

Technical Report

Title: *Porewater and Gas Analyses in DGR-1 and DGR-2 Core*

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1 Introduction

The results described in this Technical Report (TR) constitute one component of Intera Engineering Ltd. (2006) Geoscientific Site Characterization Plan (GSCP) for the Bruce Deep Geologic Repository (DGR) program. A potential DGR site is being investigated for disposal of low and intermediate level radioactive waste at the Bruce site near Tiverton Ontario. The GSCP describes recommended methods and approaches to acquire the necessary geoscientific information to support (1) the development of descriptive geosphere models of the Bruce Nuclear site; and (2) the preparation of an environmental impact statement and site preparation and construction license application for submission to the Canadian Nuclear Safety Commission.

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), and following the general requirements of the DGR Project Quality Plan (Intera Engineering Ltd., 2009).

2 Background

During the drilling operations associated with the DGR-1 and DGR-2 boreholes, drill core samples were collected for the analysis of the pore fluids. The objectives of the fluid analyses are to provide data that test the hypothesis outlined in the GSCP that porewaters and gases in the Ordovician shales and limestones are old, highly saline and that pore fluid movement is dominated by diffusion. By definition within the Bruce DGR program, “groundwater” is that water that flows under positive pressure into the borehole without artificial stimulation; “porewaters” are defined as water contained in void spaces between mineral grains in a rock or soil (Ontario Power Generation, 2008). The results of groundwater samples, which are also called opportunistic groundwater samples, are described in TR-07-11 Opportunistic Groundwater Sampling in DGR-1 & DGR-2 (Intera Engineering Ltd., 2010a).

The GSCP identified solid-core porewater extraction to be undertaken on cores recovered during the drilling of DGR-1 and DGR-2 (Intera Engineering Ltd., 2006, Task HG.9, pp. 58-62). Most porewater and gas extraction and analysis was performed for core samples obtained from DGR-2 from the Ordovician shales and carbonates, which are anticipated to form the caprock and host rock for the proposed repository, and samples obtained from the underlying Cambrian rocks. The Devonian and Silurian strata were also analysed using core from DGR-1, with the understanding that the presence of evaporite minerals would pose some analytical challenges and uncertainties.

The methods to be employed for porewater and gas extraction from DGR-1 and DGR-2 cores were established on the basis of method development work using the Bowmanville Quarry surrogate core (i.e., TR-07-02, Intera Engineering Ltd., 2008a). However, due to the time elapsed between drilling and analysis of that core, sampling methods for volatile components including He and CH₄ gases were developed during the early stages of drilling the DGR-1 core.

This Technical Report summarizes the environmental isotope results for porewaters extracted by vacuum distillation of crushed core material, hydrogeochemical results produced by leaching of the vacuum extracted (dried) crushed core material, CO₂ and CH₄ trapped and sampled during vacuum distillation of porewaters, and He concentrations and isotopes sampled from micro-cores drilled from preserved core samples.

3 Analytical Methods

3.1 Vacuum Packaging of Core in Field

Drill core sections selected in the field following recovery, rinsing and photography were packed in polyethylene with an N₂ flush and vacuum sealed, then packed into a second aluminum/plastic liner which was then vacuum

sealed (Figure 1). Cores were shipped to the University of Ottawa within a few days of drilling in most cases, and stored at 4°C until analysis. Analysis of cores was undertaken as quickly as possible, with up to three samples processed per week. This rate engendered a backlog at some points, with time between coring and analysis approaching four months (Figure 2).



Figure 1 Vacuum Sealed Core as Received from Field. Core Sample Shown Here is ~15 cm Long

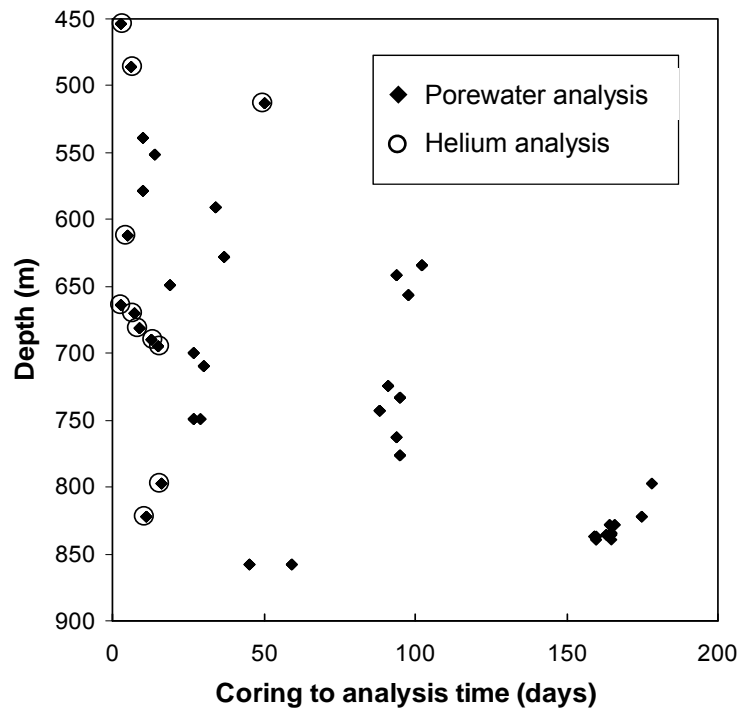


Figure 2 Time in Days Between Coring and Analysis of Samples from DGR-2

Additional cores were requested from archived samples on two occasions for further porewater extractions. During shipment, the vacuum seal on some cores was breached, although the cores remained humid and therefore unaffected by desiccation. This situation was noted, but not considered to affect porewater analysis, as the exterior 1 cm of the drill core was removed in sample preparation.

3.2 Vacuum Distillation and Stable Isotope Analysis of Porewaters

Vacuum distillation was determined by an earlier evaluation of methods with Bowmanville Quarry core to produce the most reliable results for stable water isotopes for the low-porosity Ordovician clays and limestones. The temperature of distillation is critical to assure that as close to 100% of the porewaters are collected. Preliminary testing at the University of Ottawa demonstrated that a temperature of 150°C provided reproducible results. Comparison between opportunistic groundwater samples and similar-depth porewaters suggests that accurate values are measured (see section 4.1). This temperature was also proven to yield the most reliable stable isotope results for the Tournemire argillite in a method comparison study (40% clay minerals (illite, mixed layers illite/smectite and kaolinite), 20% quartz, 20% calcite, 20% pyrite and siderite; water content 2 to 5% by weight; Altinier et al., 2007). In their study of a clay-rich rock with similar petrophysical and geochemical properties to the Ordovician rocks beneath the Bruce Nuclear Site, analysis was tested using low (50°C and 105°C) and high (150°C) vacuum distillation, liquid-phase radial diffusion and vapour-phase diffusive exchange. Vacuum distillation at 150°C provided $\delta^{18}\text{O}$ and δD results closely matching results from local fracture waters, which Altinier et al. (2007) assumed were in equilibrium with the porewaters. However, low-temperature vacuum distillation results were isotopically depleted, and both radial diffusion and diffusive exchange were anomalously enriched in ^{18}O . Furthermore, diffusive exchange provided greater than expected estimates of water content. Vacuum distillation also provides a much lower degree of post-extraction analytical uncertainty compared with diffusive methods, which incorporate a significant dilution with spiked water that increases the mass spectrometer analytical error by two- to four-fold (Waber et al., 2007). By contrast, vacuum distillates are close to pure water and are analysed directly with no dilution with spiked water.

Vacuum distillation was undertaken on core that has been crushed to approximately sand-sized particles (i.e., ~ 2 mm diameter). A mass of 30 g of crushed rock is loaded into each of five sample vessels and attached to individual vacuum extraction lines – each paired with a high-vacuum septum vial ('exetainers') on the other side, and all with a common pumping port (Figure 3). The sample vessels are initially cooled with liquid N_2 and evacuated to produce a high vacuum throughout the extraction system. The lines are then closed to the pump and a glass bead bed is placed around the sample vessels. Heating tape in the glass bead bed is used to ramp the bed temperature to 150°C. On the other side of the extraction lines, the septum vials are attached by syringe needles to the extraction line and partially submersed in a liquid N_2 bath. The water vapour distilled from the core material and condensed in the septum vial over a 6 hour period. The water yield is later weighed, which is compared with the weight loss in the core material.

Weights of the core material, both pre-distillation (wet) and post-distillation (dry) were taken, which together with the weight of distillate water provide a measure of volumetric water content for the analysed rock mass, according to:

$$\text{Volumetric water content} = (\text{weight water}) / ([\text{weight rock/mineral density}])$$

The volumetric water content is a key parameter for normalizing both measured gas contents and geochemical results to the porewater volume. Because this value was observed to vary several-fold for different aliquots of the same core sample, it is important that measured concentrations are normalized to measured porewater contents and not to average values for different geological formations. Figure 4 compares the water contents of Ordovician shales and limestones with their stable isotope values. No statistical correlation exists between these variables, suggesting that the depleted $\delta^{18}\text{O}$ values in the limestones are not an artefact of extraction from samples with low water content.



Figure 3 Distillation Line for the Vacuum Extraction of Porewaters.

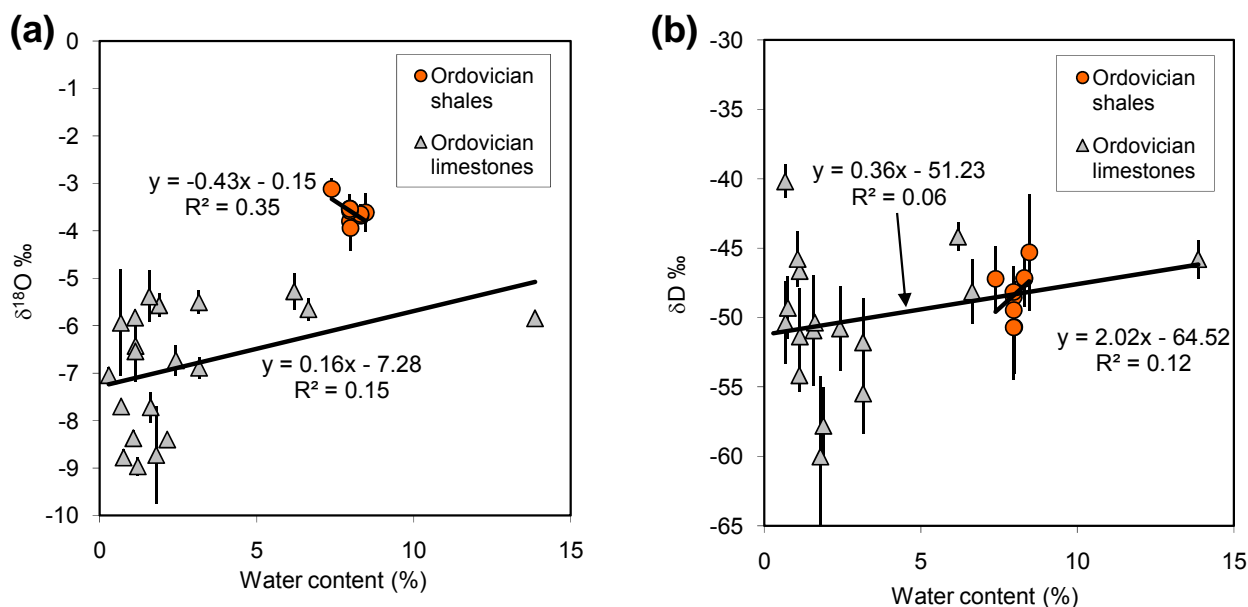


Figure 4 Comparison of Water Content with $\delta^{18}\text{O}$ (a) and δD (b) in the Ordovician shales (Queenston and Georgian Bay) and Argillaceous Limestones (Cobourg to Gull River).

The contents of the exetainer are then analyzed for ^{18}O and ^2H by isotope ratio mass spectrometry (IRMS). The analysis of $\delta^{18}\text{O}$ is done by equilibration of the water with CO_2 (2% in He in the vial headspace). Analysis of CO_2 for $\delta^{18}\text{O}$ of the water is undertaken by continuous-flow IRMS on a Finnigan-Mat Delta XL with GasBench using calibrated standards and blind reference waters. The septum vials with the distillate waters then have Pt catalyst (Hoko beads) added and are re-flushed with He gas, and filled with a 2% H_2 gas in He. Following an over-night equilibration period, the H_2 gas is analysed for δD . Poorer reproducibility for δD may be in part related to interference from hydrocarbons released during the vacuum distillation. Some samples contained hydrocarbons which follows water vapour during distillation and interferes with the equilibration and mass spectrometer analysis for δD , and required the addition of some activated charcoal in some vials was required to sorb any hydrocarbons.

The vacuum distillation method at elevated temperature provides two particular advantages over other methods for the DGR-2 rocks at the Bruce site. The first is the greater likelihood of extracting, and therefore analysing virtually all of the pore fluid from materials that have very low water contents. The second is that the method provides a very precise measurement of water content that is required for normalization of geochemical and gas data.

As water content can vary by several percent or more between different sections of the same core sample, particularly for the limestones, it is imperative that porewater content is not an average or proxy value, but the actual value for the subsample from which solutes and gases were extracted. A third advantage of high temperature extraction of porewaters at the Bruce site is the suitable mineralogy of the DGR-2 shales and limestones. There has been no clear and unequivocal detection of gypsum in these Ordovician rocks (Intera Engineering Ltd., 2008b) to contribute crystallographic water to the extracted water. Further, as the clay fraction is illite/chlorite (Intera Engineering Ltd., 2008b), there is no concern for significant contribution of interlayer waters.

Considering these suitable conditions for vacuum distillation, a higher temperature experiment was undertaken to test whether the reproducibility could be improved for the very low water content limestones by using a temperature of extraction even greater than 150°C. The two isotopically depleted samples at 797.5 m and 844.42 m depth (water contents less than 2%) were reanalyzed by extraction at 200°C. The results (Table 1) reproduced the low $\delta^{18}\text{O}$ values from the routine 150°C analysis (Appendix A). Additional extractions are currently being undertaken to further test this higher temperature method (see TR 08-37, Intera Engineering, 2010b). Noteworthy is the difference in water content for the two extractions. Given the very close isotope values for the two extractions, this is considered to represent variability in water content in the cores.

Table 1 Comparison of Vacuum Distillation at 150°C vs. 200°C

Sample Depth	Extraction Temperature	Yield (g)	Water Content (%)	$\delta^{18}\text{O}$ (‰)	Average $\delta^{18}\text{O}$ (‰)
797.50	150°C	0.147	1.02	-8.30	
797.50	150°C	0.129	0.94	-8.47	
797.50	150°C	0.161	1.21	-8.14	
797.50	150°C	0.163	1.08	-8.37	
797.50	150°C	0.147	1.10	-8.58	-8.37
797.50	200°C	0.187	1.22	-9.10	
797.50	200°C	0.186	1.20	-8.83	-8.97
822.42	150°C	0.102	0.81	-8.71	
822.42	150°C	0.101	0.79	-8.65	
822.42	150°C	0.116	0.89	-8.98	-8.78
822.42	200°C	0.343	2.32	-8.43	
822.42	200°C	0.305	2.01	-8.43	
822.42	200°C	0.332	2.11	-8.34	-8.40

Testing for complete extraction of water was undertaken on a series of core samples with varying water contents (Table 2). Each of the samples were heated for 6 hours, weighed, and heated for an additional 5 hours (11 hours total heating time) and re-weighed. The additional weight loss (third column in Table 2) was attributed to residual water produced over the additional extraction period. The $\delta^{18}\text{O}$ of this residual fraction was modelled as a Rayleigh distillation using the fractionation factor for 150°C ($\epsilon^{18}\text{O}_{\text{water-vapour}} = 3\text{‰}$) and the resulting error on the $\delta^{18}\text{O}$ of the porewater determined by simple mass balance. This can be considered to be a worst-case model as the residual water fraction is unlikely to have remained in liquid state and so the fractionation factor between

vapour produced within the 6 hour distillation and any residual water vapour in the rock would be minimal. More likely is that any residual water resides as hydration waters on the residual salts or clays, with $\delta^{18}\text{O}$ values much lower than those modelled by the Rayleigh model (3 to 21‰).

Table 2 Calculated $\delta^{18}\text{O}$ Error due to Incomplete Water Extraction

Core sample	Water yield (g)	Residual fraction gained by additional extraction (%)	$\delta^{18}\text{O}$ of remaining water (Rayleigh model)	Error on $\delta^{18}\text{O}$ (mass balance)
DGR-2 828.01-1	6.8409	0.0681	21.88	-0.02
DGR-2 828.01-2	6.7186	1.1311	13.45	-0.21
DGR-2 828.01-3	6.5963	2.1941	5.02	-0.40
DGR-2 828.01-4	6.4740	3.2571	3.41	-0.60
DGR-2 834.05-1	14.0853	-0.1194	-	-
DGR-2 834.05-2	14.1418	-0.1149	-	-
DGR-2 834.05-3	13.9886	-0.1362	-	-
DGR-2 834.05-4	13.8426	-0.1054	-	-
DGR-2 835.73-1	6.4340	2.3189	11.29	-0.39
DGR-2 835.73-2	6.1425	1.8022	12.05	-0.31
DGR-2 835.73-3	7.0921	0.8992	14.13	-0.17
DGR-2 835.73-4	7.0101	0.3580	16.90	-0.08
DGR-2 836.63-1	0.7791	6.8182	8.06	-0.96
DGR-2 836.63-2	0.7357	5.7983	8.54	-0.83
DGR-2 836.63-3	0.5836	6.4414	8.23	-0.91
DGR-2 836.63-4	0.5511	6.5678	8.17	-0.93
DGR-2 839.89-3	6.0991	0.5045	15.87	-0.11
DGR-2 724.16-1	2.9787	1.6997	12.22	-0.30
DGR-2 724.16-2	3.0840	0.9257	14.05	-0.18
DGR-2 551.75-1	9.2377	0.6578	15.07	-0.13
DGR-2 551.75-2	9.0063	0.5481	15.62	-0.11
DGR-2 551.75-3	8.3493	0.9392	14.00	-0.18
DGR-2 551.75-4	8.5529	0.2720	17.72	-0.06
DGR-2 724.16-3	1.0509	4.0765	9.60	-0.62
DGR-2 724.16-4	1.1159	2.5943	10.96	-0.42

Following leaching, the rock samples were rinsed extensively with deionized water and dried. These samples were then crushed to powder and leached with a mild acetic acid. Sr was then removed from these solutions on ion exchange columns and re-eluted for preparation of filaments for analysis by thermal ionization mass spectrometry (TIMS) on a Triton instrument at Carleton University.

3.3 Sampling and Analysis of CO₂ and CH₄

The extraction of both CO₂ and CH₄ were carried out at the same time as porewater extractions on DGR-2 samples. CO₂ released from the rock samples during heating is trapped with water vapour in the “exetainer” septum vials at liquid N₂ temperature. Following vacuum distillation, each exetainer was removed from the line and warmed to release the condensed CO₂. This was then analysed for both concentration and $\delta^{13}\text{C}$ on a Finnigan MAT Delta XL continuous flow mass spectrometer interfaced with a GC to purify the gas.

Standard gas mixtures were used to generate a calibration curve for concentration measurements. As core samples were analysed in quintuplicate for most DGR-2 samples, this allowed CO₂ to be analyzed in quintuplicate as well for each sample depth. Total yields, in mmol, were then normalized to the water mass produced from the rock mass following vacuum distillation, giving units of mmol CO₂/kg H₂O.

