$ Mixing Model

Sample ID	Tritium (TU)	% Modern Carbon (pMC)	Apparent ^{14}C Age (RCYBP)	$\delta^{13}\text{C}$ (‰ VPDB)	Corrected ^{14}C Age (RCYBP)
US3-32.30	1.9	20.96 ± 0.18	12,550 ± 70	-2.28	4,878
US8-40.60	3.7	48.50 ± 0.30	5,810 ± 50	-11.24	4,576
US3-68.50	1.8	22.16 ± 0.19	12,100 ± 70	-2.24	4,598
US7-68.90	<0.8	16.54 ± 0.16	14,450 ± 80	-2.89	7,501
US8-120.80	33.8	36.79 ± 0.27	8,030 ± 60	-7.66	4,801
US8-158.00	12.5	19.16 ± 0.17	13,270 ± 70	-4.63	7,933
US8-179.40	<6	22.25 ± 0.19	12,070 ± 70	-2.72	4,870
DGR-3 339.66 A1	9.4	67.03 ± 0.33	3,210 ± 40	-4.8	N/A (drill fluid contamination)
DGR-4 327.08 A1	3.0	18.49 ± 0.18	13560 ± 80	-2.5	5,442

The $\delta^{13}\text{C}_{\text{carb}}$ value is usually close to 0‰ (Clark & Fritz, 1997); however, for the purposes of our correction an enriched value of 5‰ was applied, given evidence that this reflects conditions during the Devonian and Silurian periods in North America (Saltzman, 2002). The $\delta^{13}\text{C}_{\text{rech}}$ term was determined to be -14.25 using a value of -23‰ for the $\delta^{13}\text{C}_{\text{soil}}$, and an estimated value of 8.75‰ for $\epsilon^{13}\text{C}_{\text{DIC-CO2(soil)}}$. The greatest corrections are then calculated for groundwaters with the most enriched $\delta^{13}\text{C}$ values. This increase in $\delta^{13}\text{C}$ (and therefore dilution in ^{14}C) is attributed to carbonate weathering. In Figure 2 this corresponds with the samples with highest Mg^{2+} concentrations, which is used here as an indication of dolomite weathering.

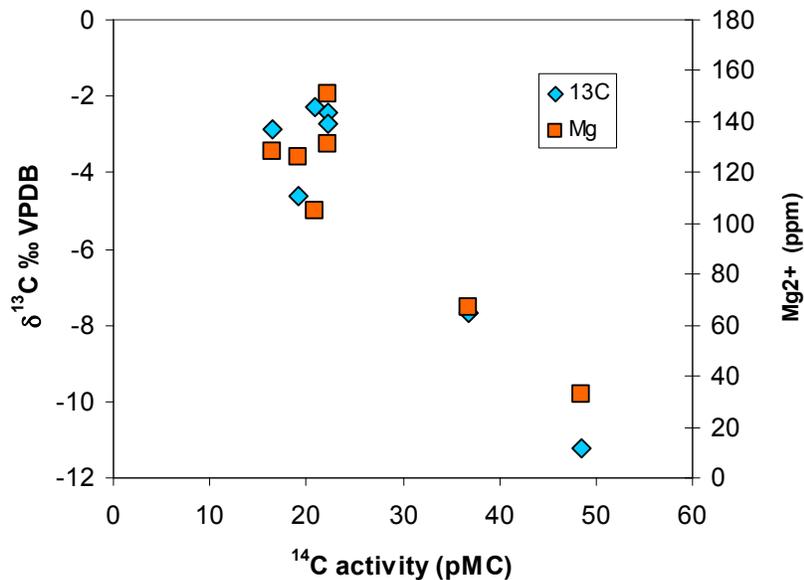
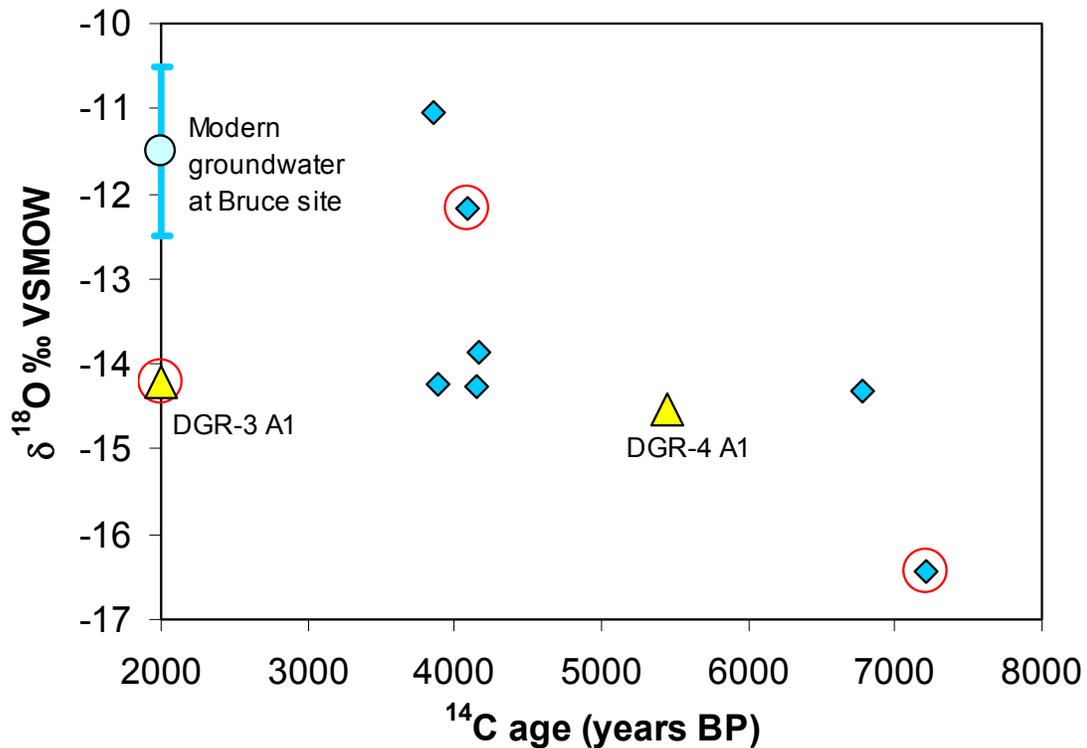


Figure 2 Cross Plot of Radiocarbon Activity with $\delta^{13}\text{C}$ and with Mg^{2+} as Indicators of ^{14}C Dilution by Dolomite Weathering; Greatest Age Corrections are Made for the Groundwaters with Most Enriched $\delta^{13}\text{C}$

Stable isotope data complement the radiocarbon data with regards to the estimation of the age and origin of the shallow groundwaters at the Bruce nuclear site (Figure 3). Up until about 12 thousand years before present this region was ice covered, and so the paleo-groundwaters of Table 4 generally post-date glaciation. The isotope data show both glacial and meteoric water signals, and suggest that there may be meteoric water mixing with waters that infiltrated during the last glaciation. This is consistent with the corrected radiocarbon ages and suggests a mean recharge period in the mid Holocene. It is also interesting to note that one of the “oldest” samples, US8-158.00, has one of the strongest glacial isotopic signatures, but also contains tritium contamination from drilling water. The similarly aged US7-68.90, also has an ^{18}O signature that lies between a glacial and meteoric origin.



Note: Red-circled points indicate high tritium in the water sample. Therefore these samples may have incorporated anthropogenic radiocarbon and ages will be too young.

