

Technical Report

Title: *Porewater Analyses in DGR-5 and DGR-6 Core*

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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, 2008).

As part of its NWMO contract, Geofirma Engineering Ltd. contracted with the University of Ottawa for determination of water isotopes and solute concentrations in groundwaters as well as porewaters extracted from intact DGR borehole cores collected at the Bruce nuclear site. This Technical Report presents the results and initial interpretation of the porewater chemistry from rock core samples collected from DGR-5 and DGR-6 as part of Phase 2B of the GSCP.

Work described in this Technical Report was completed in accordance with Test Plan TP-09-09 – Laboratory Testing of DGR-5 & DGR-6 Cores for Pore-Water Extraction and Analysis (Intera Engineering Ltd., 2010a), and following the general requirements of the Intera DGR Project Quality Plan (Intera Engineering Ltd., 2009). Core sampling and distribution was completed under TP-09-02 – DGR-5 and DGR-6 Core Sampling and Distribution (Intera Engineering Ltd., 2010b).

2 Background

By definition within the Bruce DGR program, “groundwater” is that water that flows under positive pressure into the borehole without artificial stimulation. Groundwater was sampled through the opportunistic groundwater sampling, described by TR-08-18 (Intera Engineering, 2010c). The term porewater is defined as water contained in void spaces between mineral grains in a rock (Ontario Power Generation, 2008), which can be removed from the pore space only by laboratory sampling procedures.

During the Phase 2B drilling operations associated with drilling the DGR-5 and DGR-6 boreholes, rock core samples were collected for porewater analysis. The purpose of determining the porewater chemistry is to provide data to complement similar data produced through analysis of DGR-1, DGR-2, DGR-3 and DGR-4 cores that can be used to develop porewater chemistry and tracer profiles. Such profiles can assist in improving our understanding of the origin and subsurface history of porewaters in the Silurian to Cambrian strata at the DGR site.

The Phase 2A porewater extraction program was undertaken to complement porewater data obtained from cores recovered during the drilling of DGR-1 and DGR-2. The methods employed for porewater extraction from the Phase 2A cores are based on methods developed in Phase 1 for the DGR-1 and DGR-2 cores. The geochemical parameters that are considered most representative and most suitable for interpretation include the stable water isotopes (δD and $\delta^{18}O$), chloride (Cl^-), sodium (Na^+), and bromide (Br^-).

This Technical Report (TR) summarizes the environmental isotope results for porewaters extracted by vacuum distillation of crushed core material and hydrogeochemical results produced by leaching of the vacuum extracted (dried) crushed core material. Additionally, this report examines the effectiveness of carrying out solute leaching in an anaerobic atmosphere designed to minimize the impact of sulphide oxidation on porewater chemistry. While analysis of gases in DGR-5 and DGR-6 rock core samples is beyond the scope of work outlined in Test Plan TP-09-09 (Intera Engineering Ltd., 2010a), steps were taken to seal rock samples in Isojars during the preparation process for possible analysis of CH_4 at a later time.

3 Methodology

3.1 Vacuum Packaging of Core in Field

Drill core samples were photographed, then vacuum packaged (including nitrogen flushing) in the field and stored at temperatures below 8 °C before shipping. 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 eight samples processed per week. Field sampling, handling, preservation, and shipping protocols are described in TP-09-02 (Intera Engineering Ltd., 2010b).

3.2 Vacuum Distillation and Stable Isotope Analysis of Porewaters

The vacuum distillation method was evaluated in a series of tests on both carbonate and shale samples, using a range of extraction times and temperatures. The detailed methodology of this vacuum distillation testing is presented in TR-08-37 (Intera Engineering Ltd., 2010d). From these results it was concluded that vacuum distillation at 150°C for 6 hours provided accurate and reproducible values for both porewater isotopes and geochemistry. A salt dehydration ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) experiment showed complete salt dehydration when pure salt was heated at 150°C for 6 hours.

Rock core samples were crushed and sieved (with a 2mm to 4mm grain size distribution). A mass of ~40 g of crushed rock was loaded into each of four sample flasks (four ~40 g aliquots per sample x 2 core samples) and attached to eight individual vacuum extraction lines. Each line was paired with a high-vacuum septum vial ('exetainers'), and all lines used a common pumping port. The sample flasks with the crushed rock were initially cooled with liquid N_2 and evacuated to produce a vacuum throughout the extraction system. The extraction system was then closed to the pump and each individual extraction line isolated from the rest. An oven was placed around each bank of four sample flasks to ramp the extraction temperature to 150°C. The septum vials were attached by syringe needles to the extraction line and partially submersed in a liquid N_2 bath.