CH₄ does not condense at liquid N₂ temperatures on glass surfaces, and so was not trapped with water vapour and CO₂ in the sample exetainers. It is, however, adsorbed by activated charcoal cooled with liquid N₂. Methane in the vacuum distillation line was collected on pre-cleaned activated charcoal in an exetainer attached to the vacuum line and cooled with liquid N₂. All five sample ports were opened to the charcoal trap and CH₄ was thus trapped as a composite sample. This provided sufficient CH₄ for analysis from most samples. Methane was analysed on the same mass spectrometer and interface as the CO₂. Concentration, δ¹³C and δD were all analysed. Standards were used to produce a calibration curve for determining CH₄ concentrations on the mass spectrometer.

3.4 Out-diffusion Leaching for Solutes Following Vacuum Distillation

The crushed rock material from each of the subsamples following vacuum distillation was rinsed from its distillation vessel with ~20 mL of distilled water directly into a plastic centrifuge tube. Care was taken to collect the entire rock sample and to rinse each distillation vessel into the plastic centrifuge tube three times to assure quantitative collection of salts from the experiment. The centrifuge tube was then weighed to determine the precise amount of leach water added to the dry rock. The transferred samples were allowed to leach for on average 60 days with occasional (bi-weekly) shaking, and were then filtered and analysed for major ions. Cations were measured in the University of Ottawa geochemistry laboratory on a Varian Vista ICP-OES and anions were measured by ion chromatography with a Dionex 100 liquid chromatograph. The mass of each solute in the leachate was determined from its measured concentration and mass of leach water added to the dried rock, and normalized to the mass of water yielded by vacuum distillation to give molal concentrations for the original porewaters. These results are tabulated in Appendix B.

3.5 Strontium Isotopes in Porewaters and Rock

Selected aliquots of leachate from 3.4 above, along with their respective rock sample, were analyzed for their ⁸⁷Sr/⁸⁶Sr isotope ratio as an indication of the source of Sr²⁺ and therefore Ca²⁺ in porewaters. Measurements were made by solid source thermal ionization mass spectrometry at the Ottawa-Carleton Geoscience Centre Radiogenic Isotope Laboratory. Porewater strontium was analyzed on the leach solutions discussed in 3.4 above which were produced by addition of deionized (6.7 mega-ohm-cm) water. Strontium was extracted from the leach water samples on a strontium-specific column then eluted and loaded onto a degassed Ta filament and analyzed on a Thermo Finnigan Triton multi-collector thermal ionization mass spectrometer. Rock samples were analyzed by partial dissolution with a weak acetic acid leach followed by column extraction of Sr²⁺ as for water samples.

3.6 Diffusion Extraction of He and Ne

The objective of the noble gas measurements is to determine the concentration of He and the ³He/⁴He isotope ratio in the connected porosity. The He concentration and ³He/⁴He ratio profiles can then be used to evaluate the dominant transport mechanisms for solutes and gases in the Ordovician section of DGR-2.

He is a highly diffusive gas that originates in porewaters from both in-situ production resulting from alpha decay of U and Th in the minerals adjacent to the pore spaces, and through migration from other production zones such as the Precambrian gneisses, which have abundant U and Th as well as fluids with long residence times. The extraction and measurement of He in pore spaces requires rapid delivery of core to the laboratory and a correction for delay in analysis from the time of drilling.

Early testing with DGR-1 core showed that sub-sampling of core material into He-tight vessels in the field provided good results, although the relatively slow rate of loss from these very low permeability materials also permitted sub-sampling in the laboratory with only minor loss of gas. Further, the advantage of sub-sampling in the lab allowed more complex He release-rate experiments to be undertaken. Given this advantage, plus the constraints on sub-sampling in the field (personnel and equipment), it was decided that DGR-2 cores would be sub-sampled in the lab for the He experiments.

For DGR-2 He experiments, cores were analyzed in the laboratory usually within 10 days of coring, although delays sometimes occurred due to a higher rate of drilling than the rate of analysis in the lab (Figure 2). Further, a second core-request was made to provide additional detail to the porewater profiles being generated, resulting in a delivery of material with delays up to 3 weeks. Helium data (discussed in Section 3.5) show significant He remaining in the cores after sample storage up to 4 weeks. This is considerably longer than the 'relaxation time' of 5 to 6 days reported by Rübél and Lehmann (2003, p. 246) for Opalinus Clay samples from Mt. Terri. Nonetheless, loss of He over this time required correction calculations which increase the analytical uncertainty of each measurement.

Figure 5 summarises the sampling procedure following receipt of the wrapped and sealed parent cores from the field. The parent core sample, typically a ~15 cm long cylinder of 6 cm diameter, is split into three blocks. The central block is micro drilled in the laboratory using a Diamant® diamond-faced coring tool mounted on a bench-top drill press with water circulation system. The remaining core blocks are resealed in evacuated plastic bags for other chemical and stable isotopic studies.

The micro core is typically a cylinder of ~3 cm long and 0.6 cm diameter. It is air dried with a hand blower, weighed and transferred into a 1cm I.D. x 13 cm long copper tube or a 2.5 cm I.D. x 10 cm long conflat-flanged stainless steel nipple and evacuated to a rough vacuum < 1.33 Pa. The evacuated sample is isolated from the vacuum pumps either by using stainless steel knife edges (for copper tubes) or by closing a valve (stainless steel container) until the experiment starts. A micro coring operation (parent core splitting to sealing) typically takes ~15 minutes.

Room temperature diffusion experiments involve diffusion from the ~1 cm³ micro-core for varying periods of time. For each sub-sample micro-core taken from the larger drill core, four He-diffusion steps were made followed by an overnight accumulation. Thus, typically five individual ambient-temperature measurements of He concentration and isotopes were made for each core sample. Data from such experiments produce an estimate of the rate of helium diffusion from a sample, which is very useful in assessing gas loss from the parent core near the regions of micro coring. Estimating the rate of gas loss minimises the uncertainties in true gas concentrations. Following the ambient (20°C) out-diffusion experiments, the microcore was then heated in four steps to observe the release of He and Ne with increased temperature.

Sample gases in the line, mostly He and Ne and other residual gases (e.g., H, CO, CO₂, H₂O etc.), are cleaned by exposing in succession to hot Ti (300°C) and Fe-V-Ti alloy getter at room temperature. The remaining gases, i.e., He and Ne, are then separated by regulating the temperatures (42 and 90 °K) of the cryodynamic traps. Mass spectrometric analysis follows using standard procedures (Kotzer et al. 1998; Kotzer et al., 2000; Hendry et al., 2005).

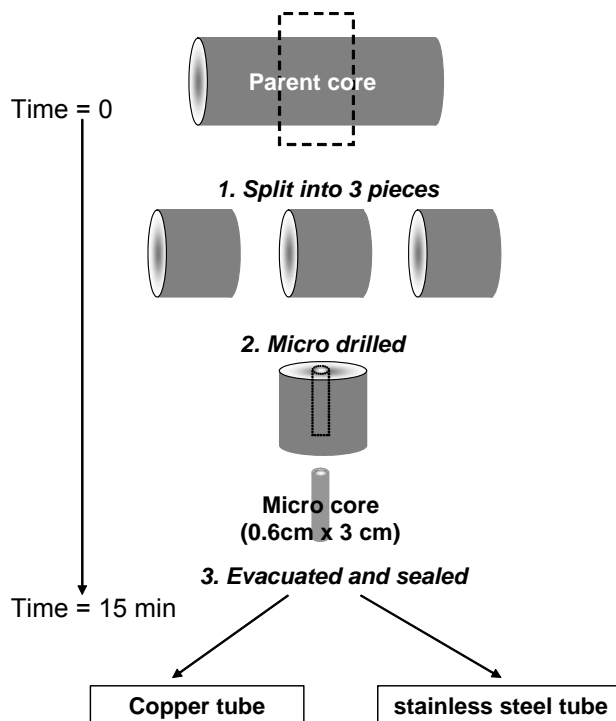


Figure 5 Sampling Protocol for Isolating a Micro-core Sample in a High Vacuum Sample Vessel for He Out-diffusion Experiments.

Procedural blanks simulating the sample runs are interspersed among sample runs. Typical blanks for the stepped heating experiments in Line 1 that involves an all components of the ultra-high vacuum line are: $^4\text{He} = 2 \times 10^{-9} \text{ cm}^3 \text{ STP}$; $^3\text{He} = 7 \times 10^{-15} \text{ cm}^3 \text{ STP}$; $^{20}\text{Ne} = 1 \times 10^{-9} \text{ cm}^3 \text{ STP}$. Blanks for the room temperature diffusion experiments, in Line 2, that involve combination of high vacuum and UHV line are typically: $^4\text{He} = 2 \times 10^{-8} \text{ cm}^3 \text{ STP}$; $^3\text{He} = 3 \times 10^{-14} \text{ cm}^3 \text{ STP}$; $^{20}\text{Ne} = 2 \times 10^{-8} \text{ cm}^3 \text{ STP}$. Aliquots of air standards are analysed following the sample run protocols to calibrate the experiments. The sensitivities of the Mass Analyzer Products Ltd (MAPL) are: $(8.87 \pm 0.42) \times 10^{-16} \text{ cm}^3 \text{ STP / cps}$ for ^3He , $(5.01 \pm 0.24) \times 10^{-6} \text{ cm}^3 \text{ STP / V}$ for ^4He and $(2.73 \pm 0.15) \times 10^{-6} \text{ cm}^3 \text{ STP / V}$ for ^{20}Ne .

4 Results

4.1 Porewater Isotopes

The $\delta^{18}\text{O}$ and δD of porewaters are tabulated in Appendix A. Results are plotted with depth in Figure 6 ($\delta^{18}\text{O}$ and water content) and Figure 7 (δD). Error bars represent the standard deviation (1σ) of the five 30 g subsample replicates (for most samples) undertaken for each core sample. Opportunistic groundwaters (Intera Engineering Ltd., 2010a) are shown in dark blue triangles and the Cambrian opportunistic groundwater sample (844 m) was corrected for salinity according to Horita et al. (1993). The sample DGR2- 775.99 m may be enriched by evaporation in the exetainer during analysis preparation, due to very small sample size (0.04 mL – smallest of all samples; the rest are $>0.1 \text{ mL}$). Comparison between the $\delta^{18}\text{O}$ and D for the groundwater samples and similar-depth porewaters suggests the porewater results are accurate.

Water contents in the Salina E through A2 units in the Upper Silurian (Figure 6) are anomalously high and probably include waters of crystallization from gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), where present in the section, i.e., (Intera Engineering Ltd., 2008b). Nonetheless, stable isotope values show a trend (Figure 8) from values for local modern meteoric waters at this site (~ -12 to -13‰ for $\delta^{18}\text{O}$) to that of the upper Ordovician shales ($\sim -3.5\text{‰}$).

The $\delta^{18}\text{O}$ profile in the Ordovician Queenston and Georgian Bay shales is very constant and suggests stable conditions over a long period of time have allowed diffusive equilibration to be established throughout this relatively high water-content zone. The profile follows a negative trend in the Blue Mountain shales towards more depleted values in the middle Ordovician argillaceous limestones as deep as the Gull River limestone. This trend towards more negative values occurs in the region where volumetric water content decreases to low values. However, careful examination demonstrates that there is no systematic correlation between porewater isotopes and water content that would suggest an analytical artefact (see Figure 4). Replicate extractions of the two most depleted samples (797.5 m and 822.42 mBGS, i.e., Gull River Formation.) at higher temperature provided very consistent isotope results (Table 1).

The profile for δD through the Devonian and Silurian section (Figure 7), like $\delta^{18}\text{O}$, shows a systematic enrichment trend from depleted values similar to local modern meteoric waters to the enriched values measured for the upper Ordovician shales (Figure 7). The larger enrichment in δD compared to $\delta^{18}\text{O}$ may reflect the enhanced diffusion of HDO over H_2^{18}O over a long diffusion profile.

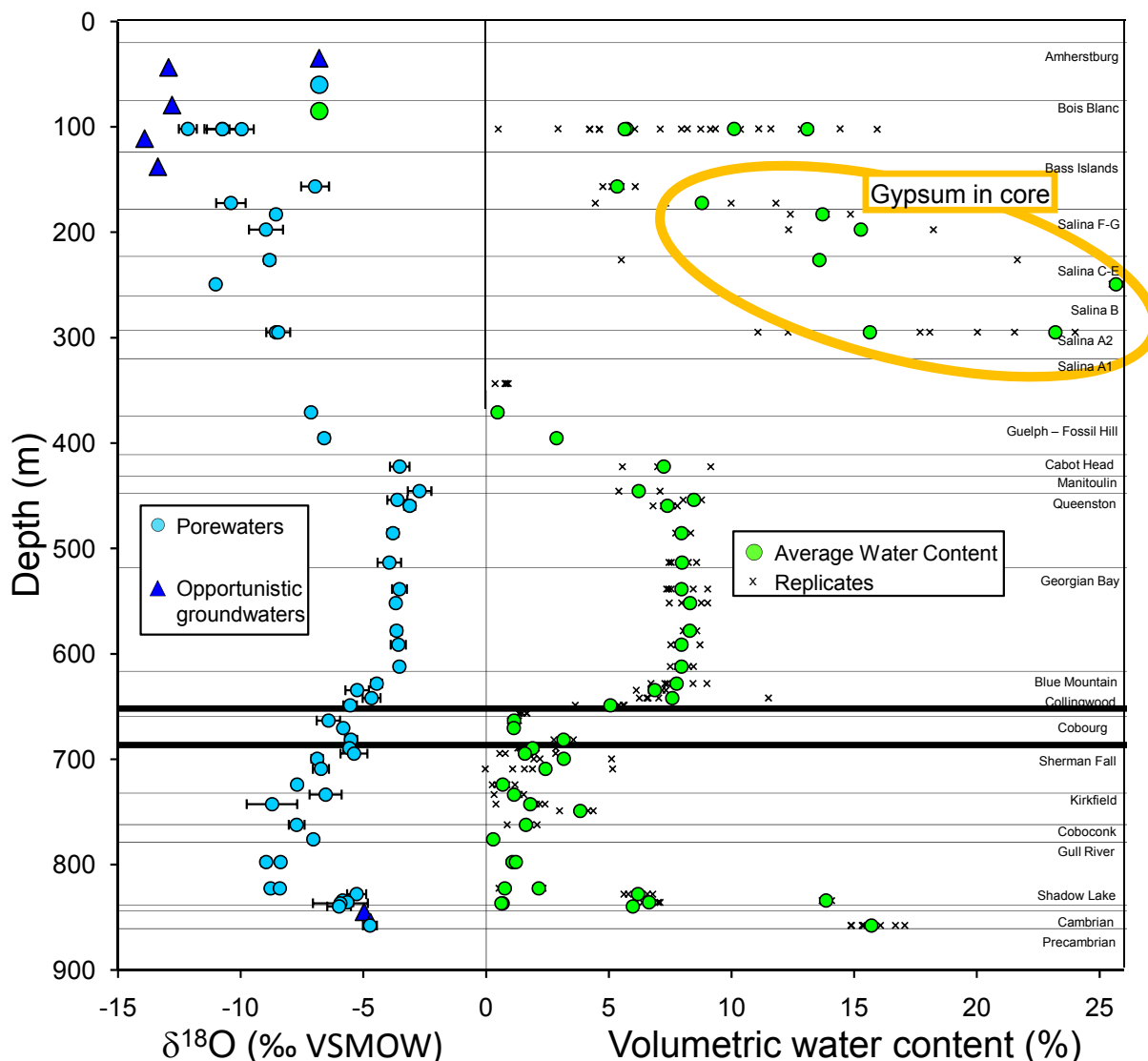


Figure 6 Average $\delta^{18}\text{O}$ in Porewaters by Vacuum Extraction from DGR-1 and DGR-2 (blue circles) and Volumetric Water Content of Core Samples (green circles). Sample replicates shown with small x, mean value shown with green circle.

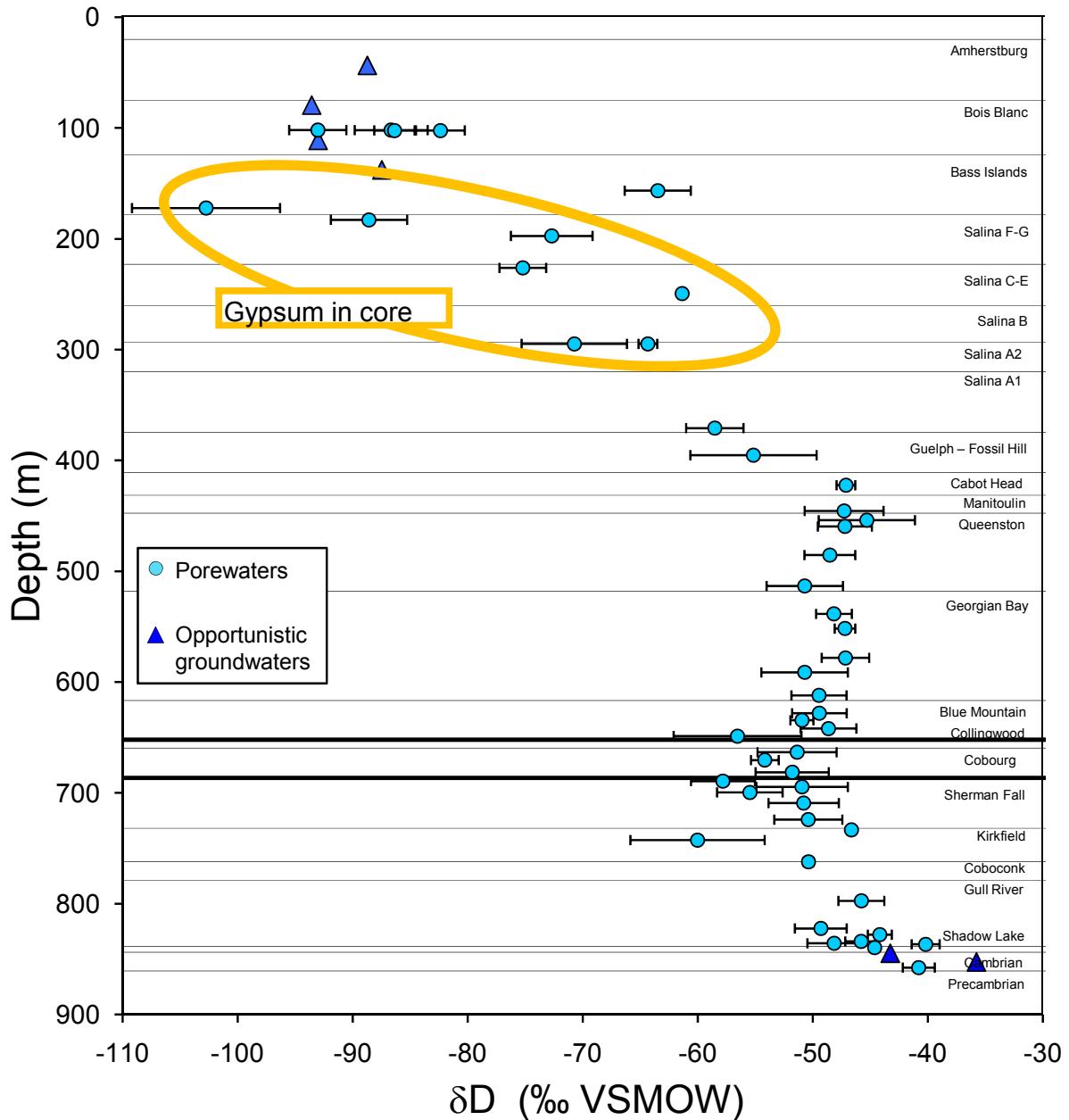


Figure 7 δD in Porewaters by Vacuum Extraction from DGR-1 and DGR-2.