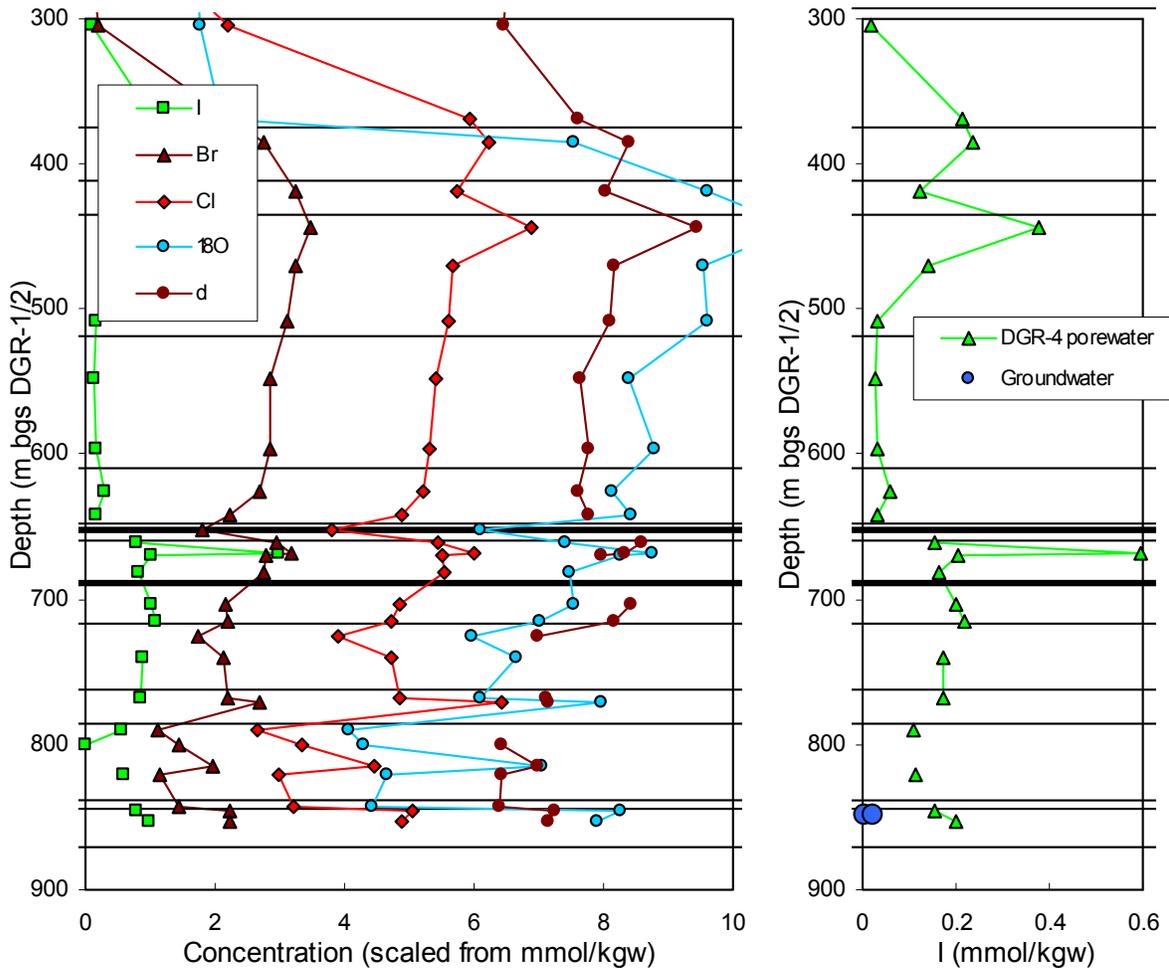
Figure 3 Correlation of $\delta^{18}\text{O}$ with Corrected Radiocarbon Ages of US-8 Groundwaters

Radiocarbon measurements for Salina Upper A1 Unit groundwaters from DGR-3 and DGR-4 are given in Table 4. The Upper A1 Unit groundwater was identified as having low salinity (29 to 33 g/L TDS) and depleted $\delta^{18}\text{O}$ and δD suggesting a mixture of glacial recharge mixed with minor subsurface brine. The DGR-3 Upper A1 Unit sample has 9.4 TU and a modern ^{14}C age due to contamination. DGR-4 Upper A1 Unit has only 3.0 TU and a mid Holocene ^{14}C age, which can be considered to be a minimum age.

4.2 ^{36}Cl

The comparatively short half-life of ^{36}Cl (301,000 years) provides a good constraint on the age and movement of fluids that complements the much longer-lived ^{129}I radionuclide. As both are halides, they share similar geochemical characteristics including the solubility and relatively conservative transport characteristics. This similar behaviour is illustrated by the strong correlations seen in Figure 4. The ingrowth of ^{36}Cl and ^{129}I are also

strongly dependent on the concentration of U in the rocks, although their modes of production differ (Table 1).



Note: Abscissa values are concentrations scaled for comparison and the values shown have no geochemical meaning. Profile with measured I concentrations is presented in right hand chart. The DGR is proposed for the Cobourg Formation, which is outlined in bold between 660 and 690 mBGS.

Figure 4 Profiles for Stable I, Br⁻, and Cl⁻ along with δ¹⁸O and Deuterium Excess for DGR-4 Porewaters

The evidence (below) demonstrates that the shale porewaters are much older than the approximate 1 million years required to reach secular equilibrium for ³⁶Cl in these rocks, and so these low measured ³⁶Cl contents can be reasonably assumed to have reached secular equilibrium. In the case of very old systems, which are anticipated to be at equilibrium for ³⁶Cl production, the measured ³⁶Cl concentration can be used to determine the U and Th concentrations as a basis for more precise calculation of secular equilibrium ¹²⁹I concentrations (Udo Fehn, University of Rochester, pers. comm.).

The in-situ ³⁶Cl, for secular equilibrium, is based on the following calculation from Andrews et al. (1986):

$$\frac{^{36}\text{Cl}}{\text{Cl}} \times 10^{-12} = J_n \times 4.55 \times 10^{-10} \quad (2)$$

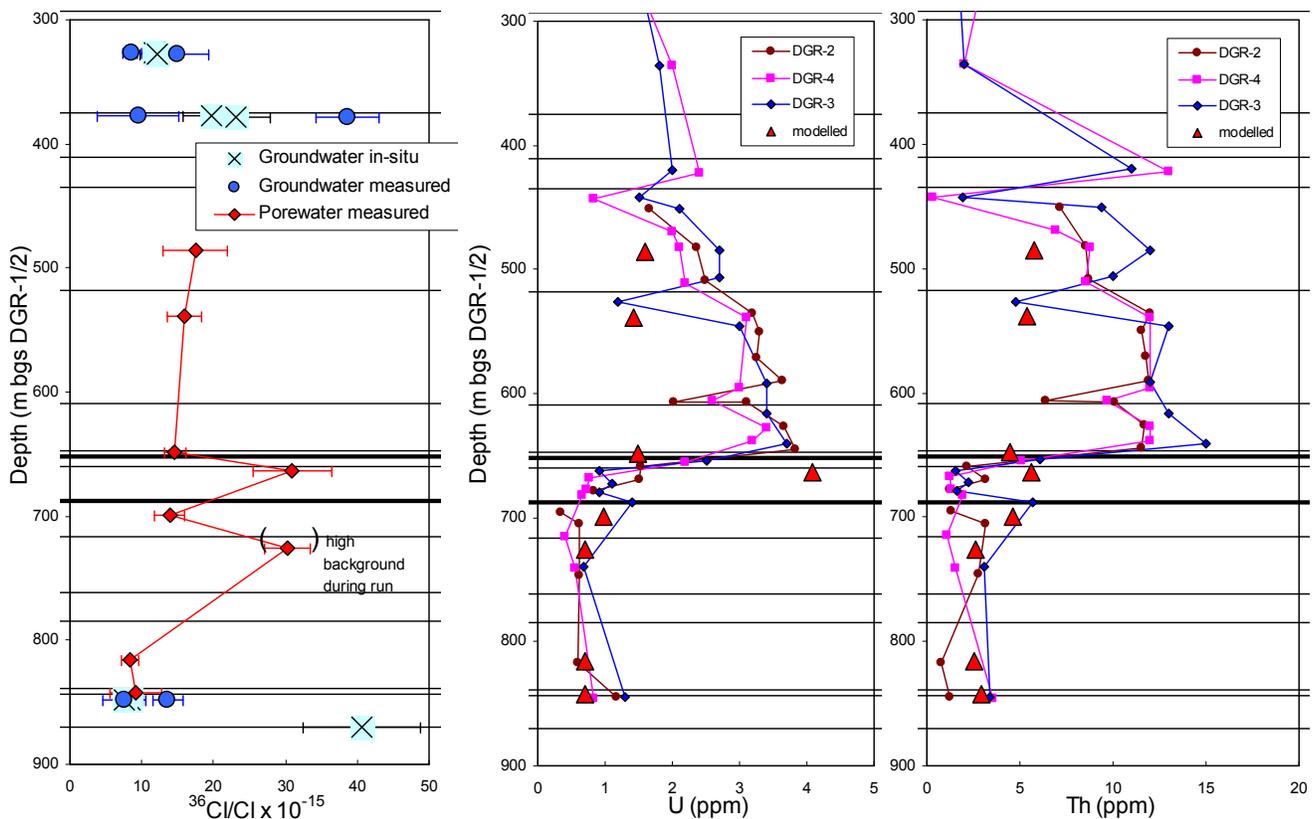
Where J_n = in-situ neutron flux, and

$$J_n = 10^{-12} (aU + bTh) \text{ in } \text{cm}^{-2} \text{s}^{-1} \quad (3)$$

(U and Th concentrations are in ppm).