The syringe needle attachment was changed during the program to a system of cored-septum caps which allowed direct attachment to the ¼" Pyrex port. This removed the constriction to vapour transfer presented by the syringe needle. However, this method prevented sampling and analysis of CO_2 , which was not proposed for the DGR-5 and DGR-6 cores. The water vapour was distilled from the core material and condensed in the septum vial over a 6 hour period. The gravimetric water loss and water recovered were determined following extraction.

The volumetric water content is a key parameter for normalizing porewater concentrations 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 gravimetric water loss for the actual sample aliquot, and not to values from different aliquots of the core sample. Both the rock flasks and exetainers are weighed to determine water loss and water gain, as well as dry-rock mass. These measurements are used to calculate gravimetric water loss, which is normalized to percent volumetric water content using a mineral density of 2.7 (approximate average of densities for calcite, quartz, illite and dolomite) according to the following equation and using a density for water, $\rho_w = 1 \text{ g/mL}$, and the mineral density, $\rho_{\text{rock}} = 2.7 \text{ g/mL}$:

$$\text{Volumetric water content, } w_{c,\text{vol}} = \frac{(m_{\text{wet rock}} - m_{\text{dry rock}}) / \rho_w}{m_{\text{dry rock}} / \rho_{\text{rock}}} \quad [1]$$

The recovered water contents of the exetainer were analyzed for ^{18}O and D 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% H₂ gas in He. Following an over-night equilibration period, the H₂ gas was analysed for δD . For samples yielding greater than 1 mL of porewater during distillation, a Los Gatos Research instrument was used to analyze both $\delta^{18}O$ and δD by off-axis cavity ring down laser spectroscopy. This instrument has proven to be of equal accuracy and precision (Wassenaar et al., 2008).

3.3 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 pre-weighed plastic Falcon centrifuge tube. Care was taken to collect the entire rock sample and to rinse each distillation vessel three times to assure quantitative collection of salts from the experiment. The centrifuge tube was then re-weighed to determine the precise amount of water. The transferred samples were allowed to leach for an average of 60 days with occasional (bi-weekly) shaking, and were then filtered and analysed for major ions.

The majority of samples were removed from the vacuum distillation line and placed in an anaerobic chamber prior to opening the centrifuge tube. The samples in the anaerobic chamber remained in the chamber for the duration of the leaching period to inhibit sample oxidation. Based on the petrography of DGR-3 and DGR-4 rock core samples (Intera Engineering Ltd, 2010e; 2010f) sulphide oxidation was considered to be the primary oxidizing agent. Sulphide minerals were primarily iron sulphides including monosulphides (e.g., mackinawite) and disulphides (e.g., pyrite). Anaerobic rinsing and storage was not done on all samples and replicates due to restrictions on the space available in the anaerobic chamber. Those leached aerobically are above the Manitoulin Formation and are identified in the sulphate concentration column of Appendix A by a blue highlight.