The cross plot of $\delta^{18}O$ vs δD (Figure 8) provides an additional perspective on the isotope trends between the different formations. Figure 8 shows the relationship between the Devonian and Silurian porewaters, which trend between the shallow meteoric groundwaters sampled from DGR-1 (opportunistic groundwater samples, Intera Engineering Ltd., 2010a) and the upper Ordovician shale porewaters.

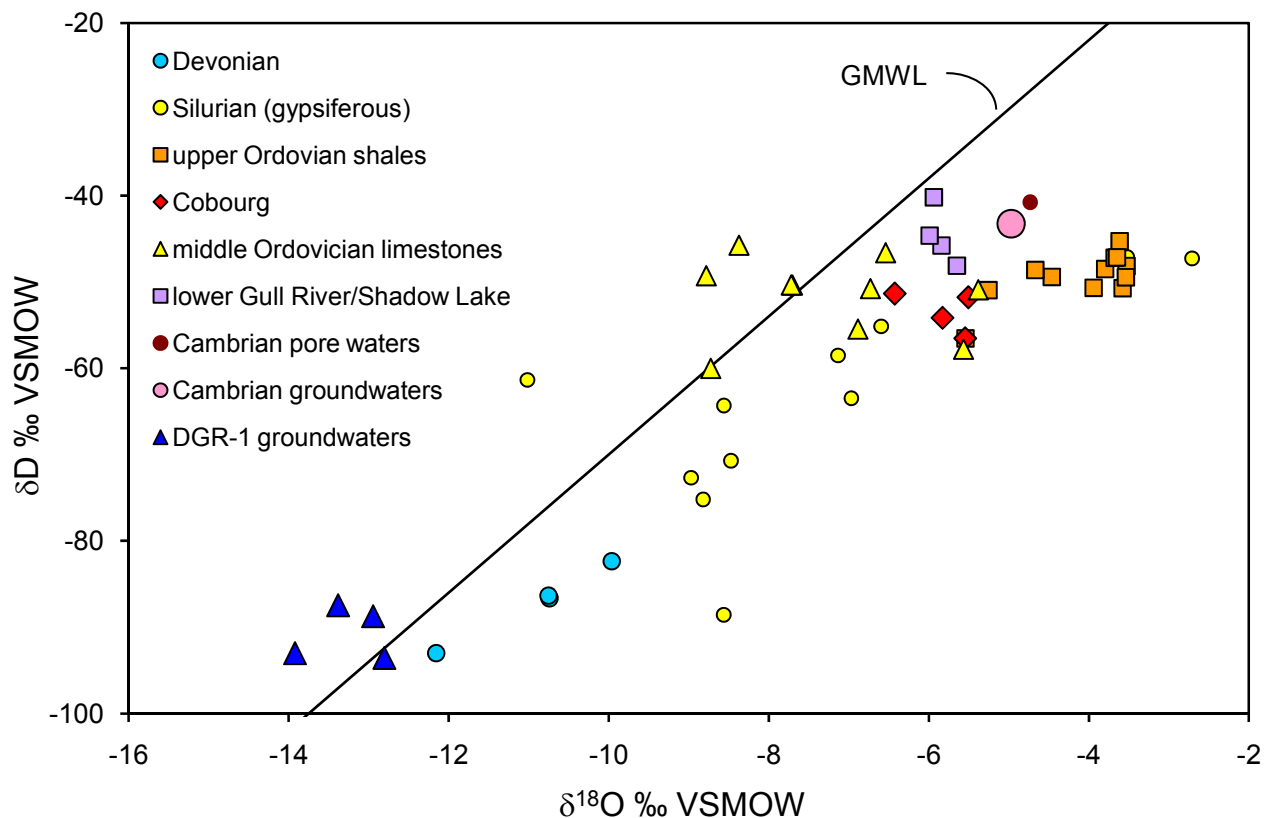


Figure 8 $\delta^{18}\text{O}$ vs δD Plot for DGR-1 and DGR-2 Porewaters and Groundwaters.

4.2 Porewater Geochemistry

The major ions show trends (Figures 9 and 10) that are similar to the $\delta^{18}\text{O}$ profile, featuring increasing values through the Silurian section (Figure 9) to the high, steady values through the upper shales (Georgian Bay Formation), and a shift to lower Cl^- and Ca^{2+} but increased Na^+ in the middle Ordovician limestones (Figure 10). The base of the profiles shows a reversal of these trends back towards the solute concentrations in the Cambrian groundwater.

Potassium shows a remarkably stable concentration in porewaters, despite the highly variable water content in the Ordovician section (Figure 10). However, below the Cobourg, K^+ experiences a gradual, then rapid depletion towards the very low concentration in the Cambrian brine. This brine, in addition to low K^+ , is distinct from the upper and middle Ordovician porewaters by a decrease in Na^+ and increase in Ca^{2+} .

Figure 11 presents results for total sulphur, magnesium and bromide. Trends in major ions are more apparent by examining ion ratios (Figure 12). Here, the positive downward trend in Na/Ca and negative downward trend in Cl/Na are both reversed in the Shadow Lake and Cambrian porewaters.

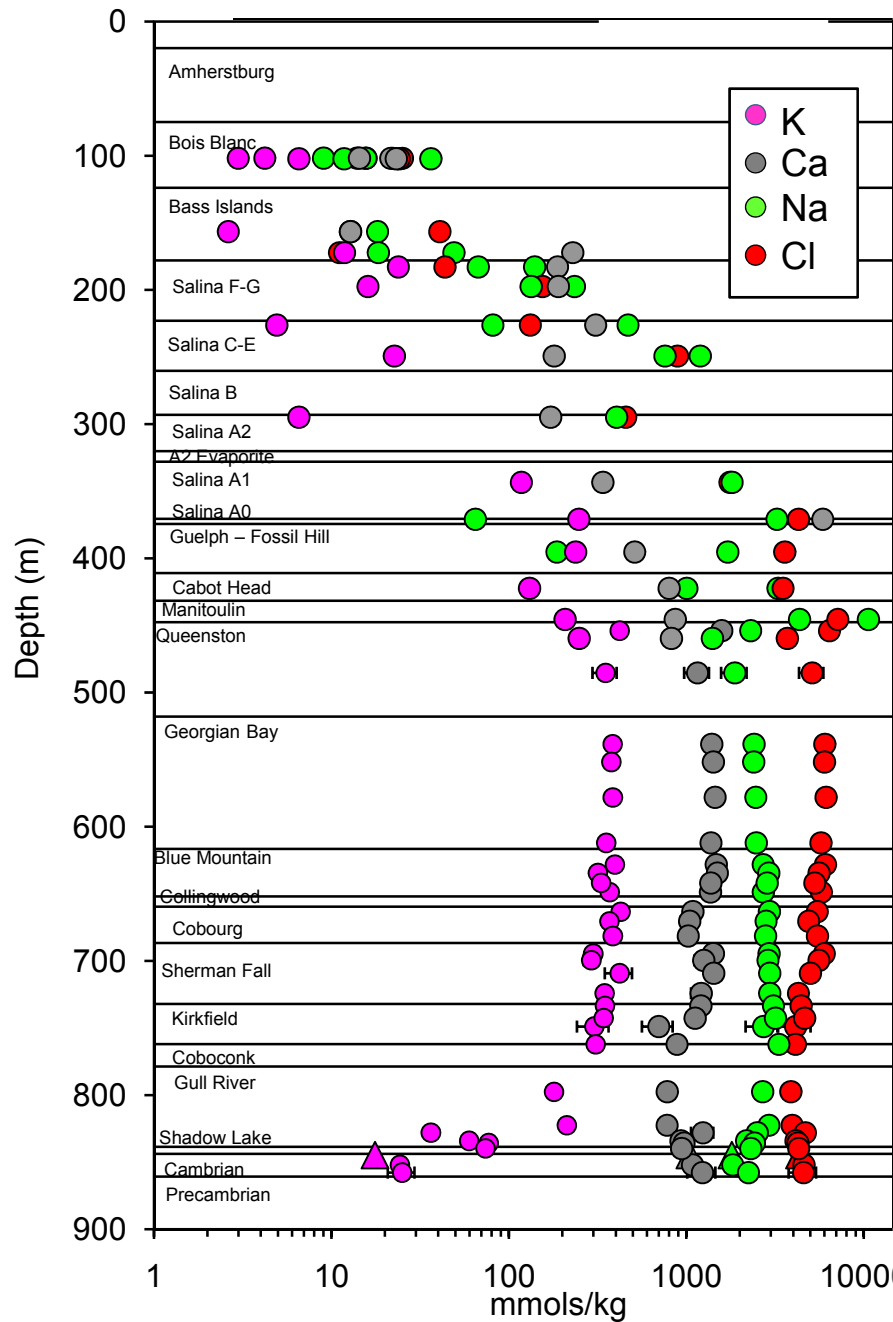


Figure 9 Concentration Profile for DGR-1 & 2 of Cl^- , Na^+ , K^+ and Ca^{2+} Leached by Out-diffusion from Dry Crushed (~2 mm fraction) Rock Following Vacuum Distillation. Concentrations Plotted on Log Scale.

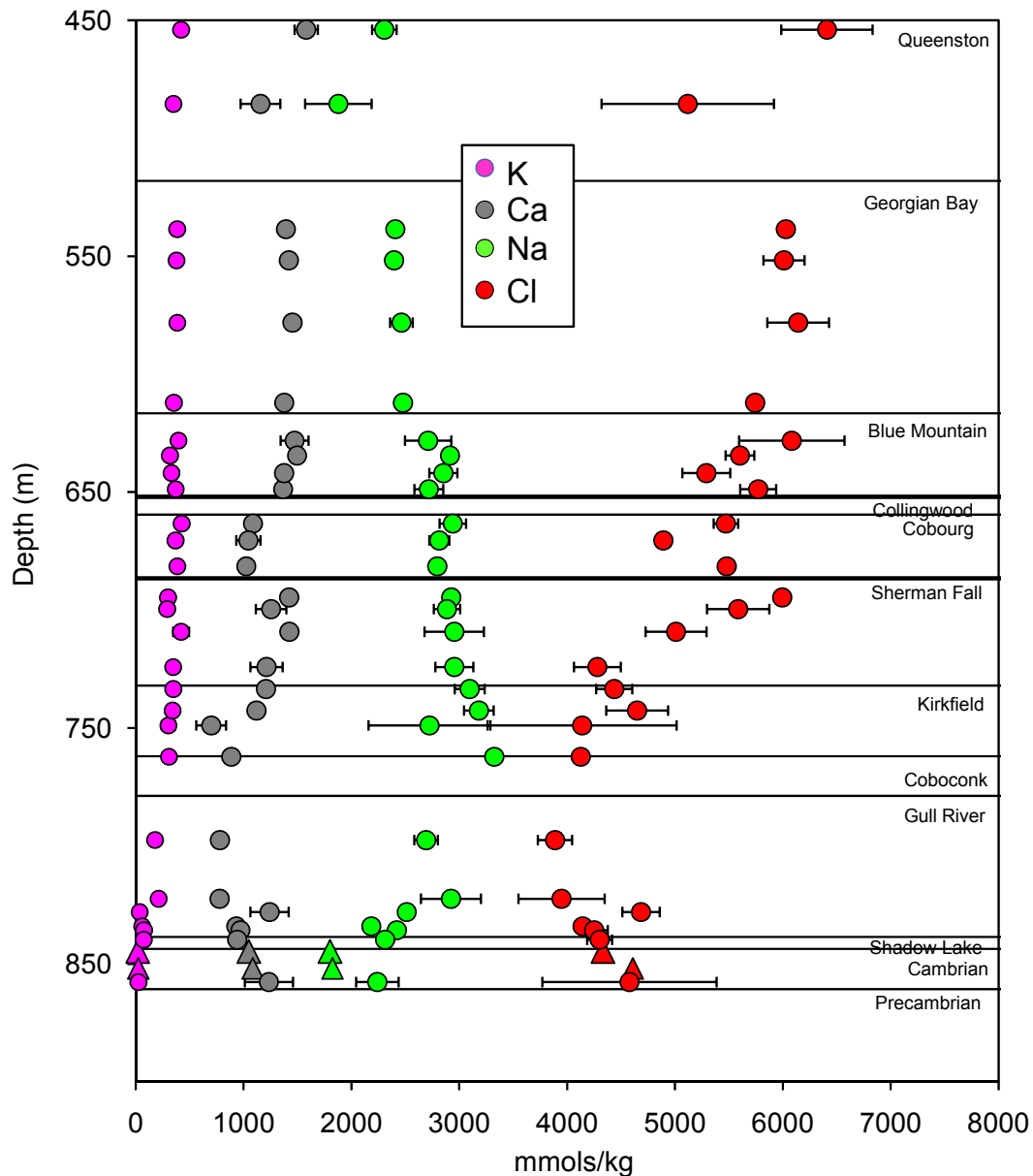


Figure 10 Detailed Profile for DGR-2 of Concentrations of Cl^- , Na^+ , K^+ and Ca^{2+} Leached by Out-diffusion from Dry Crushed (~2 mm fraction) Rock Following Vacuum Distillation. Error bars represent the standard deviation of replicate samples (see Appendix B for sample-specific details)

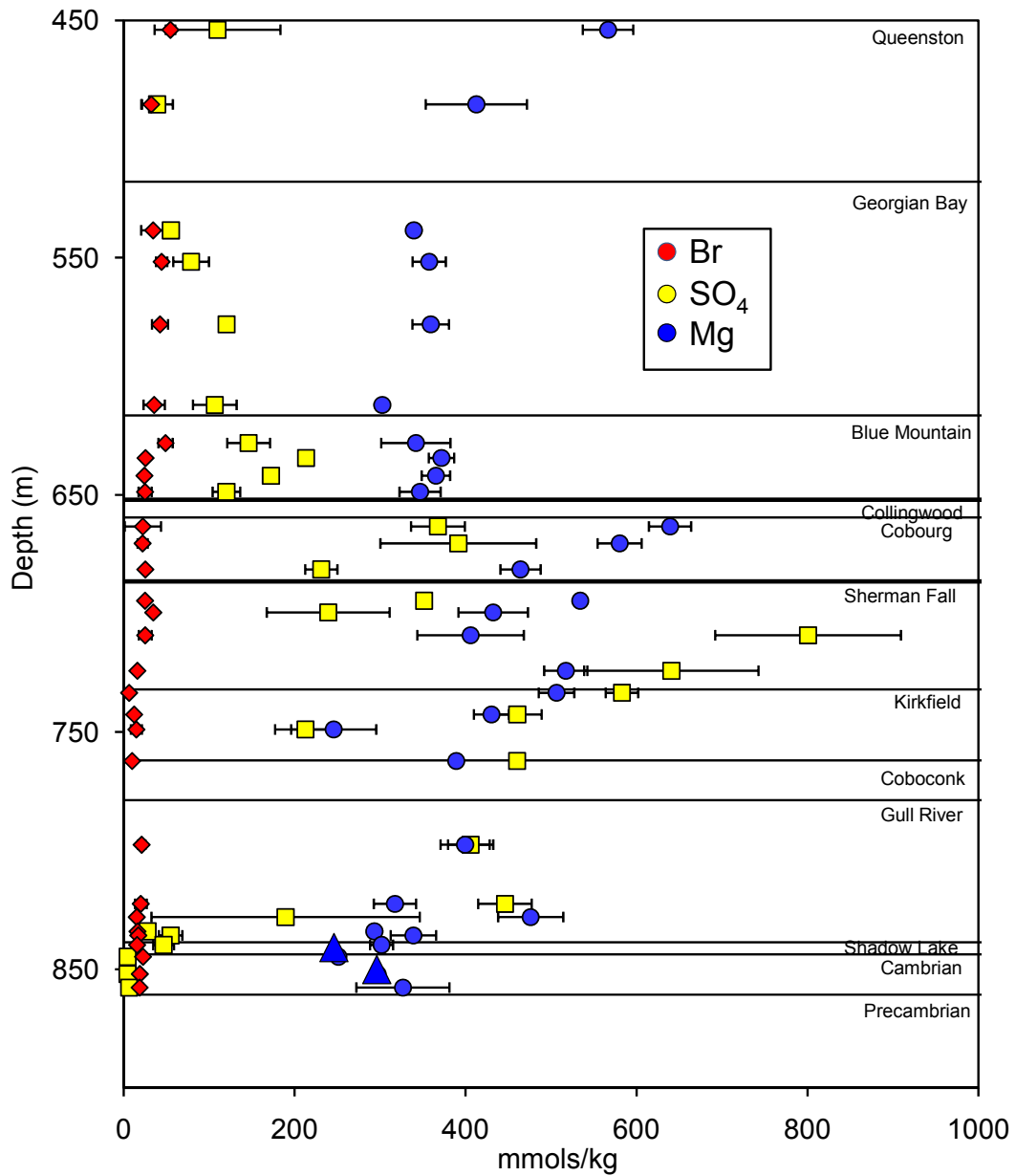


Figure 11 Concentrations of Br^- , SO_4^{2-} and Mg^{2+} Leached by Out-diffusion from Dry Crushed (~2 mm fraction) Rock Following Vacuum Distillation.