The constants a and b are derived from the capacity of given light elements in the rock matrix (O, Na, Mg, Al, Si and K) to slow neutrons to the thermal energies required for absorption by the target ^{35}Cl , according to equations in Andrews et al. (1989) from irradiation by alpha particles from the U (a) and Th (b) decay series. Accordingly, these constants have been calculated for the light element composition of the DGR rock types ($a_{ls} = 1.07$, $b_{ls} = 0.43$, $a_{sh} = 0.92$, $b_{sh} = 0.41$, $a_{ss} = 0.89$, $b_{ss} = 0.37$) using lithochemical data from DGR-3 and DGR-4, and used to calculate the in-situ thermal neutron flux at each sample depth. These constants compare with values calculated by Andrews (1989) for the Stripa granite ($a = 1.06$ and $b = 0.48$ neutrons $\text{g}^{-1}\text{yr}^{-1}$).

In Figure 5, measured $^{36}\text{Cl}/\text{Cl}$ ratios are plotted with depth (left hand chart) for both porewater samples and groundwater samples. One measurement (DGR-4, 725.92 m depth) had a low ^{36}Cl mass and is considered to have been contaminated during analysis by a high ^{36}Cl background signal during the analytical procedure and so is considered anomalous. Calculations for the U and Th concentrations at this depth were taken from the next lower sample.



Note: Error bars are +/- 1 sigma for run. One porewater sample excluded from calculation of in-situ production due to high background (Marc Caffee, PRIME Lab, Purdue, pers. comm).

Figure 5 ^{36}Cl Concentrations in Porewaters from DGR-2 and DGR-4 and Groundwater Samples

The center and right hand panels of Figure 5 present measured U and Th concentration (for DGR-2, DGR-3 and DGR-4, corrected to DGR1/2 reference depths) together with the back-calculated U and Th concentrations modeled to provide values for secular equilibrium that are the same as the measured porewater ^{36}Cl contents. For the one anomalous ^{36}Cl analysis, the U content calculated for secular equilibrium is the adjacent (lower) sample. For the shale samples, the calculated U concentrations fall near or below the range of measured U concentrations. In the Ordovician limestones, they fall near or above the range of measured U concentrations.

For the groundwaters, secular equilibrium values were calculated using the same modeled U and Th concentrations as for similar units (Upper A1 Unit and Guelph Formation as limestone and Cambrian as shale). ^{36}Cl contents in the Upper A1 Unit are close to secular equilibrium values, suggesting that Cl in this formation has had a significant local residence time. The higher of the two $^{36}\text{Cl}/\text{Cl}$ ratio measured in the Guelph Formation groundwater is likely due to drill fluid contamination, which was estimated to be 24% drill fluid based on tritium results (TR-08-18). The lower ^{36}Cl value for groundwater in the Guelph Formation is close to that measured in the Upper A1 Unit, suggesting a common source of Cl in this section. The higher values for secular equilibrium may reflect a poor understanding of the actual U and Th content for the Guelph Formation. The range of values for the Cambrian groundwaters gives no clear indication that the chloride in this brine has achieved secular equilibrium or whether it has contributions from an underlying Precambrian brine.

4.3 ^{129}I

^{129}I measured in groundwaters can be a mixture of both cosmogenic production, through interaction of cosmic rays with ^{129}Xe in the atmosphere, and spontaneous fission of ^{238}U in the subsurface. The increase in nuclear activities since the 1950s represents a third source of anthropogenic ^{129}I in the environment. Cosmogenic ^{129}I in groundwaters is difficult to assess due to the overprint from nuclear era ^{129}I , but has been estimated to be in the range of 1000 to 20,000 atoms per kg water (Rao and Fehn, 1999). Pre-nuclear era seawater has a $^{129}\text{I}/\text{I}$ ratio of about $1.5 \text{ E}-12$ or about 11.4 million atoms per kg water. Geogenic production can be similar to, or higher than, this (Rao and Fehn, 1999; Renaud et al., 2005). In the case of halides in DGR porewaters and groundwaters, no residual ^{129}I from atmospheric or marine sources is anticipated, and so measured ^{129}I can be attributed to geogenic production.

The movement of ^{129}I in pore fluids and groundwaters is closely linked with halide movement, in general, and specifically with stable I (^{127}I). Therefore, the $^{129}\text{I}/\text{I}$ ratio is of interest for the interpretation of ^{129}I production and movement. In the DGR porewaters, stable I was measured by ICP-MS and the data are presented with the other stable halides in Figure 4. The profiles for the halides and isotopes are scaled for ease of comparison, showing their strong coherence. This suggests common processes controlling the distribution of halides in porewaters that align with the isotopes. The movement of ^{129}I in the profile should then follow that of stable I and therefore of all the halides.

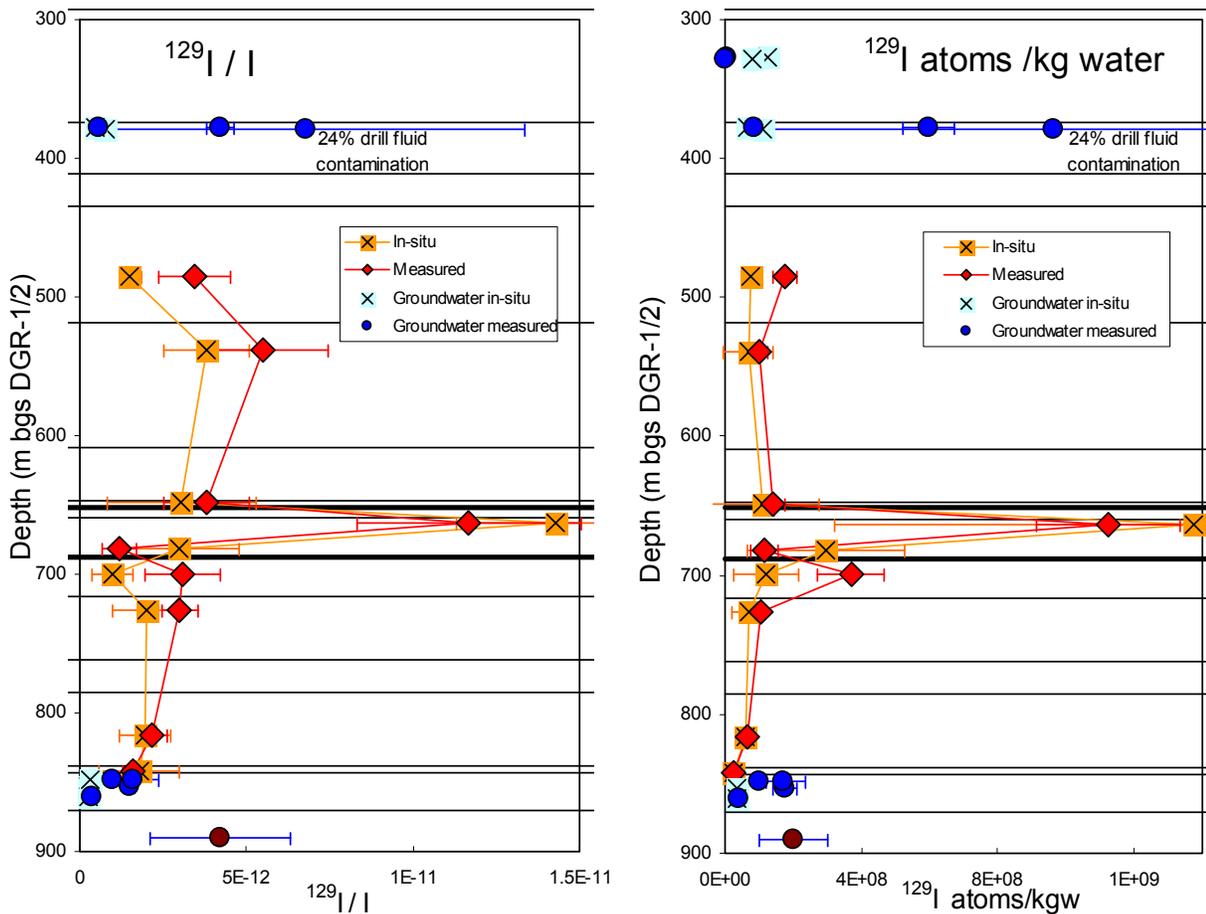
Measurements of ^{129}I concentrations are presented in Figure 6 for both porewaters and groundwaters from DGR-2 and DGR-4. Values are expressed both as atoms ^{129}I per litre of water (molal concentration) and as the atomic ratio of ^{129}I to total iodine (essentially stable ^{127}I). For groundwaters these were measured directly on submitted samples. For groundwaters from the Upper A1 Unit (~330 m depth) stable iodine measurements were below detection of 0.3 ppm, which was used to calculate a minimum $^{129}\text{I}/\text{I}$ ratio for comparison with the calculated secular equilibrium values. The reported values for I in the Cambrian (0.6 and 2.8 ppm; TR-08-18, Intera Engineering Ltd., 2010) are low. Their analysis was likely affected by the high salinity of the samples, which reduces the counts measured. For the porewaters, measurements were made by ICP-MS on leach solutions with the measured mass of ^{129}I normalized to the porewater content from that sample.