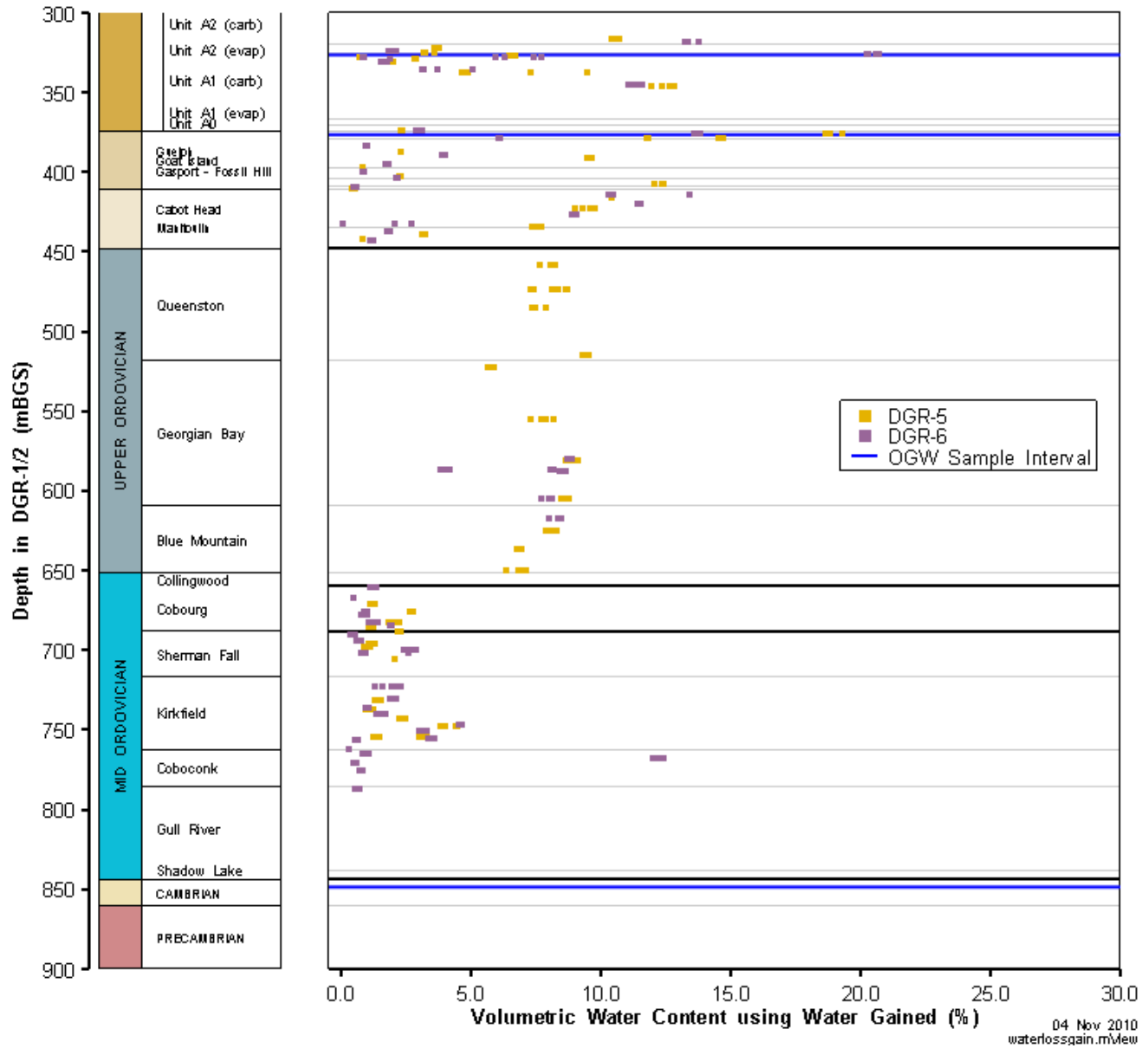
Cations were measured in the University of Ottawa geochemistry laboratory on a Varian Vista ICP-OES, and anions were measured by ion chromatography with a Dionex instrument. Br was measured using an HP 4500 ICP-MS to allow accurate measurements without interference from Cl. Br results are shown in Appendix A.

The total mass of each ion leached from the dried rock was normalized to the gravimetric water gain yielded by vacuum distillation, giving molal porewater concentrations (moles per kg water). These results are tabulated in Appendix A. In porewater extractions for DGR-3 and DGR-4, solute mass was normalized to the gravimetric weight loss, which was determined to be the more consistently reliable representation of water content (TR-08-19, Intera Engineering Ltd., 2010g). However, in DGR-5/6 extractions, the gravimetric water gain was considered to provide the most consistently reliable measurements of water content. This is due to two changes in testing protocol; (1) the improved vapour transfer using the cored-septum exetainers which assured a greater number of successful transfers, and (2) a systematic error in the post-extraction weight of the dried rock sample. The error in the post-extraction weight was due to the requirement to retain the rock sample flask under vacuum by weighing with the vacuum valve still joined. The combined weight was close to the upper limit of the mass range for which the laboratory balance was capable and imparted a systematic 0.05 to 0.01 g addition to recorded weights.

4 Results

4.1 Gravimetric Water Content

The gravimetric water loss and water recovered following vacuum distillation are tabulated in Appendix A. Due to the errors associated with weighing gravimetric water loss, gravimetric water gain results are plotted in Figure 1. The volumetric water content shown in Figure 1 was calculated using the gravimetric water gain and Equation 1. These results reproduce the major features of the DGR-1/2, DGR-3 and DGR-4 profiles, including variable water contents in the Silurian sections.



Note: Replicate data for each sample is shown. Horizontal blue lines show the depth of opportunistic groundwater (OGW) samples in the Salina Upper A1 Unit, the Guelph Formation and the Cambrian sandstone.

Figure 1 DGR-5 and DGR-6 Volumetric Water Content by Water Gain Results

Figure 1, and all depth profiles given in this Technical Report, plot data with reference depth to DGR-1/2. For inclined boreholes DGR-5 and DGR-6 this requires determination of true vertical depth for each sample obtained from DGR-5 and DGR-6 and then conversion of these true vertical depths to equivalent depths in DGR-1 and DGR-2.