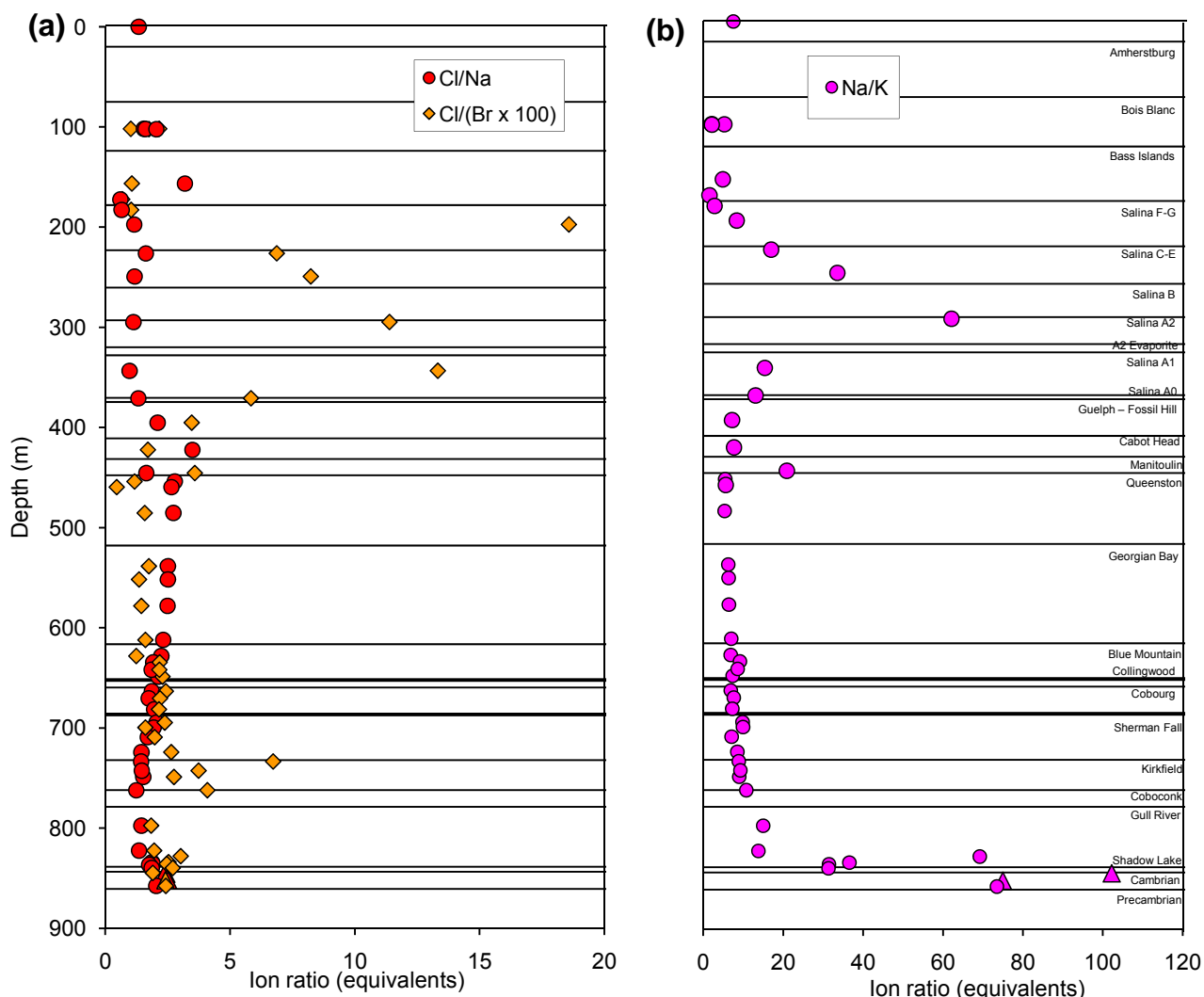


Figure 12 Major Ion Molal Ratios from Concentrations in Porewaters in Figure 9 and 10. All Br values were multiplied by 100 to scale the results and the triangles represent opportunistic groundwater sample results.

4.3 CO₂ and CH₄ from Vacuum Distillation

The concentrations and isotopes measured for CO₂ and CH₄ extracted and trapped during vacuum distillation of porewaters from DRG-2 are tabulated in Appendix C, and plotted with depth in Figures 13, 14 and 15. The methane concentrations (Figure 13) are shown with formation pressure measurements collected following the installation of Westbay equipment. Methane concentrations are low in the Queenston, possibly due to oxidation by the presence there of hematite (Intera Engineering Ltd., 2008b). The maximum methane concentration was observed in the Blue Mountain and upper Collingwood Member of the Cobourg Formation. Future work on organic matter content and evidence for any possible separate gas phase are required to establish the source of CH₄ in this section.

The stable isotope profiles for methane (Figure 14) show a mixing trend through the Middle Ordovician between an apparent thermocatalytic signature in the Cambrian groundwaters (i.e., thermal cracking of hydrocarbons to form methane) with a biogenic component in the Upper Ordovician shales. This biogenic signature in the lower Georgian Bay and Blue Mountain shales is further supported by the $\delta^{13}\text{C}$ profile of CO_2 (Figure 15), in which a strong enrichment in ^{13}C in the 570 m to 650 m zone is diagnostic of bacterial CO_2 reduction.

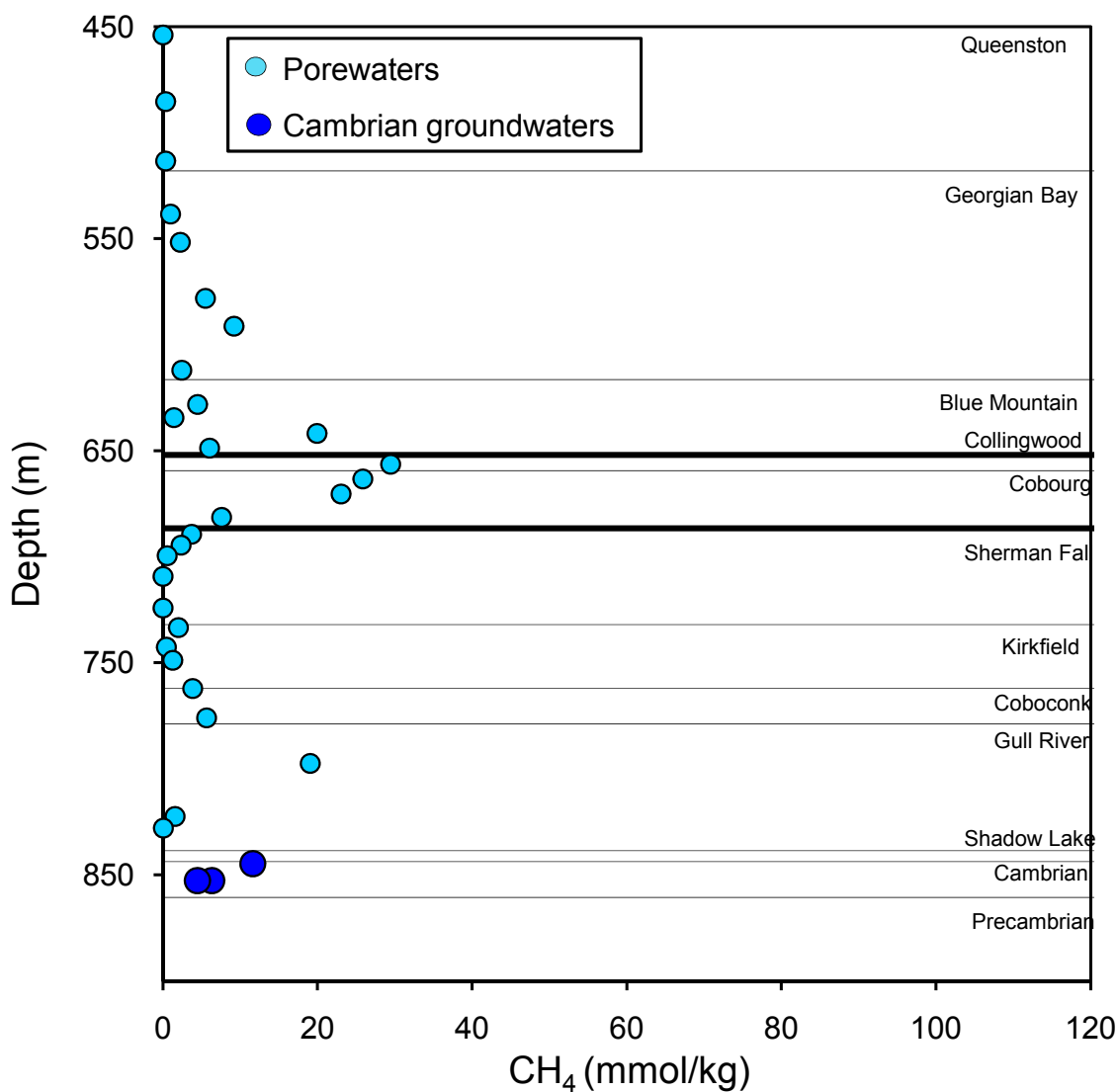


Figure 13 DGR 2 Porewater CH₄ Concentrations Normalized to Water Content.

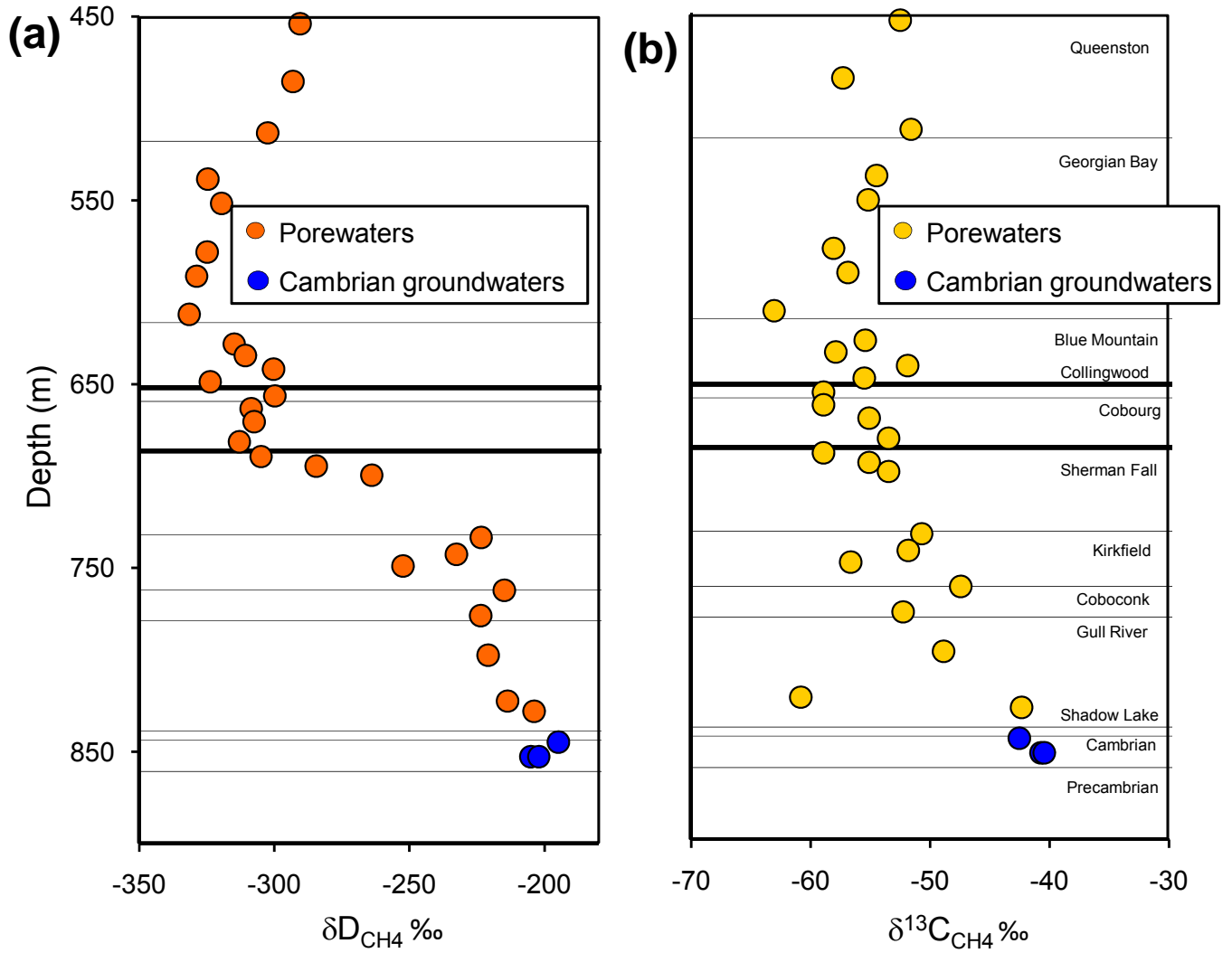


Figure 14 Isotopes of CH₄ in DGR-2 Core.

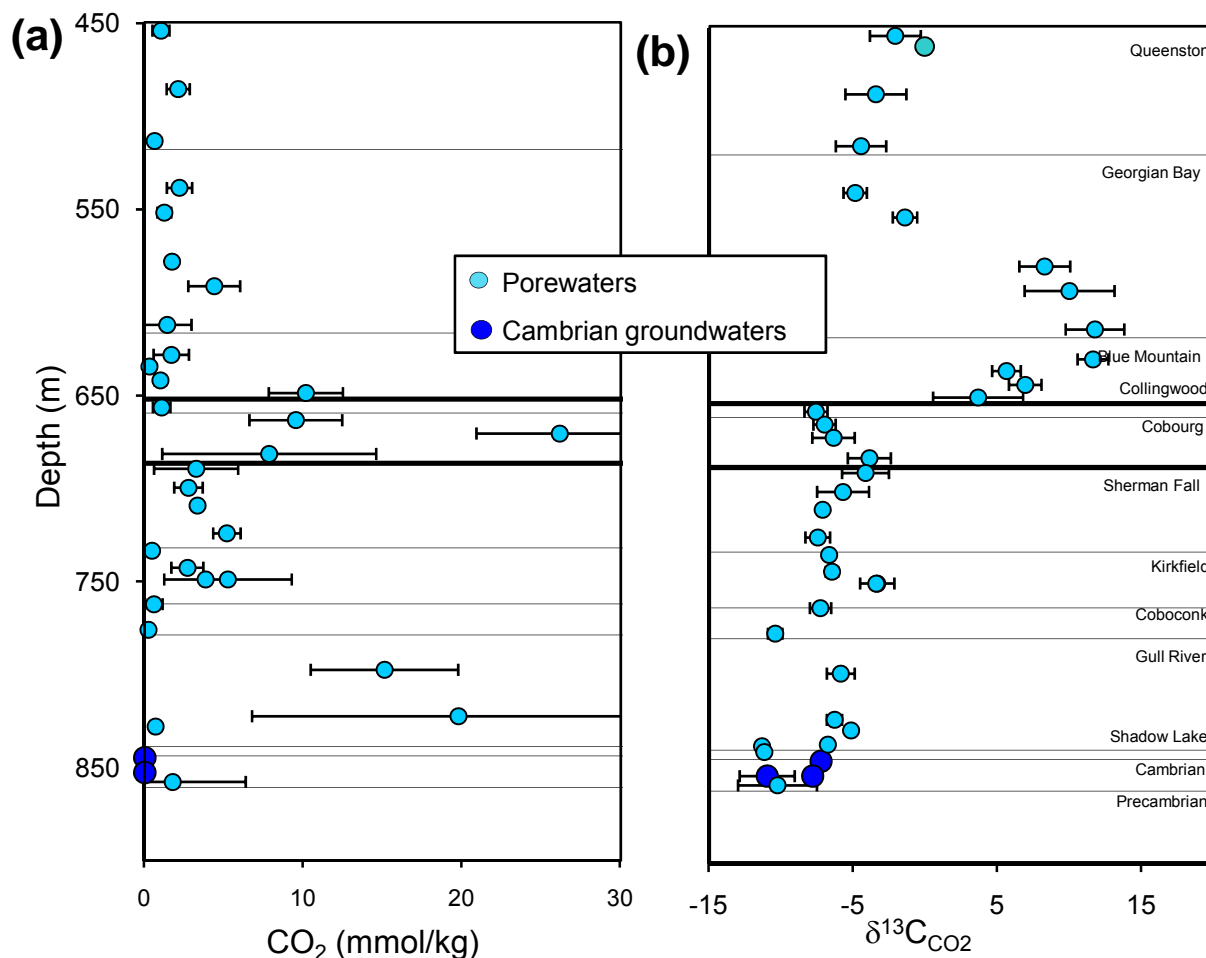


Figure 15 DGR-2 CO₂ Concentration in Pore Fluids Extracted by Vacuum Distillation (a) and δ¹³C of CO₂ from Pore Fluids (b).

4.4 Helium Gas in Pore Fluids

The helium (He) release curves of the multi-step out-diffusion experiments are plotted in Appendix D for each extraction of total He measured in the 20°C out-diffusion experiments. These curves provide an estimate of the total He in the sample at the time of analysis. To account for diffusive loss of He during core shipment following drilling in the field, a correction was made for each that takes into account the rate of degassing and the time delay between drilling the core in DGR-2 and sample analysis in the laboratory at University of Ottawa.

The rate of degassing from the Ordovician shale samples was derived from the Queenston Shale samples (Figure 16). Corrections for the limestones were similarly derived from the exponential rate of degassing from samples with varying time delays. The uncertainties are derived from the variations in porewater content, water saturation of total porosity (from CoreLab data) and an estimated 50% uncertainty in the derived rate of degassing of the limestone samples.

Total He in the core samples with depth is shown in Figure 17 together with the (provisional) measured He in the Cambrian groundwater, sampled in November, 2007. Although total He per g of rock is readily measured by our method, normalizing to porewater content requires a precise measurement of both the brine volume and any separate gas phase that exists. The low solubility of He in brines makes this an important measurement in

establishing the pore-scale partial pressure of He that would drive diffusion through the section. He isotopes are independent of the pore fluid normalization. The helium isotope ratios are also shown in Figure 17, expressed as the $^3\text{He}/^4\text{He}$ ratio in the sample over that for ambient air. The profile suggests a two component system that is separated by a low diffusion zone below the Cobourg (bold dashed lines).