In addition to measured values are ^{129}I concentrations calculated for ingrowth to secular equilibrium (concentration of ^{129}I to the point where production is matched by radioactive decay in a closed system). Values for $^{129}\text{I}_{\text{se}}$ were determined using: 1) the U concentrations of the rock, calculated above from ^{36}Cl measurements

(modelled concentrations in Figure 5) based on the assumption of secular equilibrium for the measured ^{36}Cl ; 2) the decay constant for spontaneous fission of ^{238}U (8.50×10^{-17} , Decarvalho, 1982); and 3) the fractional fission yield of ^{129}I from ^{238}U spontaneous fission, using the approach of Fabryka-Martin et al. (1989) as shown below.

$$C_{129} = \frac{N_{238} \sigma_{SF} Y_{SF} \rho \varepsilon [1 - \exp(-\lambda_{129} t_f)]}{\theta \lambda_{129}} \quad (4)$$

where C_{129} is the ^{129}I concentration in the porewater or groundwater (atoms/L); N_{238} is the atomic concentration of ^{238}U (atoms/ g of rock); σ_{SF} is the decay constant for spontaneous fission of ^{238}U ($8.5 \times 10^{-17} \text{ yr}^{-1}$); Y_{SF} is the fission yield at mass 129 from spontaneous fission of ^{238}U (0.0003); ρ is the dry bulk density of the rock (2.64 g/mL); ε is the ratio of the rate of escape to the water to the rate of production in the solids and is also called the emanation efficiency (dimensionless); λ_{129} is the decay constant for ^{129}I ($4.4 \times 10^{-8} \text{ yr}^{-1}$); t_f is the residence time of water; and θ is the measured water content. Concentrations of U, Th and Li in the DGR rocks are shown in Figure 7. The U concentrations calculated in the previous section were used to carry out the ^{129}I secular equilibrium concentrations (example calculation in Appendix B).



Note: Left chart: ^{129}I normalized to stable iodine concentration. Right chart: ^{129}I as atoms per kg porewater or groundwater. Uncertainty in stable I concentrations for the Guelph and A1 groundwaters precludes determination of their $^{129}\text{I}/\text{I}$ ratio. Brown circle at 870 m represents Precambrian brine measured at Sudbury mines (Bottomley et al., 2002). Error bars on secular equilibrium values based on uncertainties in uranium concentrations through section.

Figure 6 ^{129}I Measured in DGR-2 and DGR-4 Porewaters and Groundwaters Together with Secular Equilibrium ^{129}I Calculated from U Concentration and Assuming Secular Equilibrium

Note, that the residence time, t_r , requires an independent measurement of residence time for Equation (4) to be employable; in the present study, this independent measurement is provided by He age dating. If an independent measurement of t_r is not available, C_{129} cannot be estimated independently, and therefore ^{129}I cannot be used for age dating, and instead can only be used as an “age tracer”.

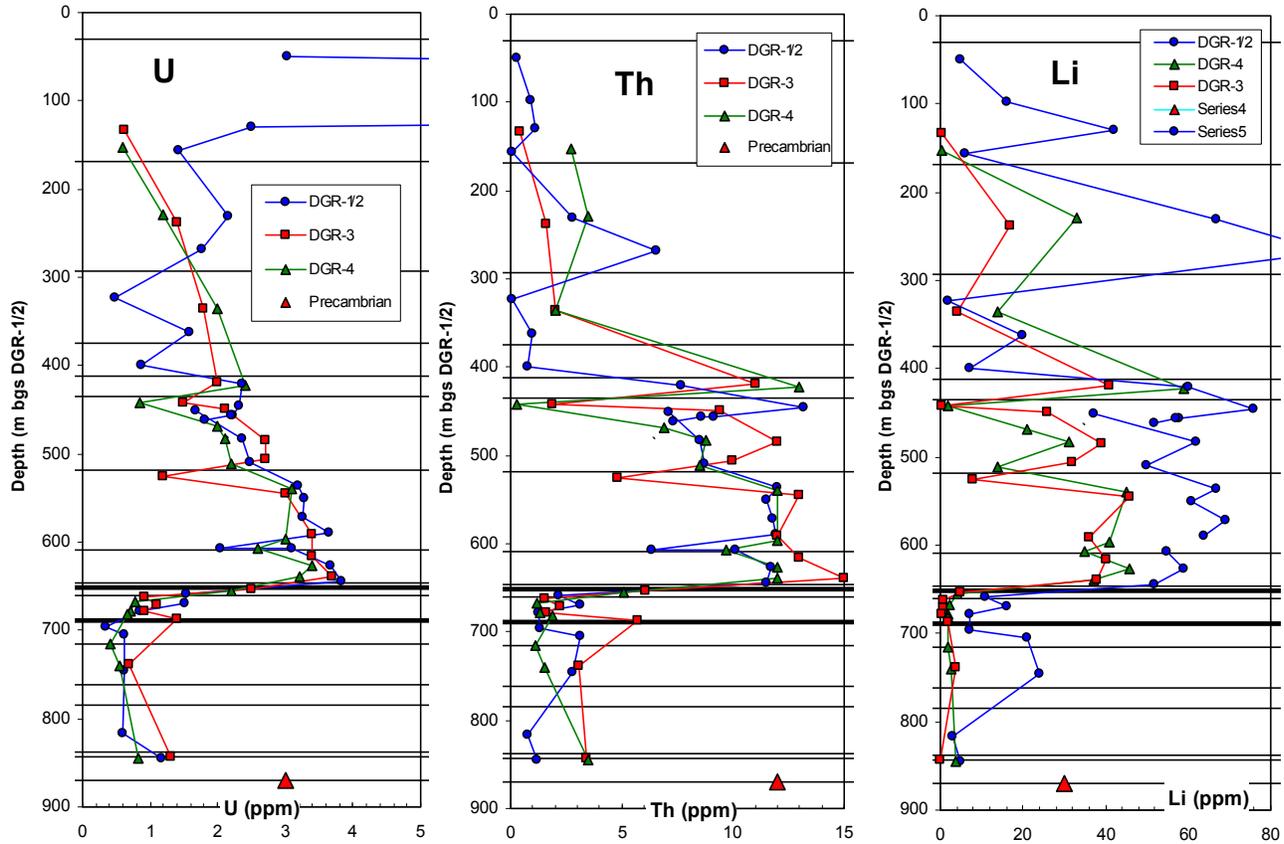


Figure 7 Uranium, Thorium and Lithium Concentrations in Cores from DGR-2, DGR-3 and DGR-4; Concentrations in the Precambrian are Approximations for Shield Terrain (Ma et al., 2009 and references therein; Faure, 1998)

The concentration of ^{129}I in porewaters or groundwaters is a function of the uranium content as well as the release factor from the mineral lattices to the open pore water from which it is leached. The release factor is a dimensionless value between 0 and 1 and represents for the rate of loss of ^{129}I by decay during the lag between production and transport to the connected fluid phase.

$$\varepsilon = \frac{\lambda_d N_{129} (C_U)}{N_{238} \lambda_{sf} Y_{sf}} \quad (5)$$

Values of 1 for ε are used in Equation (4) above, representing the greatest loss from the system. Values near 0 would indicate ^{129}I is fully retained in the rock. Given the intimate association of the porewaters and rock matrix, we have assumed a release factor of 1 (complete release). This means that the movement of ^{129}I from the production sites to the open porosity is rapid, on the time scale of ingrowth (80 million years). In fractured rock

settings, such as granite, this value is less than 1 reflecting the longer diffusion pathway from the mineral lattices to a fracture pore fluid (Bottomley et al., 2002). A release factor of 1 is also the most conservative, or base case, as it results in maximum calculated values for ^{129}I in the porewaters. This can be expressed by Equation (5) where λ_d is the rate of loss of ^{129}I from the rock (yr^{-1})

Ratio calculations ($^{129}\text{I}/\text{I}$) for the Upper A1 Unit groundwaters were not possible because the measured concentration of stable I was below the analytical detection limit. Both samples from the Upper A1 Unit had ^{129}I concentrations below the values calculated for secular equilibrium. This is consistent with the dilution of groundwater in this aquifer by the incursion of glacial meltwater, and is consistent with radiocarbon dating which shows these groundwaters to be late Pleistocene to Holocene in age. Guelph Formation groundwater analyses were complicated by the high salinity in these samples, and therefore the measured ^{129}I concentrations and ratios are accompanied by large errors. The sample with the highest value (964 E06 atoms L^{-1}) is contaminated with 24% drilling fluid (133 TU, TR-08-18) and so can be discounted. The remaining two Guelph Formation groundwater samples had contrasting ^{129}I concentrations (82.9 E06 atoms L^{-1} at Purdue; and 598 E06 atoms L^{-1} at IsoTrace) which are similar to or greater than the secular equilibrium concentration. There are no adjacent formations with sufficiently high U to account for the higher ^{129}I measurement.