Samples collected in the vicinity of the Salina Upper A1 Unit permeable horizon have low water contents, with values near the depth of 325 mBGS less than 5%; water contents were higher above and below the Salina Upper A1 Unit permeable horizon. Below the Salina Upper A1 Unit, water contents increase towards the permeable horizon at the top of the Guelph Formation, to values of up to 20%. Below the Guelph Formation

permeable zone, water contents decrease down to the Gasport Formation to values below about 5%. At the base of the Gasport Formation and top of the Cabot Head Formation dolostones, there is a sharp increase in water content, with values up to and above 12%.

Below the lower Gasport Formation, water content drops through the Cabot Head and Manitoulin formations in both DGR-5 and DGR-6 to less than 1% at the top of the Queenston Formation. The Upper Ordovician shales are characterized by values similar to DGR-2, DGR-3 and DGR-4, averaging close to 7-8% water content. The range of water contents measured in DGR-5 and DGR-6 is consistent with that observed in DGR-2, DGR-3 and DGR-4.

Water contents in the Cobourg Formation range between 0.5 and 2.6%, with no discernable trend with depth. These variable but low porewater contents are measured in the Sherman Fall and upper Kirkfield formations. Throughout this section, these very low water yields compromise the samples for analysis of stable isotopes in these materials, with some 25% of samples having insufficient yield for a reliable analysis. Contributions from clay hydration waters in the Ordovician limestones are unlikely to be significant due to low clay content (Intera Engineering Ltd., 2010e; 2010f).

In the lower Kirkfield Formation (DGR-5 and DGR-6), water contents are variable, with some samples measured at up to 5%. The high water content of 12.2% observed in the Coboconk Formation represents the ash layer. Below the ash layer through to the bottom of the core holes in the Coboconk Formation (DGR-6 only), water contents are below 1%.