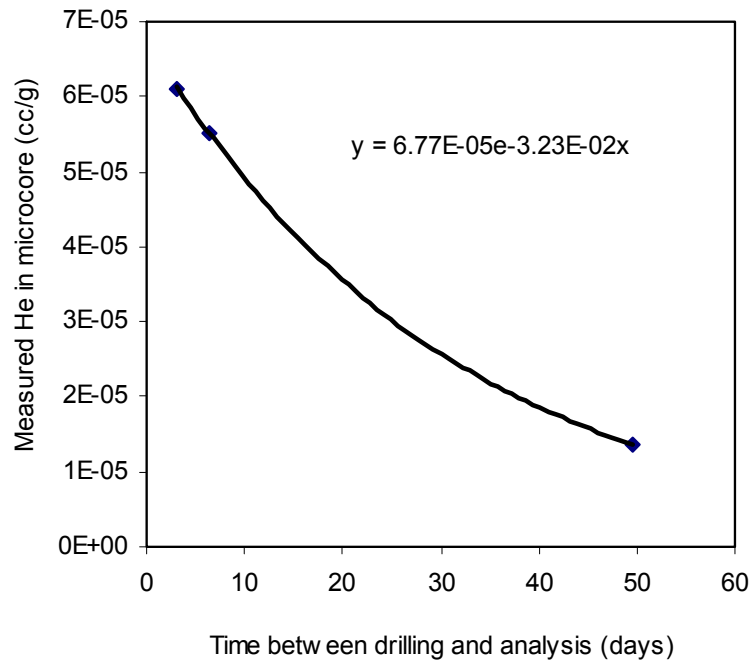


Figure 16 **Degassing of the Queenston Shale Samples due to Storage Time (in days).**

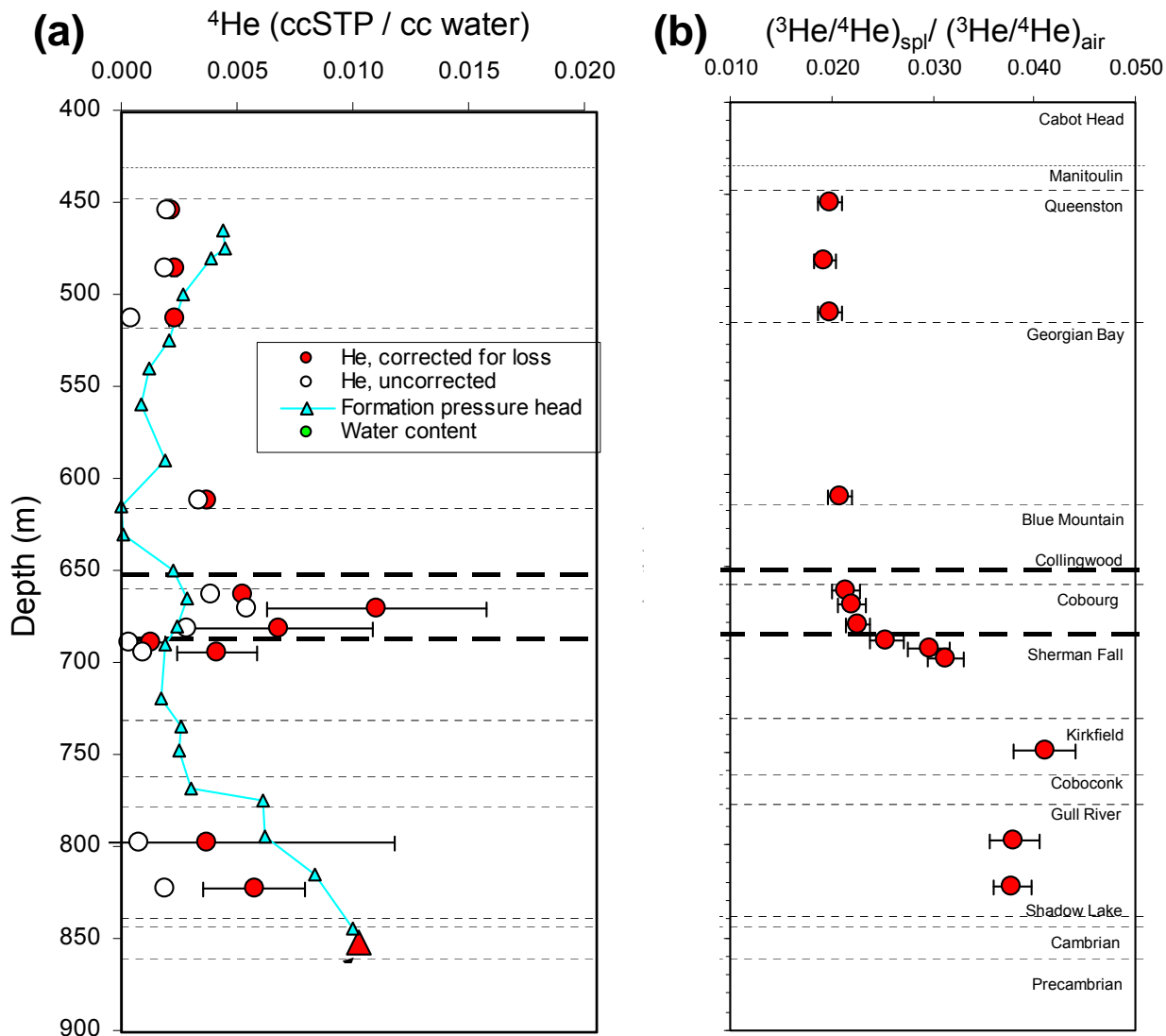


Figure 17 Total Excess He in Pore Spaces (a), Normalized to Volumetric Water Content, for DGR-2 Core; (b) $^3\text{He}/^4\text{He}$ Ratio in Sample Normalized to the Ratio for He in Air.

4.5 Strontium Isotopes in Pore Fluids

Strontium isotopes were measured in four rock samples, 5 opportunistic groundwater samples and 11 porewater samples (Appendix E). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is a reflection of the source of Sr in the rock or water. The present $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in seawater is a relatively constant value of 0.709 although this has varied over the Phanerozoic. The Ordovician to Devonian strontium isotope curve for sea water varies between about 0.7077 and 0.7087 (Veizer, 1989). Increases in this value represent greater contributions of Sr from weathering of the continental crust, which displays enrichments in radiogenic ^{87}Sr from the decay of ^{87}Rb .

The Sr isotopes in porewaters were measured on the acid leachates derived from the vacuum distillation material for porewater geochemistry (presented above). The acid leachates extract strontium from the carbonate matrix of the rock samples. Acid leaching does not sample the Sr in the clastic components of rocks (e.g. clays).

Figure 18 shows the concentration of Sr in porewaters and groundwaters, together with concentrations of Ca^{2+} . Measurements of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio are shown in the right hand diagram of Figure 18. The concentration profiles for Sr and Ca in DGR-2 porewaters both show a depletion trend with depth through the Middle Ordovician limestones, with a reversal to higher values in the lower Gull River and Cambrian. The Sr profile is also very similar to the Cl^- profile observed in Figure 9.

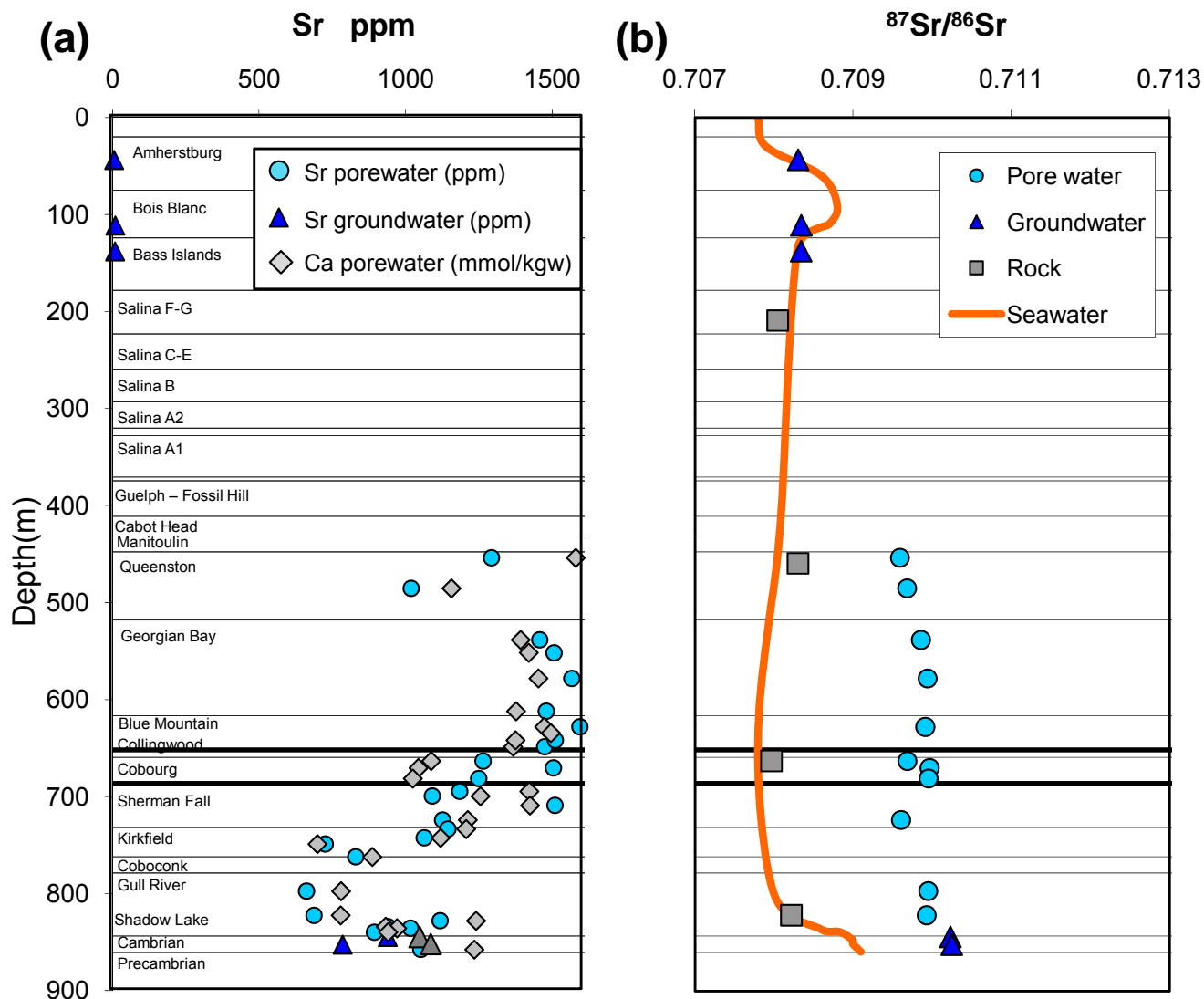


Figure 18 Sr Concentrations (a) and Isotopes (b) in Porewaters, Groundwaters and Selected Rock Samples from DGR-1 and DGR-2 (seawater strontium isotope curve from Veizer, 1989).

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio shows that the DGR-1 opportunistic groundwaters are close to equilibrium with the average value for the rocks, possibly reflecting dissolution and exchange by these meteoric waters. A greater characterization of the shallow formations, including both carbonate and sulphate phases, is required to improve this interpretation.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the DGR-2 porewaters appear to be considerably out of equilibrium with the Sr in the carbonates in the rocks in part of the DGR-2 section. Assuming Sr in the clastic components of the rock is negligible, the samples through the Upper Ordovician shales do show a slight trend towards equilibrium with the

host rock. However, deeper samples through the Middle Ordovician limestones show equilibrium with a more radiogenic source, and are closer to the Cambrian groundwater samples than the sea water curve.

4.6 Level of Confidence in Vacuum Distillation for Stable Isotopes and Geochemistry

Vacuum distillation is routinely used as a method to extract porewaters for isotope analysis from soils and other high permeability materials. Extracting pore fluids from low permeability materials is challenging and several additional methods have been developed to compare with vacuum distillation. However, the very low water content (less than 2% by volume), the very low permeability, and high salinity of the Ordovician formations in DGR-2 make vacuum distillation an appropriate method providing the temperature of extraction is suitably high. The method was applied in this study using a temperature of 150°C, which provided the most accurate results in an inter-comparison study for the Tournemire argillite (Altinier et al., 2007). The following points support the use of vacuum distillation in this study:

- Up to five replicates of each core sample were run routinely on each sample, with standard deviations that varied between 0.1 and 0.5‰ for the Ordovician shales (cap rocks forming the 'upper barrier') and 0.05 to 1‰ for the limestones (average standard deviation of sample replicates was 0.3‰ for DGR-2).
- A risk in vacuum distillation is the incomplete extraction of the porewaters, which can impart an isotopic depletion on the extracted water. Such fractionation is reduced at elevated temperature and so is minimized by the extraction temperatures used. Moreover, an extended extraction time of 6 hours was used in the method. The isotope results, compared with water yields (Figure 4) show that there is no significant trend between low water contents and low $\delta^{18}\text{O}$ values. This lack of correlation suggests that the trend to low $\delta^{18}\text{O}$ values in Figure 6 is real and not an artefact of the method.
- High temperature vacuum distillation will extract all labile water, and not just the free water in open pores. That is to say hydrous minerals including gypsum and smectite clays will contribute to the extracted water. In the Silurian sections of DGR-1 (172 m to 294 m depth; Figure 6), there is clear evidence from both the water yields (exceeding 15% by volume) and the Ca-SO_4 facies of the leach water (i.e., at gypsum saturation) that gypsum water has contributed to the extracted water. However, in DGR-2 the Ordovician rocks are free of gypsum (Intera Engineering Ltd., 2008b) and are dominated by illite, which is considered to be essentially free of interlayer water.
- The depletion observed for $\delta^{18}\text{O}$ in the Ordovician limestones is not paralleled with a depletion in δD , as would be expected for an experimental artefact related to incomplete distillation. This was demonstrated by Altinier et al. (2007) where their low temperature extractions resulted in depletion for both $\delta^{18}\text{O}$ and δD . If vacuum distillation was fractionating ^{18}O , then D would be similarly affected. From a comparison of Figure 6 and Figure 7, this is not the case.
- A complete extraction and analysis of core material was repeated for the two samples with the most depleted $\delta^{18}\text{O}$ and low water content (797 m and 822 m depth). The repeat extraction was undertaken using a longer extraction time and higher temperature (200°C). The results were all within analytical uncertainty for the mass spectrometer, and were very close to the originally extracted samples (Tables 1 and 2).
- A high degree of confidence is provided by the similar profiles for $\delta^{18}\text{O}$ and major ions. In particular, the observed trend for $\delta^{18}\text{O}$ to more negative values through the Ordovician limestones, with characteristic shift towards the Cambrian values is also found in the geochemical profiles for Cl^- and Ca^{2+} (with opposite profile for Na^+). That very similar trends are found in data derived by fundamentally different analytical means (isotopes of extracted porewaters vs. solutes leached from the dried bulk rock and

normalized to the extracted porewater mass) gives confidence that the observed trends are real, and not artefacts of the methods.

- The profiles for the stable isotopes and for solutes extracted by vacuum distillation all trend at the deepest levels in DGR-2 to the value for the Cambrian groundwater collected from DGR-2 (e.g., Figure 6). The convergence of the profiles from porewater analysis with the actual Cambrian groundwater at the base of the profile demonstrates that the data accurately represent in-situ porewater values.

5 Data Quality and Use

As discussed in Section 4.6, there is evidence to believe that the data presented in this Technical Report are reliable and representative of isotopic characteristics of porewaters and gases in the cores collected from boreholes DGR-1 and DGR-2.

6 Conclusions

Porewaters and gases were extracted for isotope analysis by vacuum distillation at 150°C from 17 core samples in DGR-1 and from 34 in DGR-2. Good reproducibility (quintuplicate analysis for most samples), good repeat analysis (two samples), and results close to values for associated opportunistic groundwater samples (Devonian and Cambrian samples) indicate reasonable precision and accuracy with the method.

Volumetric water contents calculated from water yields following vacuum distillation correspond closely with those obtained from other methods. Samples were analyzed for major ion concentrations by leaching dry rock samples following vacuum distillation, and the leached ion masses were then normalized to extracted water volume to give porewater concentrations in ppm. Low variability for most replicates and very close correspondence with solute concentrations in the Cambrian brine provide confidence in both precision and accuracy of the results.

The results for $\delta^{18}\text{O}$ and major ions in DGR-2 provide very similar depth profiles, with uniformly high concentrations through the upper Ordovician shales, a trend to lower values in the middle Ordovician limestones, and a reversal to more elevated concentrations in the Shadow Lake Formation and Cambrian. CO_2 and CH_4 were separately trapped during vacuum distillation. Results (concentrations and isotopes) demonstrate in situ gas production by bacterial methanogenesis in the Georgian Bay shales, with little diffusive migration up or down section. He concentrations and $^3\text{He}/^4\text{He}$ ratios suggest two major He production zones in the Collingwood shale and the Precambrian bedrock.

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APPENDIX A

DGR-1 and DGR-2 Porewater Mass and Stable Isotopes

(yellow highlighted cells not used in profiles)

Extraction date	Sample ID	#	Wet rock (g)	Dry Rock (g)	Weight lost (g)	Water yield (g)	fraction yield	Water content (% vol.)	$\delta^{18}\text{O}$ ‰ VSMOW	δD ‰ VSMOW
30-Mar-07	DGR1-101.89	1	31.8982	30.8253	1.0729	1.07	0.99	9.3	-11.61	-90.6
30-Mar-07	DGR1-101.89	2	32.5657	32.5077	0.058	0.35	6.08	2.9	n/a	n/a
30-Mar-07	DGR1-101.89	3	33.7211	31.9492	1.7719	1.71	0.96	14.4	-12.38	-96.1
30-Mar-07	DGR1-101.89	4	30.8349	29.8027	1.0322	0.91	0.88	8.2	-17.63	-143.1
26-Mar-07	DGR1-101.89	5	34.017	32.6092	1.4078	1.40	1.00	11.6	-12.01	-90.6
26-Mar-07	DGR1-101.89	6	31.9749	30.4809	1.494	1.49	0.99	13.2	-12.22	-93.1
26-Mar-07	DGR1-101.89	7	33.7211							
26-Mar-07	DGR1-101.89	8	30.5125	29.2977	1.2148	1.20	0.99	11.1	-12.56	-94.8
21-Mar-07	DGR1-101.99	1	26.8905	26.1229	0.7676	0.77	1.00	8.0	-10.42	-86.9
21-Mar-07	DGR1-101.99	2	28.4949	27.5967	0.8982	0.89	1.00	8.7	-11.75	-88.8
21-Mar-07	DGR1-101.99	3	31.8319	31.1247	0.7072	0.70	0.99	6.1	-9.36	-82.4
21-Mar-07	DGR1-101.99	4	32.0167	31.3722	0.6445	0.64	1.00	5.5	-10.82	-82.1
9-Mar-07	DGR1-101.99	5	23.4607	23.228	0.2327	0.04	0.18	0.5	-21.80	-153.1
9-Mar-07	DGR1-101.99	6	29.152	28.693	0.459	0.45	0.98	4.2	-10.93	-87.8
9-Mar-07	DGR1-101.99	7	30.4404	29.8031	0.6373	0.63	0.98	5.7	-11.16	-90.1
9-Mar-07	DGR1-101.99	8	28.6003	27.8581	0.7422	0.73	0.99	7.1	-10.75	-88.5
28-Feb-07	DGR1-102.26	1	33.0679	31.1888	1.8791	1.84	0.98	15.9	-11.44	-88.4
28-Feb-07	DGR1-102.26	2	33.4104	31.8225	1.5879	1.56	0.98	13.2	-10.60	-85.2
28-Feb-07	DGR1-102.26	3	32.4296	31.2235	1.2061	1.20	0.99	10.4	-10.21	-85.5
28-Feb-07	DGR1-102.26	4	36.4569	34.7469	1.71	1.65	0.97	12.8	-13.20	-106.1
5-Mar-07	DGR1-102.26	5	33.3636	32.801	0.5626	0.56	0.99	4.6	-10.43	-84.3
5-Mar-07	DGR1-102.26	6	32.0269	30.9727	1.0542	1.05	0.99	9.1	-10.24	-83.8
5-Mar-07	DGR1-102.26	7	31.1082	30.5697	0.5385	0.52	0.97	4.6	-9.30	-79.7
5-Mar-07	DGR1-102.26	8	33.0518	32.5344	0.5174	0.51	0.98	4.2	-9.88	-81.7
2-Apr-07	DGR1-156.56	1	34.7864	34.0045	0.7819	0.77	0.98	6.1	-7.76	-67.5
2-Apr-07	DGR1-156.56	2	39.6054	38.8223	0.7831	0.75	0.96	5.2	-7.19	-63.2
2-Apr-07	DGR1-156.56	3	37.8199	37.1029	0.717	0.70	0.98	5.1	-6.33	-60.8
2-Apr-07	DGR1-156.56	4	41.561	40.7224	0.8386	0.83	0.99	5.5	-7.04	-65.0
2-Apr-07	DGR1-156.56	5	36.9246	36.2644	0.6602	0.64	0.97	4.8	-6.52	-60.8
18-Apr-07	DGR1-172.32	1	33.8412	32.711	1.1302	0.89	0.78	7.3	-12.52	-127.0
18-Apr-07	DGR1-172.32	2	37.2501	35.9199	1.3302	1.33	1.00	10.0	-10.17	-106.6
18-Apr-07	DGR1-172.32	3	32.1767	30.8224	1.3543	1.35	1.00	11.8	-11.24	-108.9
18-Apr-07	DGR1-172.32	4	32.6396	31.5895	1.0501	1.04	0.99	8.9	-10.34	-101.0
18-Apr-07	DGR1-172.32	5	35.7818	35.1972	0.5846	0.58	0.99	4.4	-9.84	-94.5
1-May-07	DGR1-182.89	1	36.7903	34.8735	1.9168	1.92	1.00	14.8	-8.75	-91.8
1-May-07	DGR1-182.89	2	35.149	33.5997	1.5493	1.54	1.00	12.4	-8.37	-85.2
1-May-07	DGR1-182.89	3	35.5741	33.8308	1.7433	1.74	1.00	13.9	-8.57	-88.8
11-May-07	DGR1-197.45	4	35.3822	33.1402	2.242	2.24	1.00	18.2	-8.48	-75.2
11-May-07	DGR1-197.45	5	33.5813	32.1068	1.4745	1.47	0.99	12.3	-9.46	-70.2
8-May-07	DGR1-226.27	4	34.4132	31.852	2.5612	2.55	1.00	21.7	-8.97	-76.6
8-May-07	DGR1-226.27	5	34.8656	34.1617	0.7039	0.70	0.99	5.5	-8.67	-73.8
1-May-07	DGR1-249.33	4	34.5916	31.5663	3.0253	3.02	1.00	25.8	-11.07	-61.6
1-May-07	DGR1-249.33	5	33.9975	31.0695	2.928	2.93	1.00	25.5	-10.96	-61.1
25-Apr-07	DGR1-294.84	1	38.8089	36.3621	2.4468	2.43	1.00	18.1	-8.67	-64.2
25-Apr-07	DGR1-294.84	2	39.8799	38.3007	1.5792	1.57	0.99	11.1	-8.32	-63.9
25-Apr-07	DGR1-294.84	3	40.9413	38.6794	2.2619	2.25	1.00	15.7	-8.75	-63.7
25-Apr-07	DGR1-294.84	4	39.6913	37.2453	2.446	2.44	1.00	17.7	-8.50	-65.5
17-May-07	DGR1-294.84	5	31.7628	29.1656	2.5972	2.59	1.00	24.0	-8.11	-67.0
17-May-07	DGR1-294.84	6	34.769	32.3641	2.4049	2.40	1.00	20.0	-8.93	-67.5