The Cambrian groundwaters have 100 to 200 million atoms $^{129}\text{I} \text{ kgw}^{-1}$. Both are close to or above the calculated ^{129}I concentrations for secular equilibrium with the formational U content. These compare with an estimated value for Precambrian brine of close to 200 million atoms $^{129}\text{I} \text{ kgw}^{-1}$ based on measurements from the Victor mine in Sudbury (Bottomley et al., 2002). This enrichment in ^{129}I in the Cambrian brine toward values in the Precambrian is also seen in the $^{129}\text{I}/\text{I}$ values, which exceed the values calculated for secular equilibrium. This suggests that the Shield brine could be a potential source of ^{129}I in the Cambrian.

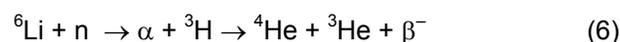
The measured porewater ^{129}I concentrations and $^{129}\text{I}/\text{I}$ ratios in the Upper Ordovician shales (Figure 6) are very close to their respective values calculated for secular equilibrium. The four Trenton Group samples, including two Cobourg limestone samples, also have measured values for both the $^{129}\text{I}/\text{I}$ ratio and concentration of ^{129}I per kg porewater that are very close to the calculated values for secular equilibrium.

The concentration of ^{129}I for the upper Cobourg at 663.34 mBGS is the most enriched sample in the profile, and coincides with a high value for ^{36}Cl in this sample. Diffusion from the overlying shales is unlikely as the $^{129}\text{I}/\text{I}$ ratio should be similar to that found in the shales. An allochthonous (external) source for this excess ^{129}I is unlikely, as no other enriched sources are identified in the section. A local, high neutron activity environment may be responsible have enhanced production of these radioisotopes in this zone, although this would require further U analyses to demonstrate.

The two deeper porewater ^{129}I values for the Gull River and upper Shadow Lake formation show $^{129}\text{I}/\text{I}$ ratios and concentrations that are lower than most of those in the Trenton group limestones. However, with lower U concentrations at these depths, the measured values are the same as values calculated for secular equilibrium. The ^{129}I contents of these two deepest porewater samples are unlike those measured in the Cambrian groundwater, as both have lower ^{129}I concentrations (atoms/kgw) and higher $^{129}\text{I}/\text{I}$ ratios.

4.4 He results

The production of ^3He and ^4He can be used to examine solute residence time. Geogenic He is produced by ingrowth of radiogenic ^4He from the decay of U and Th, while the ingrowth of ^3He arises from neutron-induced fission of ^6Li .

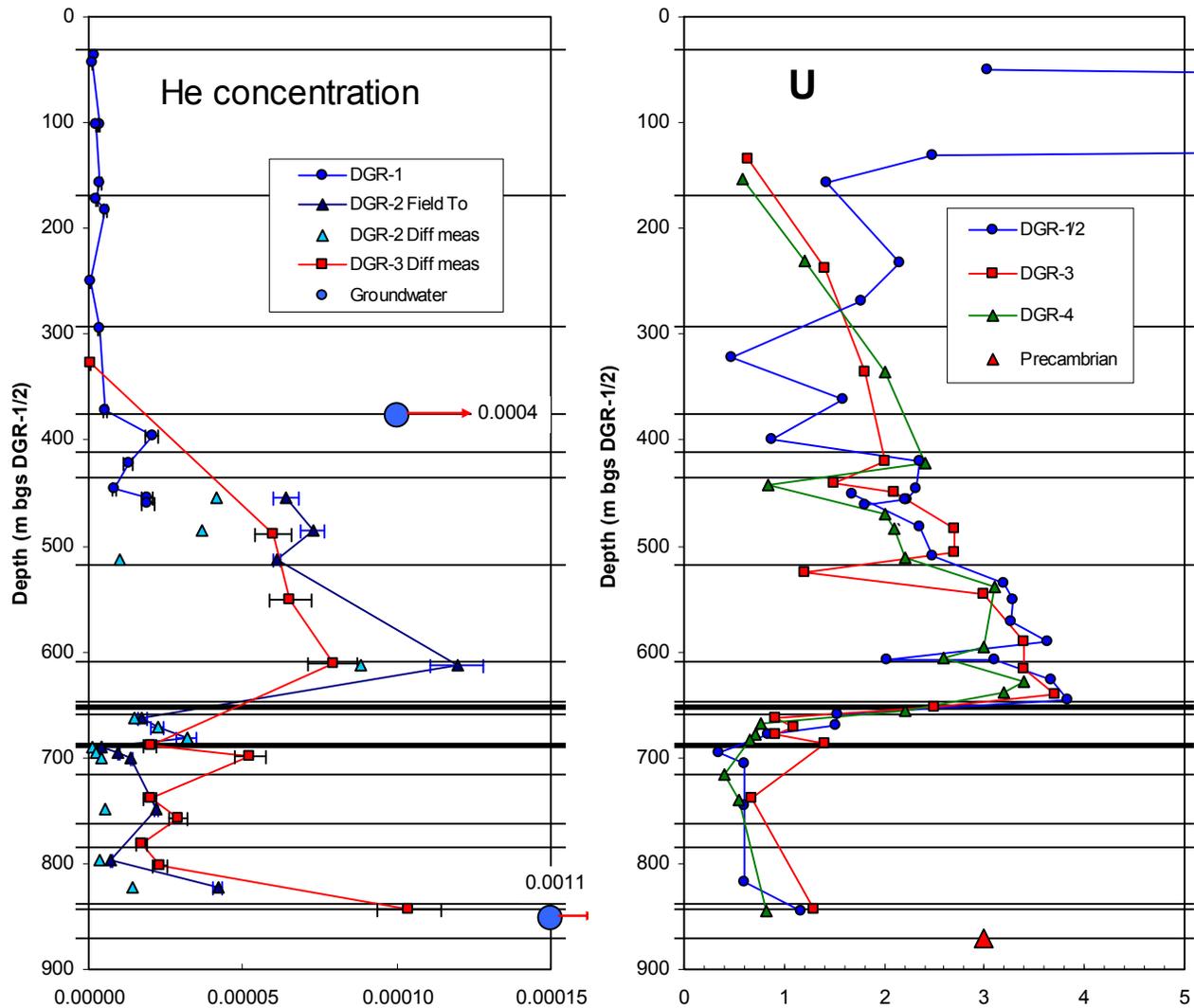


Considering the high diffusivity of He, the concentrations and ratios of these two He isotopes can be used to constrain age in very old groundwater and porewater systems. Concentrations of Li, U and Th in the DGR rocks are shown in Figure 7. Measurements of He concentrations in the DGR-2 and DGR-3 cores were undertaken by micro-drilling and encapsulation in a sealed, evacuated tube, followed by outgassing and measurement by magnetic-sector mass spectrometry on a MAPL 215-50 noble gas mass spectrometer (TR-08-19, Clark et al., 2010b). While the $^3\text{He}/^4\text{He}$ ratios were reported, concentration data normalized to porewater content were not reported because it was considered to be less reliable due to potential problems of partial gas saturation. Correction for He loss prior to analysis was also required, given the high diffusivity of the gas.

Here, concentration data collected from analysis of the DGR-2 and DGR-3 cores have been corrected for gas loss prior to analysis, and are normalized to concentration in the rock (cc He STP/g). Accordingly, they do not necessarily reflect the porewater concentration profile that would drive diffusion through connected porosity. However, the measured profiles present total He accumulation in pores in these rocks that can be used to constrain age, depending on the closure of the system.

Figure 8 presents the total concentration of out-gassed He from the samples analyzed. Note that additional He that can be derived from heating the rock samples during analysis are not added to the yields in Figure 8, because these may include He accumulated since mineral formation in the Precambrian. Accordingly, the accumulations presented here are minimum amounts for the radiogenic production. DGR-1 samples were encapsulated in the field in an initial program of method development. The DGR-2 samples were encapsulated in the lab, following a minimal core storage period after drilling. In these samples, the measured He concentration of diffusive (DGR-2 Diff meas.) has been corrected to time-zero (Field T_0) or the time of drilling the core. This correction was based on an out-gassing curve generated from the three samples in the Queenston Formation with storage times of 3.1 days, 6.5 days and 49.6 days. The amount of correction, shown in Figure 8, is not significant for most samples. The DGR-3 samples have not been so measured, because they were encapsulated in the field immediately following drilling.

The He concentration profiles for DGR-2 and DGR-3 are similar and closely resemble the U concentration profile, showing higher concentrations in the Upper Ordovician shales and lower concentrations in the Middle Ordovician limestones. This close affiliation of He concentration with the primary production term (^{238}U is the principal source of alpha decay and ^4He production, whereas ^{232}Th accounts for about one quarter of radiogenic He) suggests that the system has remained relatively closed. If so, then the accumulated He can be used to constrain age. Note that unlike ^{36}Cl and ^{129}I which are radioactive isotopes produced radiogenically, He is not radioactive and so no secular equilibrium between radiogenic production and decay is established. He will continue to accumulate unless loss by diffusion or advection under open system conditions occurs.



Note: Value for Precambrian rocks is based on estimates from Faure (1998) and Ma et al. (2009).

Figure 8 Left chart: Helium Concentrations per Gram Rock from DGR-2 and DGR-3 and for Groundwaters Samples (normalized to rock concentration with density and porosity); Right chart: Uranium Concentrations in DGR-2, DGR-3 and DGR-4 Rocks

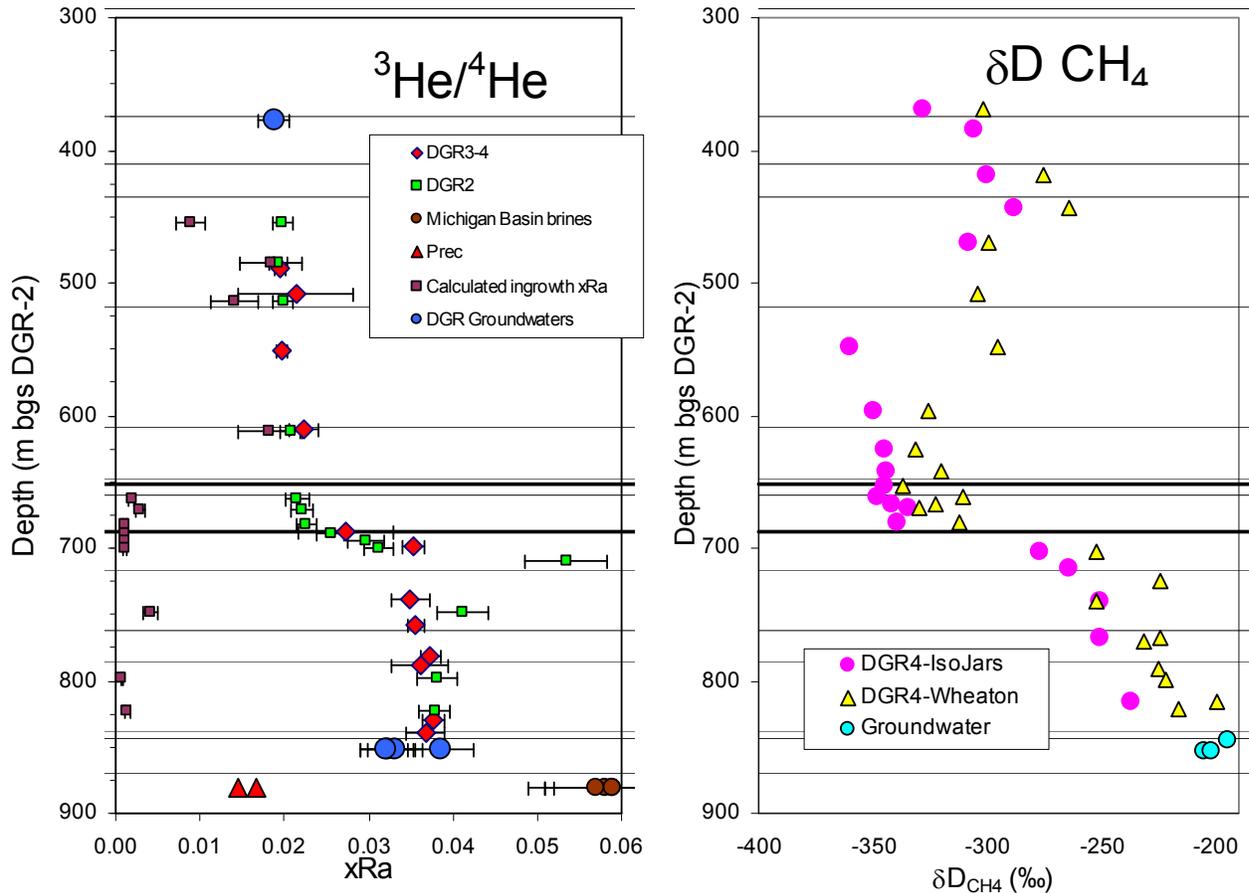
The degree of closure of the systems to He loss can be examined by comparing the measured $^3\text{He}/^4\text{He}$ ratio with the ratios calculated from the different modes of formation of these two isotopes (^3He by ^6Li fission and ^4He by alpha decay in the ^{238}U and ^{232}Th series). This is shown in Figure 9 where the measured ratios (xRa = $^3\text{He}/^4\text{He}$ normalized to the ratio in air) are shown for samples from DGR-2 and DGR-3 together with the calculated ratios based on the respective production rates of ^3He and ^4He . Calculations for the ^3He and ^4He production rates, summarized by Ballentine and Burnard (2002), are based on the production of thermal neutrons generated by alpha-n reactions together with modulation by interaction with Mg, Na, Al, Si and C in the rock matrix.

$${}^3\text{He atoms g}^{-1}\text{yr}^{-1} = 0.8 \times \left\{ \frac{0.01[\text{U}](13.8[\text{Na}] + 5.4[\text{Mg}] + 5[\text{Al}] + 1.31[\text{Si}] + 2[\text{C}]) + 0.01[\text{Th}](6[\text{Na}] + 2.45[\text{Mg}] + 2.55[\text{Al}] + 0.56[\text{Si}] + 0.83[\text{C}])}{0.01[\text{Th}](6[\text{Na}] + 2.45[\text{Mg}] + 2.55[\text{Al}] + 0.56[\text{Si}] + 0.83[\text{C}])} \right\} \times \frac{2.05 \times 10^{-4}}{9.79 \times 10^{-8}}$$

(7)

and

$${}^4\text{He atoms g}^{-1}\text{yr}^{-1} = (3.115 \times 10^6 + 1.272 \times 10^3)[\text{U}] + 7.710 \times 10^3[\text{Th}] \quad (8)$$



Note; Values for the Precambrian (Kotzer et al., 1998) and the Michigan Basin (Ma et al., 2009) shown for reference.

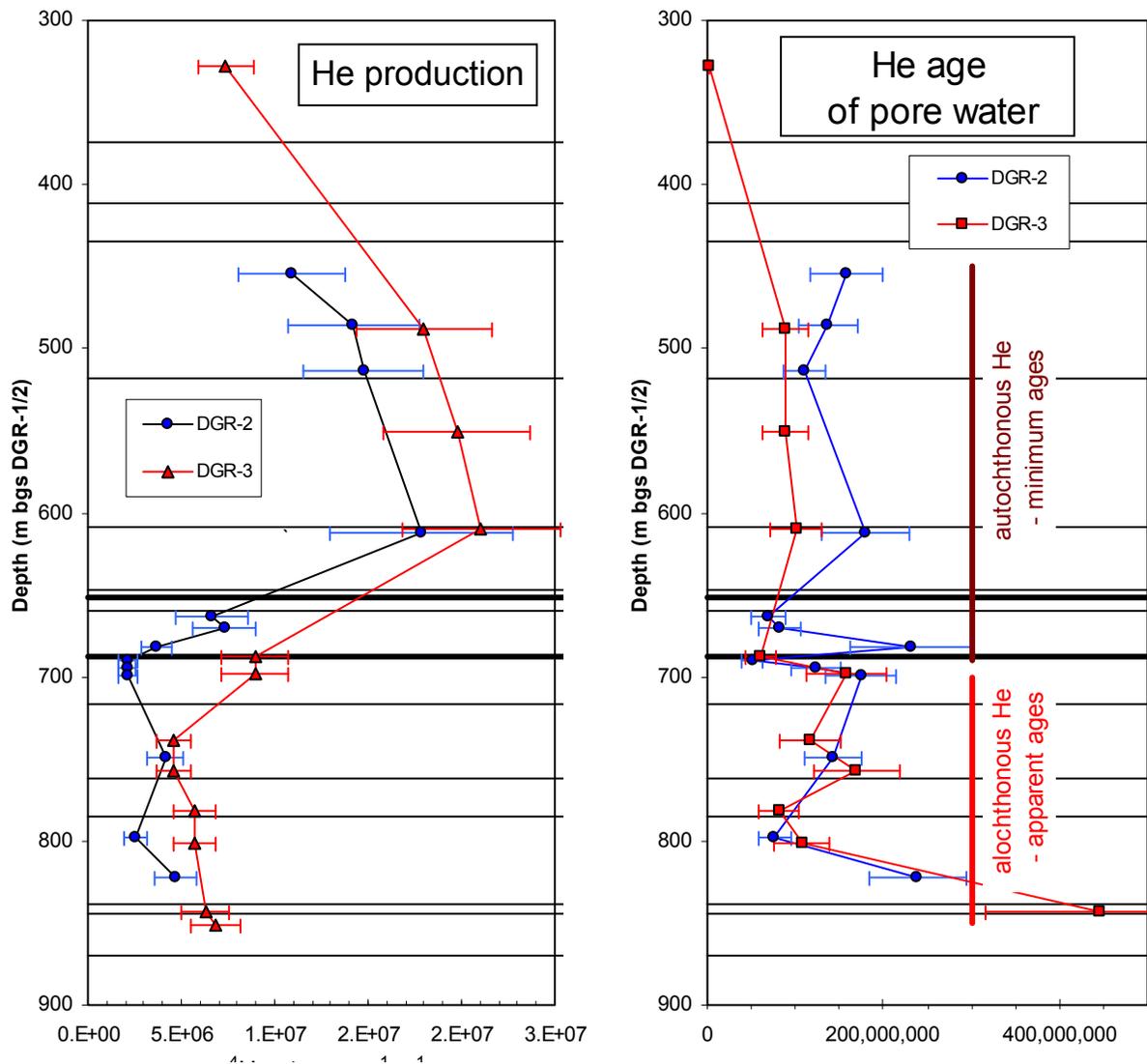
Figure 9 Left chart: Helium Isotope Ratios Measured in DGR-2 and DGR-3 Cores (TR-08-19) Together with Calculated Isotope Ratios (Based on Decay of U and Th for ${}^4\text{He}$) and Fission of ${}^6\text{Li}$ (Based on Calculations of Neutron Flux for ${}^6\text{Li}$) (Ballentine and Burnard, 2002). Right chart: δD for CH_4 from DGR-4 Core