17-May-07	DGR1-294.84	7	33.6451	31.1561	2.489	2.48	1.00	21.5	-8.68	-68.2
17-May-07	DGR1-294.84 (Gypsum)	8	25.8224	22.5921	3.2303	3.19	0.99	38.1	-8.83	-77.5
17-May-07	DGR1-294.84 (Gypsum)	9	24.1013	23.0451	1.0562	1.05	0.99	12.3	-7.81	-73.4
13-Apr-07	DGR1-343.49	1	32.5589	32.4683	0.0906	0.04	0.49	0.4	-15.18	-58.9
13-Apr-07	DGR1-343.49	2	38.9967	38.8746	0.1221	0.11	0.92	0.8	-13.52	-76.2
13-Apr-07	DGR1-343.49	3	38.611	38.4814	0.1296	0.12	0.91	0.8	-11.85	-90.9
13-Apr-07	DGR1-343.49	4	40.1095	39.9856	0.1239	0.12	0.93	0.8	-12.32	-66.1
13-Apr-07	DGR1-343.49	5	40.2929	40.1501	0.1428	0.13	0.94	0.9	-11.58	-88.0
3-May-07	DGR1-370.93	1	36.6217	36.5695	0.0522	0.05	0.98	0.4	-7.22	-61.4
3-May-07	DGR1-370.93	2	40.5811	40.5086	0.0725	0.06	0.88	0.4	-7.02	-57.3
3-May-07	DGR1-370.93	3	37.6617	37.569	0.0927	0.08	0.89	0.6	-7.16	-56.9
3-May-07	DGR1-395.29	4	36.5958	36.2168	0.379	0.37	0.98	2.8	-6.45	-51.3
3-May-07	DGR1-395.29	5	34.7783	34.3929	0.3854	0.38	0.98	3.0	-6.74	-59.0
11-May-07	DGR1-422.40	1	35.4591	34.291	1.1681	1.16	1.00	9.2	-3.24	-46.5
11-May-07	DGR1-422.40	2	37.4979	36.5446	0.9533	0.95	0.99	7.0	-3.80	-47.7
11-May-07	DGR1-422.40	3	38.5598	37.6358	0.924	0.77	0.84	5.6	-5.18	-57.0
8-May-07	DGR1-445.60	1	34.3506	33.467	0.8836	0.88	0.99	7.1	-2.37	-44.9
8-May-07	DGR1-445.60	2	37.4688	36.6277	0.8411	0.84	0.99	6.2	-3.05	-49.7
8-May-07	DGR1-445.60	3	37.5955	36.8048	0.7907	0.74	0.93	5.4	-4.82	-62.7
20-Apr-07	DGR1-459.62	1	41.6408	40.5525	1.0883	1.08	1.00	7.2	-3.18	-49.1
20-Apr-07	DGR1-459.62	2	39.0457	37.9731	1.0726	1.07	1.00	7.6	-3.32	-48.8
20-Apr-07	DGR1-459.62	3	38.9672	37.9047	1.0625	1.06	0.99	7.5	-2.74	-47.5
20-Apr-07	DGR1-459.62	4	39.0823	37.9823	1.1	1.10	1.00	7.8	-3.10	-47.5
20-Apr-07	DGR1-459.62	5	36.7145	35.8089	0.9056	0.90	1.00	6.8	-3.24	-43.2
4-Jun-07	DGR2-453.95	1	38.8227	37.5926	1.2301	1.22	0.99	8.8	-2.94	-49.4
4-Jun-07	DGR2-453.95	2	39.1512	37.943	1.2082	1.20	1.00	8.6	-3.91	-43.0
4-Jun-07	DGR2-453.95	3	37.7678	36.6149	1.1529	1.15	1.00	8.5	-3.89	-39.9
4-Jun-07	DGR2-453.95	4	38.3975	37.2232	1.1743	1.17	1.00	8.5	-3.52	-44.6
4-Jun-07	DGR2-453.95	5	36.3494	35.2975	1.0519	1.05	1.00	8.0	-3.81	-49.6
5-Jun-07	DGR2-485.40	1	30.4491	29.5328	0.9163	0.91	0.99	8.3	-4.11	-47.2
5-Jun-07	DGR2-485.40	2	36.5332	35.4777	1.0555	1.05	1.00	8.0	-3.75	-48.6
5-Jun-07	DGR2-485.40	3	34.57	33.5902	0.9798	0.98	1.00	7.9	-3.53	-47.5
5-Jun-07	DGR2-485.40	4	37.7828	36.7032	1.0796	1.07	1.00	7.9	-3.68	-47.0
5-Jun-07	DGR2-485.40	5	31.0313	30.1635	0.8678	0.86	1.00	7.7	-3.91	-52.3
8-Jul-07	DGR2-513.35	1	38.109	36.9937	1.1153	1.11	0.99	8.1	-3.18	-48.1
8-Jul-07	DGR2-513.35	2	37.2622	36.1525	1.1097	1.10	0.99	8.2	-4.08	-48.5
8-Jul-07	DGR2-513.35	3	36.5335	35.4005	1.133	1.12	0.99	8.6	-3.82	-48.2
8-Jul-07	DGR2-513.35	4	38.23	37.1844	1.0456	1.04	0.99	7.5	-4.43	-54.5
8-Jul-07	DGR2-513.35	5	37.8907	36.8661	1.0246	1.02	0.99	7.4	-4.19	-54.1
10-Jun-07	DGR2-538.51	1	35.4627	34.5003	0.9624	0.95	0.99	7.4	-3.29	-49.6
10-Jun-07	DGR2-538.51	2	31.7183	30.747	0.9713	0.96	0.99	8.4	-3.87	-48.4
10-Jun-07	DGR2-538.51	3	29.3931	28.4338	0.9593	0.95	0.99	9.0	-3.43	-46.5
10-Jun-07	DGR2-538.51	4	27.6613	26.8192	0.8421	0.73	0.87	7.4	-5.27	-61.6
10-Jun-07	DGR2-538.51	5	35.3057	34.2873	1.0184	0.96	0.94	7.6	-4.34	-52.9
15-Jun-07	DGR2-551.75	1	34.9217	33.9121	1.0096	1.00	0.99	8.0	-3.57	-48.4
15-Jun-07	DGR2-551.75	2	35.6909	34.7239	0.967	0.96	0.99	7.5	-3.81	-47.4
15-Jun-07	DGR2-551.75	3	34.8401	33.7378	1.1023	1.09	0.99	8.8	-3.82	-46.7
15-Jun-07	DGR2-551.75	4	36.7464	35.5495	1.1969	1.19	0.99	9.0	-3.51	-46.4
11-Jun-07	DGR2-578.15	1	34.6279	33.5751	1.0528	1.05	1.00	8.4	-3.65	-45.3
11-Jun-07	DGR2-578.15	2	34.4139	33.406	1.0079	1.01	1.00	8.2	-3.79	-50.1
11-Jun-07	DGR2-578.15	3	35.3873	34.294	1.0933	1.09	1.00	8.6	-3.80	-46.7
11-Jun-07	DGR2-578.15	4	35.7905	34.7527	1.0378	1.03	1.00	8.0	-3.35	-46.5
11-Jun-07	DGR2-578.15	5	31.7786	31.5243	0.2543	0.04	0.15		-19.05	-140.6

6-Jul-07	DGR2-591.33	1	36.2135	35.0733	1.1402	1.13	0.99	8.7	-3.15	-46.8
6-Jul-07	DGR2-591.33	2	38.8857	37.7894	1.0963	1.09	0.99	7.8	-3.85	-52.3
6-Jul-07	DGR2-591.33	3	34.5352	33.5419	0.9933	0.98	0.99	7.9	-3.58	-48.6
6-Jul-07	DGR2-591.33	4	37.9773	36.8902	1.0871	1.08	0.99	7.9	-3.73	-55.2
6-Jul-07	DGR2-591.33	5	32.9819	32.0786	0.9033	0.89	0.99	7.5	-4.09	-56.3
9-Jun-07	DGR2-612.09	1	37.4685	36.3439	1.1246	1.11	0.99	8.2	-3.57	-47.1
9-Jun-07	DGR2-612.09	2	38.3359	37.2504	1.0855	1.08	0.99	7.8	-3.61	-51.9
9-Jun-07	DGR2-612.09	3	34.6976	33.6334	1.0642	1.05	0.99	8.5	-3.43	-49.4
9-Jun-07	DGR2-612.09	4	36.5772	35.4877	1.0895	0.99	0.91	7.5	-5.12	-57.4
9-Jun-07	DGR2-612.09	5	35.9309	34.9048	1.0261	1.01	0.98	7.8	-4.30	-50.6
10-Jul-07	DGR2-628.18	1	35.5595	34.4074	1.1521	1.15	1.00	9.0	-6.64	-49.3
10-Jul-07	DGR2-628.18	2	36.0787	35.1151	0.9636	0.96	1.00	7.4	-4.40	-51.4
10-Jul-07	DGR2-628.18	3	37.8346	36.8398	0.9948	0.99	1.00	7.3	-4.28	-47.9
10-Jul-07	DGR2-628.18	4	38.8056	37.6287	1.1769	1.17	1.00	8.4	-4.38	-46.9
10-Jul-07	DGR2-628.18	5	37.1973	36.2907	0.9066	0.90	1.00	6.7	-4.79	-51.5
13-Sep-07	DGR2-634.49	1	43.711	42.6708	1.0402	0.967	0.93	6.1	-6.69	-64.3
13-Sep-07	DGR2-634.49	2	43.5615	42.4054	1.1561	1.152	1.00	7.3	-5.73	-51.8
13-Sep-07	DGR2-634.49	3	42.1381	41.0537	1.0844	1.09	1.01	7.2	-4.61	-51.0
13-Sep-07	DGR2-634.49	4	43.0342	41.9383	1.0959	1.087	0.99	7.0	-5.21	-49.5
13-Sep-07	DGR2-634.49	5	44.1652	43.0806	1.0846	1.073	0.99	6.7	-5.46	-51.4
5-Sep-07	DGR2-641.92	1	38.6211	37.6462	0.9749	0.981	1.01	7.0	-4.16	-45.8
5-Sep-07	DGR2-641.92	2	42.7716	41.7526	1.019	1.021	1.00	6.6	-4.66	-49.6
5-Sep-07	DGR2-641.92	3	41.2396	40.2638	0.9758	0.977	1.00	6.6	-4.87	-47.7
5-Sep-07	DGR2-641.92	4	41.7655	40.828	0.9375	0.944	1.01	6.2	-4.98	-51.5
5-Sep-07	DGR2-641.92	5	42.355	41.5228	0.8322	1.77	2.13	11.5	-7.23	-71.1
22-Jun-07	DGR2-648.75	1	34.6258	33.8811	0.7447	0.70	0.94	5.6	-5.54	-61.8
22-Jun-07	DGR2-648.75	2	37.691	36.9149	0.7761	0.77	0.99	5.6	-5.27	-50.7
22-Jun-07	DGR2-648.75	3	36.08	35.3315	0.7485	0.71	0.95	5.4	-5.82	-57.1
22-Jun-07	DGR2-648.75	4	34.3314	33.6505	0.6809	0.63	0.93	5.1	-6.60	-63.5
22-Jun-07	DGR2-648.75	5	39.0108	38.3312	0.6796	0.52	0.76	3.6		-62.7
14-Sep-07	DGR2-656.41	1	41.0225	40.7424	0.2801	0.205	0.73	1.4	-10.63	-84.5
14-Sep-07	DGR2-656.41	2	41.3645	41.1035	0.261	0.254	0.97	1.7	-8.17	-56.8
14-Sep-07	DGR2-656.41	3	42.3134	42.0399	0.2735	0.208	0.76	1.3	-10.45	-95.5
14-Sep-07	DGR2-656.41	4	37.908	37.6744	0.2336	0.231	0.99	1.7	-3.38	-56.8
14-Sep-07	DGR2-656.41	5	44.0621	43.7656	0.2965	0.238	0.80	1.5	-4.16	-84.9
18-Jun-07	DGR2-663.34	1	28.2753	28.1514	0.1239	0.12	0.96	1.1	-6.25	-53.9
18-Jun-07	DGR2-663.34	2	29.9053	29.7477	0.1576	0.15	0.92	1.3	-7.13	-53.4
18-Jun-07	DGR2-663.34	3	36.5859	36.4228	0.1631	0.15	0.93	1.1	-6.11	-51.9
18-Jun-07	DGR2-663.34	5	32.242	32.113	0.129	0.12	0.91	1.0	-6.21	-46.4
19-Jun-07	DGR2-670.48	1	37.9639	37.7889	0.175	0.17	0.98	1.2	-5.97	-55.3
19-Jun-07	DGR2-670.48	2	39.9608	39.7806	0.1802	0.17	0.96	1.2	-5.68	-55.0
19-Jun-07	DGR2-670.48	3	38.7276	38.5581	0.1695	0.16	0.94	1.1	-5.76	-53.7
19-Jun-07	DGR2-670.48	4	40.5083	40.3352	0.1731	0.16	0.94	1.1	-5.90	-52.7
19-Jun-07	DGR2-670.48	5	40.5071	40.345	0.1621	0.15	0.94	1.0	-6.46	-58.5
21-Jun-07	DGR2-681.45	1	36.5118	36.0935	0.4183	0.41	0.97	3.0	-5.64	-50.6
21-Jun-07	DGR2-681.45	2	36.9419	36.4897	0.4522	0.44	0.98	3.3	-5.55	-53.4
21-Jun-07	DGR2-681.45	3	36.6141	36.1789	0.4352	0.42	0.97	3.2	-5.22	-46.9
21-Jun-07	DGR2-681.45	4	37.0648	36.5706	0.4942	0.48	0.98	3.6	-5.29	-55.0
21-Jun-07	DGR2-681.45	5	37.3078	36.9199	0.3879	0.38	0.97	2.8	-5.82	-53.0
27-Jun-07	DGR2-689.45	1	36.1321	35.8547	0.2774	0.27	0.98	2.1	-5.38	-56.1
27-Jun-07	DGR2-689.45	2	37.576	37.3764	0.1996	0.19	0.96	1.4	-5.92	-55.8
27-Jun-07	DGR2-689.45	3	37.6259	37.4392	0.1867	0.18	0.96	1.3	-5.42	-57.6
27-Jun-07	DGR2-689.45	4	36.7688	36.3776	0.3912	0.38	0.98	2.8	-5.55	-61.8
29-Jun-07	DGR2-694.63	1	39.466	39.0515	0.4145	0.41	0.99	2.8	-5.47	-54.6