The ratio of these two production rates gives the ${}^3\text{He}/{}^4\text{He}$ isotope ratio for in-situ production. Important to note is the similarity between measured and calculated ${}^3\text{He}/{}^4\text{He}$ ratios in the Upper Ordovician shales, which indicates in-situ U, Th and Li to be the source term for He in the shales (see Figure 7). One can then conclude that this is autochthonous (internally-derived) He and so concentrations can be used to estimate minimum ages for pore fluids.

By contrast, He isotopes measured in the Middle Ordovician limestones are more enriched in ${}^3\text{He}$ than would be expected for in-situ production. Moreover, the measured values below the Cobourg Formation are close to that measured in the Cambrian groundwater and intermediary between literature values for Precambrian brine (Kotzer et al., 1998) and Michigan Basin brines (Ma et al., 2009). It can be concluded that He in this section is

allochthonous, by migration from a mixture of basin-derived and Shield-derived He via the Cambrian sandstone. This is consistent with the measured He concentrations (Figure 8, left chart) which show a steep gradient into the Cambrian sandstone.

Within the Cobourg Formation limestone, measured $^3\text{He}/^4\text{He}$ ratios are consistent with the overlying shales, yet enriched in ^3He over the calculated in-situ values. Here it is apparent that movement of He from the shales into the limestones has occurred, with little to no exchange with He from the underlying Sherman Fall or deeper limestone formations. This is consistent with the CH_4 profiles (TR-08-19) that show a strong impediment to migration of this gas below the Cobourg Formation. Recent hydraulic conductivity testing suggests that horizontal hydraulic conductivities in this section are as low as 10^{-15} m/s (TR-08-32) and are likely to be even lower in the vertical direction.



Note: Error bars include He measurement uncertainties (most near 9%) and uncertainties in interpolation of U and Th measurements (assessed at 20%).

Figure 10 Left chart: Helium Production Based on U and Th Concentrations. Right chart: Helium Ages Calculated for DGR Porewaters Based on Measured He per g Rock and In-situ He Production Based on U and Th Concentrations Assuming a Closed System

Considering that the calculated xRa is close to measured values, and that the He and U profiles are similar, the He in the Upper Ordovician shales can be considered autochthonous, with an age of accumulation of at least 100 million to 200 million years. This fits well with the evolution of the Michigan Basin, where Ma et al. (2009) place the timing of the last major thermal event at some 150-160 million years before present.

The calculated ages for the Middle Ordovician limestones are invalid as they assume a closed system with in-situ production and accumulation of He. From the He production profile (left chart - Figure 10) and He age profile (right chart - Figure 10), the accumulated He measured in the limestones provides ages as old or older than those for He in the Upper Ordovician shales, and ages below 800 m BGS that approach the age of the sedimentary units themselves. As the $^3He/^4He$ ratios (Figure 9, left) demonstrate, He in this section is allochthonous showing an almost uniform profile from the Cambrian up to the Cobourg Formation. Therefore it is concluded that the Middle Ordovician limestones are open to exchange with the underlying Cambrian sandstone. Porewaters in the Cobourg Formation limestone, however, must be considered to be as old as the overlying shales, given that their He isotope signature is derived from He produced in the shales and has migrated downward, presumably by diffusion. While, in-situ production has been minimal (Figure 8, left chart), He from the shales has dominated the Cobourg Formation porewaters over the past 100 to 200 million years.

5 Data Quality and Use

The analysis of radioisotopes in geological materials involves the risk of contamination in the high activity environment of the Bruce nuclear site. Local nuclear activities have raised the background in radiocarbon (Lee et al., 1995) as well as in ^{36}Cl , ^{129}I and tritium. All of the core samples and groundwater samples analyzed in the DGR program are expected to be much older than the 50 years required for tritium decay, and so tritium has been used as an indication of the degree of drilling fluid contamination in groundwaters (TR-08-18, Intera Engineering Ltd., 2010). On this basis, one groundwater sample for ^{129}I (OGW-9, also called DGR-3 389.99) was found to be contaminated, and was not used in the data interpretation.

Porewater radiohalide measurements, both as ratios and concentrations, are very similar for the shales, suggesting that analytical variability is reasonably low and measurements are reliable within the level of interpretation here. Reproducibility of three Cambrian groundwater samples for ^{129}I ($177 \pm 34.4 E-15$, $170 \pm 64.8 E-15$ and $102 \pm 16 E-15$) is acceptable for the level of interpretation in this report. Core samples are considered to be free of drilling fluid contamination because the outer core was removed prior to crushing and leaching. Helium analyses are determined by a new method that has been described in TR-07-21 and TR-08-18. There is good correlation between the DGR-2 and DGR-3/4 results, with the ratio profile produced in DGR-2 being reproduced with the DGR-3 and DGR-4 analyses. This, combined with the laboratory protocols for calibration with air standards, provides confidence that these data are reliable and accurate to the level of interpretation in this Technical Report.

6 Summary and Conclusions

The application of radioisotopes in the DGR strata supports the following observations concerning the ages of the solutes.

Devonian and Upper Silurian Groundwaters

- Measureable tritium in many of these waters is attributed to minor drilling fluid contamination, making even waters in the upper 100 m greater than 50 years old.
- Groundwaters from the US-8 monitoring wells have radiocarbon activities in the range of 16 to 50 pMC reflecting a combination of ^{14}C dilution by carbonate weathering and radioactive decay.

- Groundwater ages, corrected using a standard ^{13}C dilution model, provide ages in the range of 4000 to 8000 years BP. Many of these groundwaters have $\delta^{18}\text{O}$ values which suggest that they comprise a component of glacial meltwater. Therefore, these groundwaters are likely a variable mixture of late Pleistocene glacial meltwater and mid to late Holocene meteoric water. Beyond the elevated tritium in some deeper US-8 groundwaters, which is attributed to drilling fluid contamination, no evidence for modern recharge is found in these groundwaters.

Upper Ordovician Shales

- Age of the Upper Ordovician shales is estimated to be on the order of 100 to 200 million years or more, based on the two independent dating methods of He and ^{129}I .
- Measured $^3\text{He}/^4\text{He}$ ratios of porewater determined through micro-coring in DGR-2, DGR-3 and DGR-4 core are very similar to calculated $^3\text{He}/^4\text{He}$ ratios based on He production from U, Th and Li concentrations. This demonstrates an autochthonous source from in-situ production.
- Measured He concentrations (^4He) of the diffusive component from open porosity (cc He STP / g rock) compared to rates of production from U and Th concentrations in the rock (ppm), demonstrate that an ingrowth period of 100 million to 200 million years is required to accumulate the concentrations measured. Any diffusive loss over this time would make these minimum ages.
- This age of 100 million to 200 million years corresponds with the period of last significant heating of the Michigan Basin (Ma et al, 2009).
- ^{129}I measurements in the Queenston and Georgian Bay Formations are close to values for secular equilibrium, which requires a period of 80 million years. Values for secular equilibrium for ^{129}I are based on U concentrations derived from ^{36}Cl measurements which are assumed to have achieved secular equilibrium with the matrix ($T_{1/2} = 301,000$ years) and can be used to determine the effective U concentration for each sample.