29-Jun-07	DGR2-694.63	2	39.6889	39.4239	0.265	0.25	0.96	1.7	-6.98	-56.7
29-Jun-07	DGR2-694.63	3	37.5118	37.398	0.1138	0.11	0.95	0.8	-4.80	-46.7
29-Jun-07	DGR2-694.63	4	37.0701	36.7958	0.2743	0.27	0.98	2.0	-5.88	-51.4
29-Jun-07	DGR2-694.63	5	38.3736	38.2865	0.0871	0.08	0.90	0.6	-5.65	-47.9
9-Jul-07	DGR2-699.58	1	38.7688	38.0402	0.7286	0.72	0.99	5.1	-6.54	-52.6
9-Jul-07	DGR2-699.58	2	36.245	35.8034	0.4416	0.43	0.98	3.3	-7.00	-54.3
9-Jul-07	DGR2-699.58	3	37.409	37.1344	0.2746	0.27	0.97	1.9	-7.08	-59.9
9-Jul-07	DGR2-699.58	4	37.7521	37.2924	0.4597	0.45	0.99	3.3	-6.76	-56.5
9-Jul-07	DGR2-699.58	5	35.135	34.8426	0.2924	0.28	0.97	2.2	-7.05	-54.0
13-Jul-07	DGR2-709.21	1	36.7047	36.0091	0.6956	0.69	0.99	5.2	-6.50	-48.6
13-Jul-07	DGR2-709.21	2	34.575	34.325	0.25	0.24	0.96	1.9	-6.96	-53.0
13-Jul-07	DGR2-709.21	3	28.7865	28.6111	0.1754	0.17	0.95	1.6	-8.08	-54.0
13-Jul-07	DGR2-709.21	4	34.8323	34.6829	0.1494	0.14	0.93	1.1	-10.08	
13-Jul-07	DGR2-709.21	5	39.0245	38.9693	0.0552	-0.01	-0.09	0.0	-10.44	
12-Sep-07	DGR2-724.16	1	45.9208	45.8525	0.0683	0.073	1.06	0.4	-8.96	-51.8
12-Sep-07	DGR2-724.16	2	43.4905	43.3807	0.1098	0.114	1.04	0.7	-7.79	-47.5
12-Sep-07	DGR2-724.16	3	43.317	43.1356	0.1814	0.187	1.03	1.2	-7.67	-53.4
12-Sep-07	DGR2-724.16	4	43.8086	43.7747	0.0339	0.04	1.19	0.2	-8.26	44.2
12-Sep-07	DGR2-724.16	5	42.1731	42.0418	0.1313	0.133	1.01	0.9	-7.65	-50.3
17-Sep-07	DGR2-733.48	1	42.9065	42.831	0.0755	0.052	0.68	0.3	-10.34	-31.6
17-Sep-07	DGR2-733.48	2	40.2944		70.0338				-14.53	-77.8
17-Sep-07	DGR2-733.48	3	41.6284	41.423	0.2054	0.206	1.00	1.3	-6.08	-46.4
17-Sep-07	DGR2-733.48	4	41.8295	41.62	0.2095	0.207	0.99	1.3	-7.00	-46.9
17-Sep-07	DGR2-733.48	5	43.4321	43.2021	0.23	0.245	1.06	1.5	-4.72	-37.7
10-Sep-07	DGR2-742.61	1	40.4159	40.1407	0.2752	0.06	0.22	0.4	-24.08	-139.0
10-Sep-07	DGR2-742.61	2	37.9073	37.6083	0.299	0.304	1.02	2.2	-9.82	-67.2
10-Sep-07	DGR2-742.61	3	37.6211	37.295	0.3261	0.331	1.02	2.4	-9.25	-61.5
10-Sep-07	DGR2-742.61	4	40.9906	40.701	0.2896	0.295	1.02	2.0	-7.47	-53.3
10-Sep-07	DGR2-742.61	5	36.6464	36.3746	0.2718	0.276	1.02	2.1	-8.36	-58.0
12-Jul-07	DGR2-748.92	1	32.3978			0.48			0.44	-38.9
12-Jul-07	DGR2-748.92	2	35.8415			0.58			-13.56	-42.2
12-Jul-07	DGR2-748.92	3	37.1917			0.47			-8.96	-55.6
12-Jul-07	DGR2-748.92	4	36.2929			0.50			-10.44	-51.4
12-Jul-07	DGR2-748.92	5	37.9769			0.48			-9.50	-61.2
14-Jul-07	DGR2-748.92	6	37.6382	37.0615	0.5767	0.57	0.99	4.2	-7.89	-37.6
14-Jul-07	DGR2-748.92	7	38.414	37.9856	0.4284	0.42	0.98	3.0	4.03	-41.7
14-Jul-07	DGR2-748.92	8	37.0772	36.4827	0.5945	0.59	0.99	4.4	-6.20	-37.2
18-Sep-07	DGR2-762.19	1	40.47887	40.2161	0.2628	0.26	0.98	1.7	-7.53	-50.4
18-Sep-07	DGR2-762.19	2	41.81728	41.6746	0.1427	0.13	0.94	0.9	-6.64	-34.0
18-Sep-07	DGR2-762.19	3	40.48033	40.1662	0.3141	0.31	0.98	2.1	-7.54	-50.8
18-Sep-07	DGR2-762.19	4	39.94818	39.6719	0.2763	0.27	0.97	1.8	-8.09	-49.9
20-Sep-07	DGR2-775.99	1	42.8174	42.7758	0.0416	0.04	1.01	0.3	-6.86	-5.8
20-Sep-07	DGR2-775.99	2	39.5467	39.4964	0.0503	0.05	0.91	0.3	-6.15	13.9
20-Sep-07	DGR2-775.99	3	39.1398	39.0939	0.0459	0.05	1.01	0.3	-7.22	0.4
20-Sep-07	DGR2-775.99	4	41.7132	41.6712	0.042	0.04	0.97	0.3	-7.05	14.7
5-Jul-07	DGR2-797.50	1	38.9313	38.7753	0.156	0.15	0.94	1.0	-8.30	-47.7
5-Jul-07	DGR2-797.50	2	36.926	36.7869	0.1391	0.13	0.93	0.9	-8.47	-45.0
5-Jul-07	DGR2-797.50	3	36.2473	36.0744	0.1729	0.16	0.93	1.2	-8.14	-43.1
5-Jul-07	DGR2-797.50	4	40.7279	40.5588	0.1691	0.16	0.96	1.1	-8.37	-47.8
5-Jul-07	DGR2-797.50	5	36.4732	36.3164	0.1568	0.15	0.94	1.1	-8.58	-45.3
14-Dec-07	DGR2-797.50	6	41.4277	41.2499	0.1778	0.19	1.05	1.2	-9.10	-63.4
14-Dec-07	DGR2-797.50	7	41.9567	41.7722	0.1845	0.19	1.01	1.2	-8.83	-49.2
3-Jul-07	DGR2-822.42	1	34.0504	33.9424	0.108	0.10	0.95	0.8	-8.71	-46.9
3-Jul-07	DGR2-822.42	2	34.4847	34.3782	0.1065	0.10	0.95	0.8	-8.65	-51.4

3-Jul-07	DGR2-822.42	3	35.0823	34.9779	0.1044	0.10	0.92	0.7	-10.49	-65.7
3-Jul-07	DGR2-822.42	4	35.6165	35.4915	0.125	0.12	0.93	0.9	-8.98	-49.6
3-Jul-07	DGR2-822.42	5	32.0772	32.0005	0.0767	0.06	0.80	0.5	-12.68	-80.4
14-Dec-07	DGR2-822.42	6	40.2032	39.8646	0.3386	0.34	1.01	2.3	-8.43	-75.57
14-Dec-07	DGR2-822.42	7	41.2862	40.9818	0.3044	0.31	1.00	2.0	-8.43	-74.92
14-Dec-07	DGR2-822.42	8	42.8429	42.5072	0.3357	0.33	0.99	2.1	-8.34	-98.23
3-Dec-07	DGR2-828.01	1	47.1509	45.9763	1.1746	1.16	0.98	6.8	-5.14	-44.91
3-Dec-07	DGR2-828.01	2	45.3963	44.2912	1.1051	1.08	0.98	6.6	-5.02	-43.43
5-Dec-07	DGR2-828.01	3	43.1509	42.2261	0.9248	0.91	0.98	5.8	-5.85	-54.75
5-Dec-07	DGR2-828.01	4	46.1359	45.1821	0.9538	0.94	0.98	5.6	-5.09	-53.29
4-Dec-07	DGR2-834.05	1	42.2398	40.1455	2.0943	2.05	0.98	13.8	-5.77	-57.92
4-Dec-07	DGR2-834.05	2	43.7311	41.5546	2.1765	2.17	1.00	14.1	-5.92	-45.7
4-Dec-07	DGR2-834.05	3	43.2319	41.1024	2.1295	2.11	0.99	13.9	-5.82	-47.22
4-Dec-07	DGR2-834.05	4	44.7359	42.5542	2.1817	2.16	0.99	13.7	-5.86	-44.45
3-Dec-07	DGR2-835.73	1	44.838	43.7944	1.0436	1.03	0.99	6.4	-5.53	-63.68
3-Dec-07	DGR2-835.73	2	44.902	43.9032	0.9988	0.99	0.99	6.1	-5.56	-61.01
5-Dec-07	DGR2-835.73	3	46.9274	45.7263	1.2011	1.20	1.00	7.1	-5.51	-46.49
5-Dec-07	DGR2-835.73	4	45.2494	44.1043	1.1451	1.14	1.00	7.0	-6.00	-49.78
29-Nov-07	DGR2-836.63	1	44.3484	44.2208	0.1276	0.13	1.02	0.8	-5.19	-56.88
29-Nov-07	DGR2-836.63	2	43.7935	43.6745	0.119	0.12	1.00	0.7	-4.81	-41.05
29-Nov-07	DGR2-836.63	3	43.9087	43.814	0.0947	0.10	1.05	0.6	-6.59	-48.07
29-Nov-07	DGR2-836.63	4	46.3413	46.2469	0.0944	0.09	1.01	0.6	-7.16	-39.33
30-Nov-07	DGR2-836.63	5	44.3916	44.2876	0.104	0.10	1.00	0.6		-38.75
30-Nov-07	DGR2-836.63	6	42.7723	42.6726	0.0997	0.10	0.97	0.6	-5.55	-35.8
30-Nov-07	DGR2-839.69	1	44.3509	43.3875	0.9634	0.96	1.00	6.0	-6.38	-50.55
30-Nov-07	DGR2-839.69	2	42.0784	41.1632	0.9152	0.91	0.99	5.9	-6.14	-44.62
5-Dec-07	DGR2-839.69	3	43.0685	42.1171	0.9514	0.94	0.99	6.0	-5.45	-57.88
7-Sep-07	DGR2-857.71	1	24.7953	23.4581	1.3372	1.332	1.00	15.3	-4.59	-39.7
7-Sep-07	DGR2-857.71	2	24.9224	23.5202	1.4022	1.401	1.00	16.1	-4.55	-41.9
7-Sep-07	DGR2-857.71	3	41.2841	38.9774	2.3067	2.222	0.96	15.4	-5.06	-42.0
7-Sep-07	DGR2-857.71	4	38.1059	36.0695	2.0364	1.986	0.98	14.9	-4.48	-35.2
21-Sep-07	DGR2-857.71	5	30.5776	28.9735	1.6041	1.597	1.00	14.9	-4.93	-42.0
21-Sep-07	DGR2-857.71 Dup	6	30.0148	28.3963	1.6185	1.614	1.00	15.3	-5.61	-39.4
21-Sep-07	DGR2-857.71 Dup	7	31.332	29.5045	1.8275	1.823	1.00	16.7	-3.49	-33.0
21-Sep-07	DGR2-857.71 Dup	8	26.6729	25.0859	1.587	1.585	1.00	17.1	-4.23	-39.5

APPENDIX B

Geochemistry of Pore Fluids by Vacuum Distillation and Deionized Water Leach

Depth	Na	K	Ca	Mg	Sr	SO ₄ IC	Cl by IC	Br by IC
	mmol/kg	mmol/ kg	mmol/ kg	mmol/ kg	mmol/ kg	mmol/ kg	mmol/ kg	mmol/ kg
101.89	7.7	4	13	29	0.15	155	11.8	0.0
101.89	12.6	6	17	46	0.21	204	18.8	0.1
101.89	6.8	3	13	31	0.19	163	11.3	0.1
101.89	6.6	3	11	30	0.17	139	10.7	0.2
101.99	10.6	2	16	31	0.16	99	14.4	0.1
101.99	16.2	3	21	62	0.14	128	30.3	0.2
101.99	16.5	3	27	47	0.23	156	25.5	0.4
101.99	19.3	3	23	52	0.24	158	30.2	0.3
102.26	7.8	3	14	15	0.13	66	22.7	0.1
102.26	7.6	3	16	19	0.15	102	17.6	0.1
102.26	22.0	14	41	75	0.42	437	37.8	0.3
102.26	9.8	7	21	29	0.19	155	18.3	0.0
156.56	14.6	3	15	83	0.29	95	43.6	0.2
156.56	11.0	3	10	63	0.23	83	38.1	0.6
172.32	18.8	11	226	60	2.04	2798	12.6	0.3
172.32	17.9	13	233	62	2.38	2721	9.6	0.1
182.89	70.8	26	198	48	1.06	2524	46.6	0.4
182.89	63.8	22	178	47	0.98	2277	40.5	0.4
197.45	69.6	8	145	9	0.50	1630	90.6	0.2
197.45	197.4	24	235	31	1.30	2750	218.6	0.0
226.27	39.8	2	135	8	1.02	1304	71.1	0.1
226.27	122.8	8	482	37	3.81	5121	193.0	0.3
249.33	741.0	23	179	38	0.95	1614	891.4	0.6
249.33	777.1	23	181	38	0.89	1670	892.4	1.5
294.84	451.6	8	181	25	1.58	1911	503.1	0.5
294.84	357.6	5	163	18	1.17	1770	408.0	0.3
343.49	1857.8	118	344	180	2.34	2758	1813.4	1.5
343.49	1763.2	117	334	164	2.46	2590	1712.2	1.1
370.93	3333.0	245	7164	961	62.00	78032	4549.2	11.7
370.93	3148.1	251	4579	981	43.83	52421	4031.0	3.0
395.29	1696.2	235	488	340	5.49	552	3600.0	8.7
395.29	1730.6	240	537	333	5.72	1204	3584.6	12.0
422.4	1004.8	131	801	259	8.90	73	3506.7	20.5
445.6	4010.1	203	815	225	7.08	577	6494.6	21.9
445.6	4678.3	212	916	277	8.05	585	7775.0	17.9
459.62	0.0	0	0	0	0.00	149	0.0	0.0
459.62	1402.1	249	824	239	7.89	173	3714.6	81.1

Depth	Na	K	Ca	Mg	Sr	SO ₄ IC	Cl by IC	Br by IC
	mmol/kg	mmol/ kg	mmol/ kg	mmol/ kg	mmol/ kg	mmol/ kg	mmol/ kg	mmol/ kg
453.95	2225	400	1505	546	14	58	6110	58.8
453.95	2385	442	1656	588	16	162	6709	51
485.4	2242	414	1371	466	14	59	6073	48.8
485.4	1992	371	1228	453	12	49	5393	27.5
485.4	1524	287	942	337	9	17	4207	26.5
485.4	1758	329	1085	395	11	33	4800	27
538.51	2365	373	1406	338	17	50	5988	44.5
538.51	2448	396	1379	341	16	60	6068	24.7
551.75	2358	386	1376	344	17	94	5875	49.2
551.75	2432	370	1465	371	18	64	6145	39.9
578.15	2389	369	1415	344	17	117	5940	36
578.15	2538	401	1491	374	18	124	6344	49.3
612.09	2465	353	1373	303	17	89	5721	44.6
612.09	2489	355	1381	302	17	125	5767	27
628.18	2474	376	1292	285	16	135	5479	38
628.18	2698	383	1495	357	19	128	6100	56.3
628.18	2607	372	1450	340	18	150	5968	44.8
628.18	2722	398	1473	332	18	130	6026	58.3
628.18	3055	450	1655	396	20	188	6840	48.4
634.49	2888	311	1471	361	18	212	5508	44.6
634.49	2939	324	1520	382	19	215	5696	
641.92	2760	325	1340	354	17	169	5133.6	
641.92	2944	337	1410	377	18	176	5448	25.8
648.75	2623	360	1337	330	17	132	5654	30.6
648.75	2812	380	1397	364	17	109	5889	19.8
656.41	3275	422	860	483	13	425	4361	
656.41	3127	429	838	472	13	444	4207	
663.34	2853	424	1054	622	14	345	5392	7.6
663.34	3027	428	1121	657	15	390	5553	37.6
670.48	2749	362	965	562	17	327	4850	18.2
670.48	2881	376	1123	598	17	456	4935	26.5
681.45	2765	373	995	448	14	218	5433	24.6
681.45	2827	397	1055	481	15	245	5524	26.4
694.63	2720	311	1169	420	12	299	5228	7.7
694.63	3130	288	1675	648	15	404	6760	44.5
699.58	2760	255	1052	375	11	148	5173	39.8
699.58	2903	316	1217	429	12	220	5669	33.2
699.58	2960	292	1320	448	13	270	5685	36.5
699.58	2766	275	1248	423	12	216	5453	34.1
699.58	3039	320	1439	487	14	342	5948	30.7
709.21	2553	323	905	238	11	246	4432	29
709.21	2942	427	992	326	11	399	4831	18.3
709.21	3163	478	1655	476	21	1004	5284	13.4
709.21	3155	455	2146	584	26	1554	5492	40.9
724.16	2830	335	1107	499	12	569	4127	24.4
724.16	3079	358	1318	535	14	713	4433	
733.48	2998	335	1208	492	13	596	4318	
733.48	3195	361	1205	521	13	570	4555	
742.61	3085	333	1088	416	12	440	4446	16.2
742.61	3278	351	1152	445	13	481	4852	5.9

Depth	Na	K	Ca	Mg	Sr	SO ₄ IC	Cl by IC	Br by IC
	mmol/kg	mmol/ kg	mmol/ kg	mmol/ kg	mmol/ kg	mmol/ kg	mmol/ kg	mmol/ kg
748.92	2587	296	627	222	7	186	3844	12
748.92	1998	216	535	186	6	164	3067	13
748.92	3707	412	961	337	11	271	5765	23.5
748.92	2942	320	746	254	9	243	4461	17.2
748.92	2170	256	605	206	7	220	3383	17.2
748.92	2724	295	682	243	8	203	4087	19
748.92	2937	327	741	273	9	203	4360	3.3
762.19	3324	308	886	389	9	460	4126	7.3
797.5	2569	172	744	357	7	396	3734	19.1
797.5	2726	188	811	408	8	443	3905	28.5
797.5	2639	173	763	399	7	376	3780	18.6
797.5	2667	180	761	397	7	422	3875	18.4
797.5	2859	185	821	437	8	393	4144	21.4
822.42	2638	207	730	295	7	445	3572	20.1
822.42	2878	204	776	313	8	444	3874	17.3
822.42	3306	237	877	353	9	486	4513	13.7
822.42	2868	200	732	309	7	410	3832	29.7
828.01	2495	35	1083	486	12	54	4861	5.1
828.01	2485	35	1096	518	12	66	4447	
828.01	2549	38	1346	426	13	261	4732	
828.01	2522	38	1437	474	13	377	4701	18.3
834.05	2186	62	938	299	11	28	4230	16.1
834.05	2180	60	929	291	11	29	4090	13.9
834.05	2177	59	925	288	11	29	4076	13.7
834.05	2194	58	937	295	11	27	4182	16.5
835.73	2402	77	979	350	12	69	4253	15.7
835.73	2499	78	1022	371	12	64	4427	17
835.73	2406	76	948	319	11	42	4179	16.2
835.73	2380	77	935	315	11	45	4143	18.7
839.69	2319	75	945	308	10	50	4427	17.3
839.69	2307	76	942	311	10	57	4279	0
839.89	2310	71	935	286	10	33	4198	0
857.71	2274	25	1178	321	12	6	4515	16.2
857.71	2258	24	1218	324	12	7	4684	15.7
857.71	2190	24	1169	314	11	6	4533	15.9
857.71	1854	20	1002	261	10	6	3763	16.7
857.71	2961	32	1606	413	15	7	5992	19

APPENDIX C

CO₂ and CH₄ from Pore Fluids by Vacuum Distillation

(yellow highlighted cells not used in profiles)

ID of rock sample	CO ₂ total moles extracted	CO ₂ mmol/kg Run average, corrected for oil solubility	CO ₂ $\delta^{13}\text{C}$	CO ₂ $\delta^{13}\text{C}$ - weighted average	CH ₄ total moles extracted	CH ₄ mmol/kg	CH ₄ δD	CH ₄ $\delta^{13}\text{C}$
DGR2-453.95	4.72E-06		0.44					
DGR2-453.95	8.67E-06		-3.99					
DGR2-453.95	2.16E-05		-0.66					
DGR2-453.95	2.13E-05		-1.80					
DGR2-453.95	7.72E-06	1.10E+00	-4.35	-2.04	1.56E-07	0.03	-290.44	-52.51
DGR2-485.40	5.64E-05		-0.28					
DGR2-485.40	2.29E-05		-3.27					
DGR2-485.40	1.58E-05		-2.09					
DGR2-485.40	3.32E-05		-2.71					
DGR2-485.40	1.32E-05	2.22E+00	-6.81	-3.38	1.75E-06	0.36	-293.12	-57.31
DGR2-513.35	2.27E-05		-0.50					
DGR2-513.35	1.26E-05		-4.31					
DGR2-513.35	1.4E-05		-3.01					
DGR2-513.35	1.09E-05		-4.59					
DGR2-513.35	6.94E-06	6.91E-01	-7.18	-4.42	1.90E-06	0.35	-302.46	-51.60
DGR2-538.51	3.24E-05		-3.94					
DGR2-538.51	9.33E-06		-5.77					
DGR2-538.51	1.48E-05		-4.75					
DGR2-538.51	1.84E-05		-5.24					
DGR2-538.51	1.15E-05	2.30E+00	-5.93	-4.82	4.50E-06	0.99	-324.62	-54.49
DGR2-551.75	1.79E-05		-2.46					
DGR2-551.75	9.76E-06		-1.92					
DGR2-551.75	1.41E-05		-1.02					
DGR2-551.75	2.64E-05	1.32E+00	-0.60	-1.36	9.60E-06	2.26	-319.55	-55.20
DGR2-578.15	3.82E-05		6.49					
DGR2-578.15	1.52E-05		10.70					
DGR2-578.15	2.63E-05		8.73					
DGR2-578.15	2.11E-05		9.42					
DGR2-578.15	1.1E-05	1.82E+00	6.72	8.32	2.33E-05	5.52	-324.86	-58.10
DGR2-591.33	3.39E-05		7.00					
DGR2-591.33	1.75E-05		13.88					
DGR2-591.33	3.34E-05		9.42					
DGR2-591.33	2.2E-05		12.63					
DGR2-591.33	1.06E-05	4.54E+00	14.51	10.04	4.76E-05	9.19	-328.76	-56.89
DGR2-612.09	1.05E-05		9.70					
DGR2-612.09	4.86E-06		14.67					
DGR2-612.09	1.14E-05		11.96					
DGR2-612.09	3.38E-05		12.00					
DGR2-612.09	8.14E-06	1.49E+00	18.92	11.81	1.27E-05	2.42	-331.51	-63.07
DGR2-628.18	4.19E-05		5.50					
DGR2-628.18	1.58E-05		11.95					
DGR2-628.18	6.77E-06		9.81					
DGR2-628.18	1.82E-05		12.18					
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DGR2-634.49	3.46E-06		9.24					