Cobourg Formation Limestone

- Porewaters in the Cobourg Formation limestones are likely as old as those in the overlying shales.
- Based on the measured $^3\text{He}/^4\text{He}$ ratios, He in the Cobourg Formation is derived from the overlying shales and so porewaters in the Cobourg can be assigned a corresponding age of 100 to 200 million years.
- The $^3\text{He}/^4\text{He}$ ratios in the Cobourg Formation limestone are the same as in the overlying shales.
- ^{129}I concentrations and $^{129}\text{I} / \text{I}$ ratios in the Cobourg are within the range of uncertainty for calculated values for secular equilibrium. Further, the two measured values are very different, suggesting ingrowth (in-situ generation) rather than an external origin. Values of secular equilibrium for ^{129}I are consistent with the He age estimates.

Sherman Fall – Kirkfield Limestones (Lower Trenton Group)

- The $^3\text{He}/^4\text{He}$ ratio shifts from the baseline value of 0.02 in the shales and Cobourg Formation to 0.035 in the Sherman Fall Formation through to the Cambrian.
- This shift occurs over a narrow interval below the Cobourg Formation in the upper Sherman Fall Formation. It also occurs at the same depth as the sharp shift observed for isotopes of CH_4 from a biogenic source in the Georgian Bay Formation shales to thermocatalytic methane from the Cambrian sandstone.

- The measured $^3\text{He}/^4\text{He}$ ratio in the Sherman Fall to Shadow Lake section is enriched in ^3He over the ratio calculated for in-situ production using U, Th and Li concentrations, and indicates an allochthonous source. The measured ratios also correspond with that measured in the Cambrian groundwater indicating a probable source from below. As the ratio in the Cambrian is intermediary between literature values for the Precambrian shield brine (Kotzer et al., 1998) and Ordovician groundwaters from the Michigan Basin (Ma et al., 2009), its source is presumed to be a mixture of regional basinal He and Shield He.
- Unlike for the Upper Ordovician shales and Cobourg Formation, He in the Sherman Fall to Shadow Lake section is derived externally, and cannot be used in this section to constrain porewater ages.

Black River Group Limestones

- He isotope ratios in the Black River Group differ significantly from the calculated $^3\text{He}/^4\text{He}$ ratios of autochthonous He, indicating that He in this section is allochthonous, having migrated through the Black River from the Cambrian.
- Concentrations of He in this section increase near the base towards the very high values measured in the Cambrian groundwaters. The $^3\text{He}/^4\text{He}$ ratio in this section indicates that the source of He is a mixture of He Michigan Basin and He from the Precambrian. Ma et al. (2009) note that the ^3He -enriched He of the Michigan Basin has incorporated mantle ^3He , likely through rifting in the deep central basin region.
- ^{129}I concentrations and $^{129}\text{I}/\text{I}$ ratios in the two Black River Group samples (lower Gull River Formation and Shadow Lake Formation) are close to values for secular equilibrium. These samples are from the section characterized by decreased Cl^- and depletion in ^{18}O .
- The ^{129}I concentrations in these two Black River Group porewater samples are less than the average of measurements of the Cambrian groundwater. This is consistent with other tracers (TR-08-19 – Clark et al; 2010b) demonstrating that the Cambrian today differs from the low-salinity, ^{18}O -depleted porewaters observed in much of the lower Black River section.
- Given that the system is open to He migration within this section, and therefore a corroborative dating method is lacking, any estimate for the mean residence time of solutes in the porewaters of this section remains highly uncertain.

Summary

- Halides and He in porewaters of the Upper Ordovician shales indicate a closed system with residence times in these porewaters of greater than 100 million years.
- The Cobourg Formation has variable ^{129}I contents similar to secular equilibrium and He derived from the overlying shales. It is concluded that these porewaters and solutes have a local residence time roughly equivalent to that of the overlying shales.
- Halides in porewaters of the Sherman Fall and Kirkfield (Lower Trenton Group) suggest a residence time in excess of 80 million years, which cannot be corroborated by He ages. This section has been open to influxes of He derived from the Cambrian.
- The lower salinity, ^{18}O -depleted porewaters of the lower Black River Group (lower Gull River and Shadow Lake formations) represents an open system for He diffusion/migration, making estimates of residence time uncertain.

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APPENDIX A

LABORATORY RADIOISOTOPE RESULTS AND CALCULATED ¹²⁹I SECULAR EQUILIBRIUM VALUES

Sample I.D.	Tritium	measured		¹²⁹ I		stable I		Secular equilibrium		Secular equilibrium		Depth	
		³⁶ Cl/Cl	+/-	atoms/kgw E06	+/- E06	mmol/kg	¹²⁹ I/I E-12	+/- E-12	¹²⁹ I/I E-12	+/- E-12	¹²⁹ I/kgw E06		+/- E06
Porewaters													
DGR2-485.40 IT		17.5	4.5	175.7	37.4	0.085	3.4	1.08	3.43	0.33	88.7	24.8	485.40
DGR2-538.51 IT		16.0	2.4	99.2	25.3	0.030	5.5	1.95	5.49	1.29	79.9	73.7	538.51
DGR2-648.25 IT		14.6	1.5	140.5	33.8	0.062	3.8	1.29	3.79	2.24	127.2	163	648.25
DGR2-663.34 IT		30.9	5.5	1125.0	210	0.160	11.7	3.35	11.68	2.95	1567.7	1049	663.34
DGR2-681.45 IT				116.6	40.2	0.165	1.2	0.52	1.17	1.78	347.8	229	681.45
DGR2-699.58 IT		13.9	2.2	370.6	97.5	0.200	3.1	1.12	3.08	0.61	154.3	94.9	699.58
DGR4-725.92 P		30.3	3.2	104.6	8.4	0.058	3.0	0.54	3.00	1.02	94.4	47.2	725.92
DGR4-816.24 P		8.44	1.2	66.9	8.0	0.051	2.2	0.48	2.16	0.78	75.9	17.1	816.24
DGR4-842.27 P		9.15	3.6	23.8	2.4	0.025	1.6	0.32	1.61	1.21	33.6	2.4	842.27
Groundwaters													
DGR3-339.66 P	9.4	8.65	1.35	5.9	0.5	<0.0024	0.5	0.09	11.39	2.28	138.0	27.6	326.86
DGR4-327.08 P	2.3	15.0	4.33	0.6	0.1	<0.0024	0.0	0.01	7.60	1.52	92.0	18.4	328.07
DGR3-389.99 P	133.1	9.47	5.72	964	838	0.004	6.8	6.58	0.80	0.16	113.6	22.7	378.42
DGR4-377.42 IT	5.2			598	75.0	0.004	4.2	0.42	0.46	0.09	65.8	13.2	377.19
DGR4-377.42 P	5.2	38.6	4.32	82.9	21.6	0.004	0.6	0.21	0.46	0.09	65.8	13.2	377.19
DGR2-852.70 IT	2.5			177.0	34.0	0.022	1.5	0.15	0.28	0.06	33.2	6.6	852.70
DGR3-860.53 P	1.6	13.6	2.10	42.1	7.2	0.022	0.4	0.10	0.28	0.06	33.2	6.6	847.53
DGR4-848.50 IT	<0.8			102.0	16.0	0.022	1.0	0.10	0.31	0.06	33.2	6.6	848.50
DGR4-848.50 P	<0.8	7.64	3.00	170.6	64.8	0.022	1.6	0.77	0.31	0.06	33.2	6.6	848.50

IT = analysis at IsoTrace, uOttawa, Toronto

P = analysis at PRIME Lab, Purdue

APPENDIX B

SAMPLE CALCULATION FOR ^{129}I AT SECULAR EQUILIBRIUM

$$C_{129} = \frac{N_{238} \sigma_{\text{SF}} Y_{\text{SF}} \rho \varepsilon [1 - \exp(-\lambda_{129} t_f)]}{\theta \lambda_{129}}$$

C_{129} is the ^{129}I concentration in the porewater or groundwater (atoms/L)

N_{238} is the atomic concentration of ^{238}U (atoms/g of rock)

σ_{SF} is the decay constant for spontaneous fission of ^{238}U

Y_{SF} is the fission yield at mass 129 from spontaneous fission of ^{238}U

ρ is the dry bulk density of the rock

ε is the emanation efficiency (dimensionless)

λ_{129} is the decay constant for ^{129}I

t_f is the residence time of water;

θ is the measured water content

$$C_{129} = 7.67\text{E}+07 \text{ atoms/kgw}$$

	175,720,070 atoms/L
based on 1.59 ppm U =	4.03E15 atoms/g
	$8.5 \times 10^{-17} \text{ yr}^{-1}$
	0.0003 (fraction)
	2.7 g/mL
	1
	$4.4 \times 10^{-8} \text{ yr}^{-1}$
	80,000,000
	0.08 (fraction)