DGR2-634.49	5.84E-07		0.83					
DGR2-634.49	4.48E-06		6.14					
DGR2-634.49	9.98E-07		5.16					
DGR2-634.49	1.07E-06	3.42E-01	4.16	5.67	7.61E-06	1.42	-310.7	-57.9
DGR2-641.92	8.77E-06		7.68					
DGR2-641.92	1.85E-06		5.48					
DGR2-641.92	4.17E-06		6.14					
DGR2-641.92	2.49E-06		-3.03					
DGR2-641.92		1.05E+00		6.97	1.13E-04	19.91	-300.3	-51.9
DGR2-648.75	4.87E-05		1.44					
DGR2-648.75	1.7E-05		7.58					
DGR2-648.75	2.53E-05		5.46					
DGR2-648.75	1.81E-05		8.88					
DGR2-648.75	1.27E-05	1.05E+01	7.32	3.70	2.01E-05	6.04	-323.73	-55.51
DGR2-656.41	4.79E-06		-7.78					
DGR2-656.41	2.82E-06		-10.54					
DGR2-656.41	6.31E-06		-7.41					
DGR2-656.41	2.59E-06		-6.67					
DGR2-656.41	4.17E-06	1.15E+00	-8.27	-7.54	3.34E-05	29.44	-299.8	-58.9
DGR2-663.34	1.49E-05		-6.53					
DGR2-663.34	8.59E-06		-6.33					
DGR2-663.34	1.47E-05		-8.02					
DGR2-663.34	1.44E-05	9.85E+00	-6.64	-6.94	1.38E-05	25.84	-308.59	-58.94
DGR2-670.48	2.57E-05		-4.52					
DGR2-670.48	1.71E-05		-7.88					
DGR2-670.48	1.06E-05		-6.59					
DGR2-670.48	1.74E-05		-7.30					
DGR2-670.48	2.72E-06	2.68E+01	-12.23	-6.32	1.89E-05	23.04	-307.51	-55.12
DGR2-681.45	3E-05		-2.71					
DGR2-681.45	2.16E-05		-6.06					
DGR2-681.45	3.99E-05		-3.29					
DGR2-681.45	1.01E-05		-4.60					
DGR2-681.45	9.4E-07	8.10E+00	-13.04	-3.84	1.62E-05	7.61	-312.95	-53.48
DGR2-689.45	7.82E-06		-2.78					
DGR2-689.45	3.13E-06		-6.03					
DGR2-689.45	1.43E-05		-4.41					
DGR2-689.45	2.59E-05	3.38E+00	-0.20	-4.11	3.83E-06	3.73	-304.90	-58.94
DGR2-694.63	3.03E-05		-2.27					
DGR2-694.63	1.95E-05		-6.44					
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DGR2-694.63	1.2E-05		-7.04					
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DGR2-699.58	4.34E-05		-1.18					
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DGR2-699.58	9.98E-06		-5.10					
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DGR2-709.21	8.26E-06		-4.43					
DGR2-709.21	5.64E-06		-5.81					
DGR2-709.21	3.37E-06	3.47E+00	-9.60	-7.08	np	0.00		
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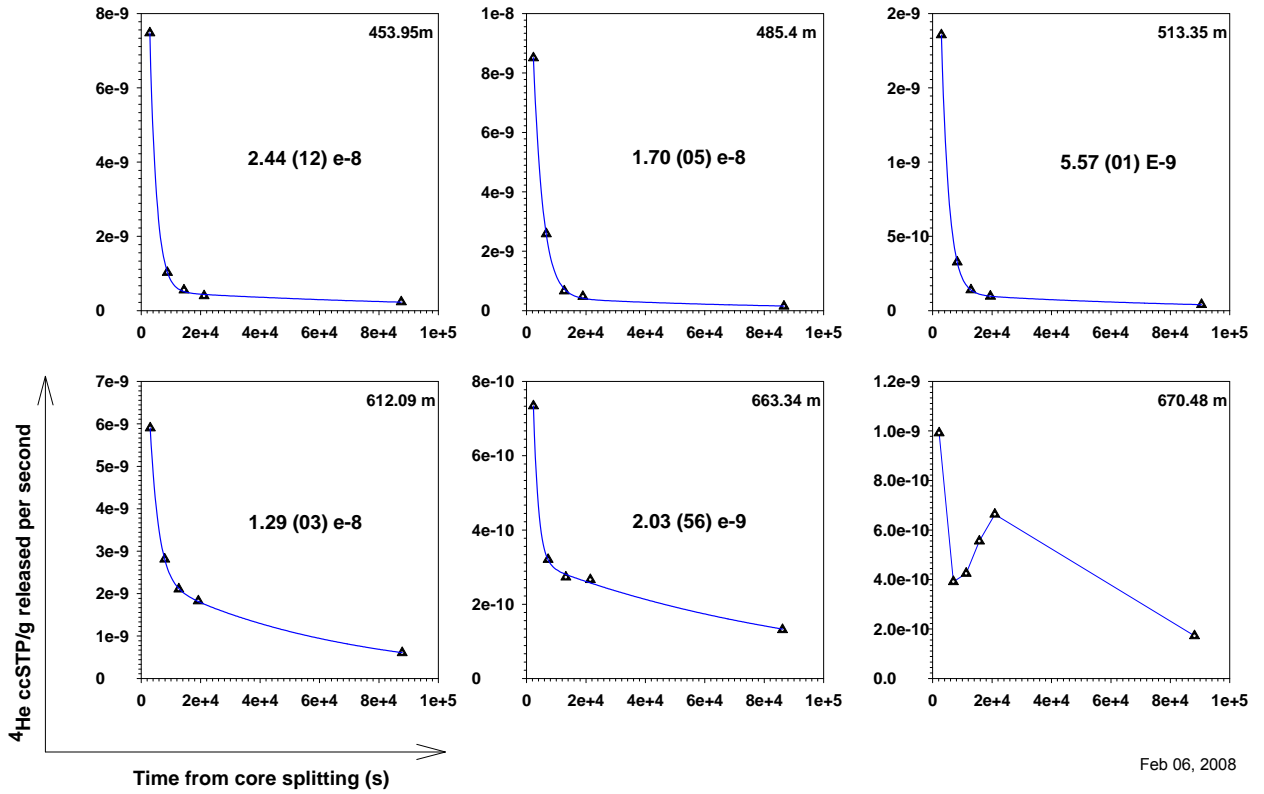
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DGR2-724.16	3.52E-06	5.38E+00	-10.75	-7.42	np	0.00		
DGR2-733.48	5.38E-06		-5.11					
DGR2-733.48	1.12E-05		-9.21					
DGR2-733.48	1.6E-06		-6.77					
DGR2-733.48	6.78E-07		-6.31					
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DGR2-742.61	1.23E-05		-7.54					
DGR2-742.61	9.98E-06		-6.64					
DGR2-742.61	1.54E-05		-6.09					
DGR2-742.61	6.38E-06		-6.93					
DGR2-742.61	4.79E-06	2.81E+00	-7.78	-6.43	5.95E-07	0.47	-232.6	-51.8
DGR2-748.92	2.82E-06		-10.54					
DGR2-748.92	4.79E-06		-7.78					
DGR2-748.92	4.71E-05		-2.88					
DGR2-748.92	1.52E-05		-4.56					
DGR2-748.92	9.38E-06	5.45E+00	-10.18	-3.29	3.22E-06	1.28	-252.34	-56.66
DGR2-748.92 - Dup	3.78E-05		-3.12					
DGR2-748.92 - Dup	1.22E-05		-6.47					
DGR2-748.92 - Dup	2.83E-05	4.01E+00	-3.69	-3.36				
DGR2-762.19	5.03E-07		-8.42					
DGR2-762.19	2.13E-06		-6.94					
DGR2-762.19	1.02E-06		-6.79					
DGR2-762.19	1.97E-06	6.41E-01	-7.44	-7.22	3.73E-06	3.86	-214.9	-47.4
DGR2-775.99	1.95E-07		-27.23					
DGR2-775.99	1.31E-07		-10.88					
DGR2-775.99	1.24E-07		-9.88					
DGR2-775.99	1.51E-07	2.82E-01	-10.33	-10.37	9.85E-07	5.63	-223.6	-52.3
DGR2-797.50	3.09E-05		-6.03					
DGR2-797.50	1.02E-05		-7.20					
DGR2-797.50	2.73E-05		-4.83					
DGR2-797.50	2.17E-05		-6.11					
DGR2-797.50	8.39E-06	1.56E+01	-11.77	-5.82	1.42E-05	19.05	-220.83	-48.87
DGR2-822.42	2.53E-05		-3.87					
DGR2-822.42	1.11E-05		-6.47					
DGR2-822.42	6.01E-06		-7.01					
DGR2-822.42	1.02E-05		-6.37					
DGR2-822.42	1.53E-05	2.04E+01	-5.73	-6.26	7.48E-07	1.57	-213.68	-60.84
DGR2-828.01	4.28E-06	7.57E-01	-5.11	-5.11	1.92E-07	0.05	-203.8	-42.3
DGR2-828.01	np							
DGR2-834.05	7.1E-06		-3.76					
DGR2-835.73	3.25E-06		-6.05					
DGR2-835.73	4.15E-06		-7.22	-6.71				
DGR2-836.63	1.71E-06		-11.27	-11.27				
DGR2-839.69	1.81E-06		-11.12	-11.12				
DGR2-857.71	1.24E-07		-6.12					
DGR2-857.71	4.99E-07		-6.25					
DGR2-857.71	1.93E-07		-5.62					
DGR2-857.71	2.43E-07		-6.11	-6.09				

DGR2-857.71						
Dup	8.09E-06	-7.72				
DGR2-857.71						
Dup	2.43E-06	-8.50				
DGR2-857.71						
Dup	7.38E-07	-6.58				
DGR2-857.71						
Dup	1.09E-05	-10.45	-10.21			
DGR2-844.73						
Cambrian						
groundwater	6.19	-7.2		11.618964	-194.88	-42.53
DGR2-852.70						
Cambrian						
groundwater	5.4	-8.35		6.322176	-205.10	-40.73
DGR2-852.70						
Cambrian						
groundwater	6.6	-10.92	-9.76	4.45941	-202.12	-40.45

APPENDIX D

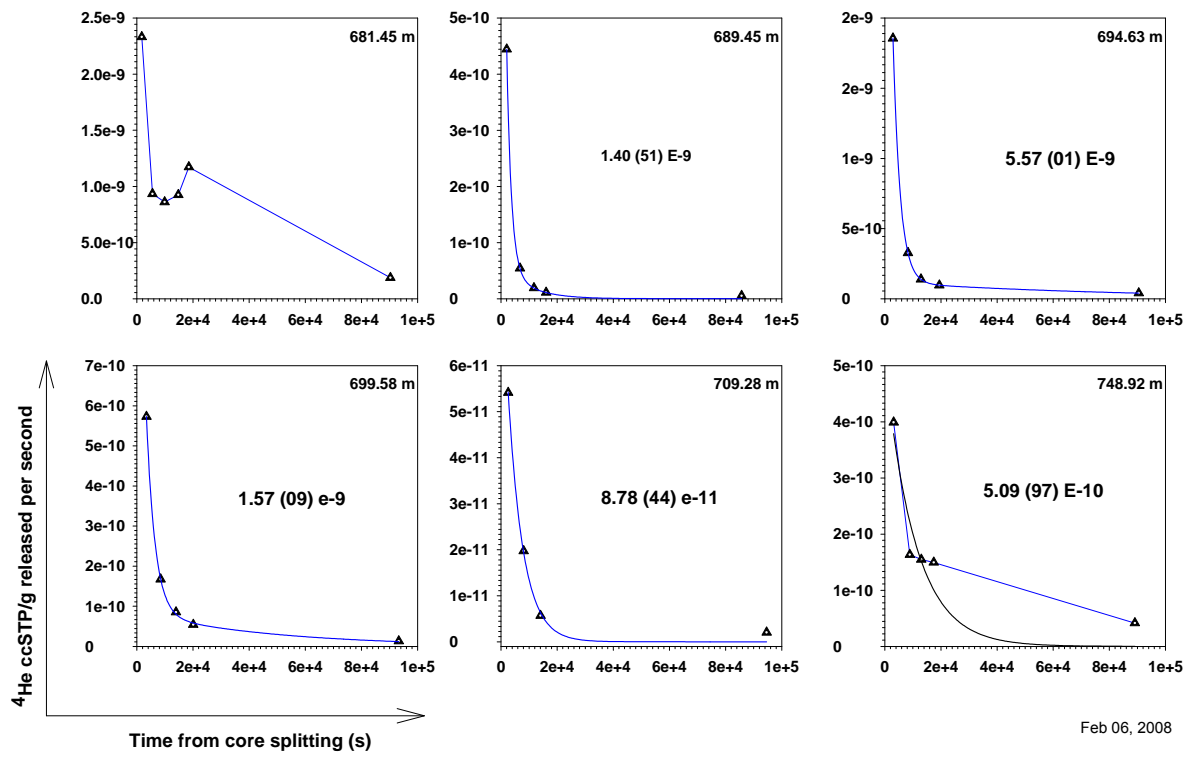
DGR-2 Helium Out-Gassing Experiments - Room Temperature He Release Curves.

DGR 2 micro core samples (2007) - room temperature (20 °C) diffusion of helium

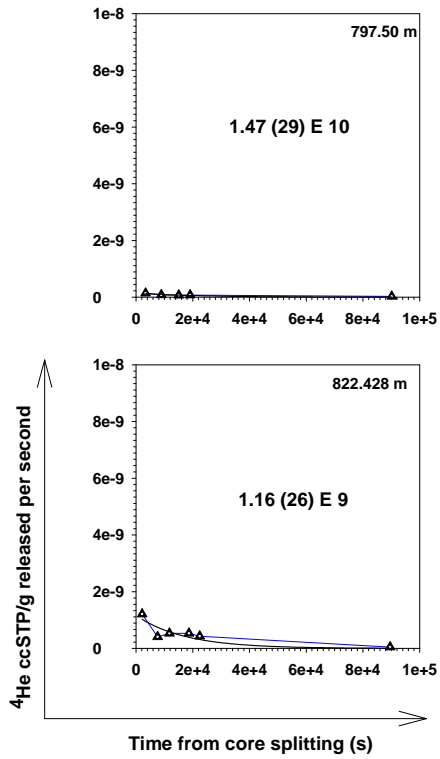


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DGR 2 micro core samples (2007) - room temperature (20 °C) diffusion of helium $5.57E-09 \square 1.35E-11$

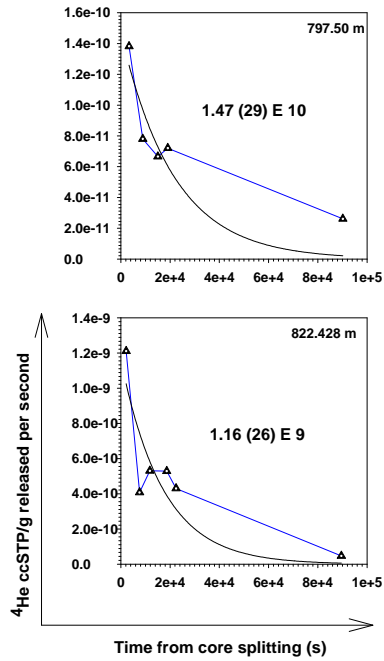


DGR 2 micro core samples (2007) - room temperature (20 °C) diffusion of helium



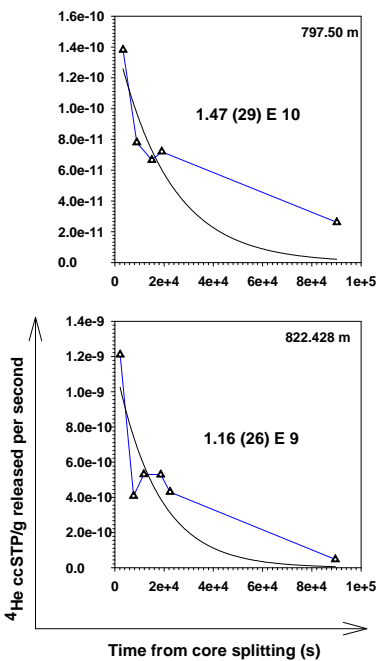
Feb 06, 2008

DGR 2 micro core samples (2007) - room temperature (20 °C) diffusion of helium



Feb 06, 2008

DGR 2 micro core samples (2007) - room temperature (20 °C) diffusion of helium



Feb 06, 2008

APPENDIX E

**Strontium Isotopes
Radiogenic Isotope Laboratory
Earth Sciences Department
Carleton University**

Sample Matrix	Depth	$^{87}\text{Sr}/^{86}\text{Sr}$	Variance of replicate analyses	Sr ppm
Groundwater	43.64	0.708310	0.00001	5.6
Groundwater	111.22	0.708349	0.000009	9.6
Groundwater	137.86	0.708347	0.000011	8.7
Porewater	453.95	0.709596	0.000011	1293
Porewater	485.40	0.709685	0.00001	1019
Porewater	538.51	0.709860	0.000012	1457
Porewater	578.15	0.709945	0.000012	1567
Porewater	628.18	0.709915	0.000011	1595
Porewater	663.34	0.709689	0.000009	1264
Porewater	670.48	0.709970	0.000009	1504
Porewater	681.45	0.709957	0.00001	1249
Porewater	724.16	0.709609	0.00001	1126
Porewater	797.50	0.709952	0.00001	662
Porewater	822.42	0.709933	0.00001	688
Groundwater	844.73	0.710233	0.000009	860
Groundwater	852.70	0.710250	0.000011	720
Rock	209.28	0.708050	0.00001	
Rock	459.62	0.708306	0.00001	
Rock	663.34	0.707972	0.00001	
Rock	822.42	0.708223	0.000011	