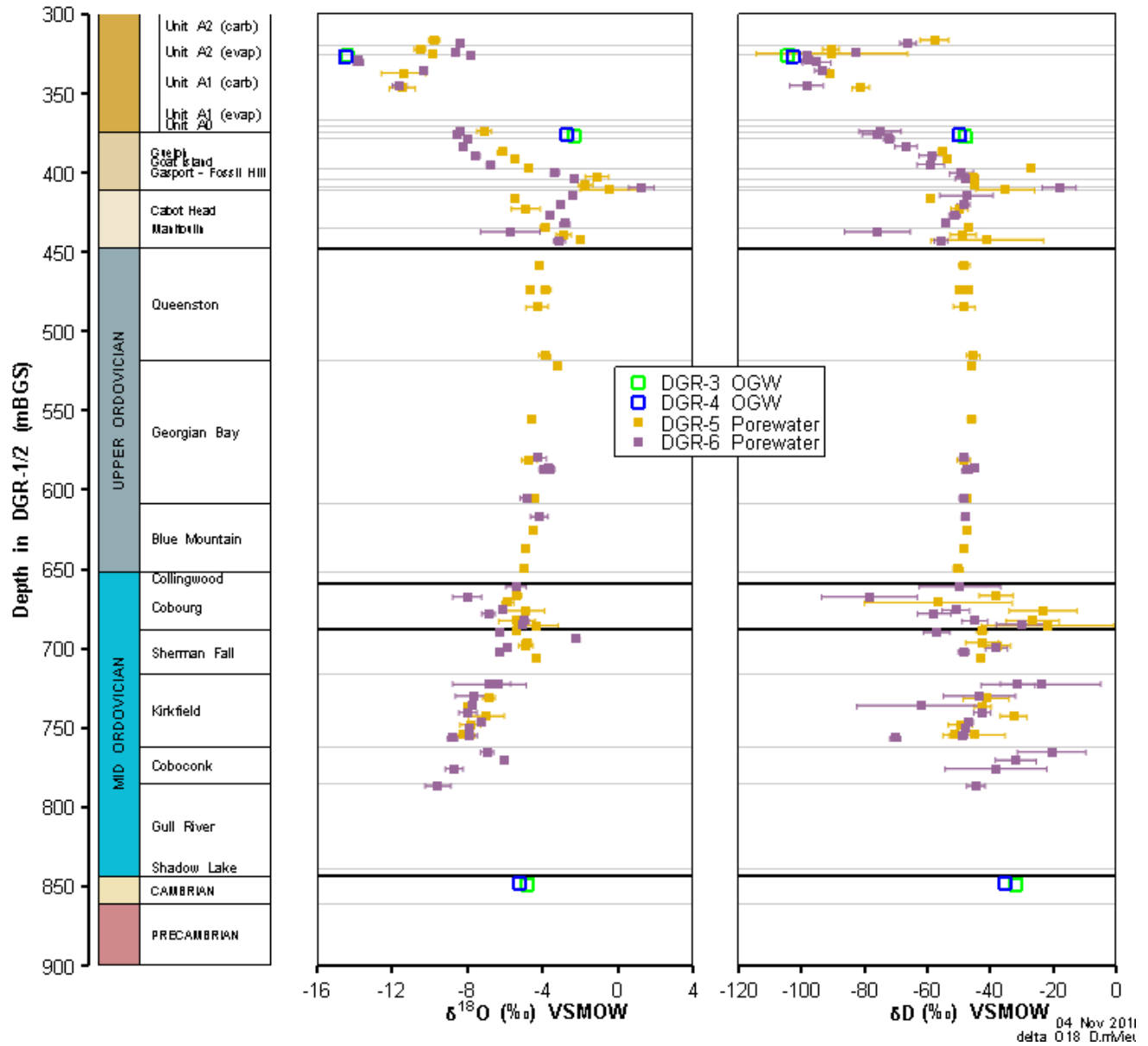
4.2 Porewater Isotopes

The $\delta^{18}\text{O}$ and δD values of porewaters for all extractions are tabulated in Appendix A. Porewater results are plotted with depth in Figure 2 as the average and standard deviation of the replicate samples. Isotope measurements plotted in Figure 2 have been filtered to remove values with poor reproducibility (standard deviation $>5\text{‰}$ for δD and $> 0.5\text{‰}$ for $\delta^{18}\text{O}$). In cases where the $\delta^{18}\text{O}$ values were acceptable, indicating no problem with the extraction, then δD values with a standard deviation marginally exceeding 5‰ were accepted. These results are evident from the error bars in Figure 2.

Opportunistic groundwater sample results from the permeable horizons in DGR-3 and DGR-4 (TR-08-18, Intera Engineering Ltd., 2010c) are also shown in Figure 2. These groundwater results were corrected for salinity following Horita et al. (1993).

The selection of DGR-5 and DGR-6 drill cores for testing was designed to improve data resolution near features of hydrogeologic interest, including (i) the Salina Upper A1 Unit permeable zone, (ii) the Guelph Formation permeable zone, (iii) the Cobourg/Sherman Fall formation interface, and (iv) the ash bed of the Coboconk Formation.

Overall, the DGR-5 and DGR-6 isotope profiles capture the essential elements of the DGR-1 to DGR-4 profiles, with a depletion trend down to the Salina Upper A1 Unit permeable horizon followed by a general increase in both $\delta^{18}\text{O}$ and δD to the Guelph Formation. Values through the Upper Ordovician shales remain enriched, at values near -4‰ for $\delta^{18}\text{O}$ and -50‰ for δD . The depletion trend observed for $\delta^{18}\text{O}$ in all other drill cores through the Middle Ordovician limestones is observed in both DGR-5 and DGR-6, with values near -8 to -10‰ in the Coboconk Formation. By contrast to $\delta^{18}\text{O}$, δD through this section in DGR-5 and DGR-6 are more scattered and show no significant trend with depth.



Note: Analytical uncertainty represented by error bars as the standard deviation of four replicates per sample. Results of opportunistic groundwater (OGW) sampling of the Salina Upper A1 Unit, the Guelph Formation and the Cambrian sandstone in DGR-3 and DGR-4 are also shown.

Figure 2 $\delta^{18}\text{O}$ and δD in Porewaters by Vacuum Distillation for DGR-5 and DGR-6 Cores

4.2.1 Salina Upper A1 Unit Permeable Horizon

The water isotopes show an irregular depletion trend towards the highly depleted Salina Upper A1 Unit in this section (Figure 2). The drill fluid analyses carried out near the Salina Upper A1 Unit shows δD near -53.3‰ and $\delta^{18}\text{O}$ between -5.3‰ and -6.4‰ for DGR 5, and δD was near -5.9‰ and $\delta^{18}\text{O}$ was near -7.3‰ for DGR-6 (Geofirma Engineering Ltd., 2011a). The enrichment in water isotopes in the porewater samples compared to the groundwater samples in the Salina Upper A1 Unit permeable horizon may be due to drill fluid contamination. This is very likely given the field observations of open interconnected porosity in core samples collected within, and near, the Upper A1 Unit.

The relatively higher permeability for the Salina Upper A1 Unit permeable zone sampled in DGR-5 and 6 may have allowed enriched drill fluid to affect the water isotopes near the Salina Upper A1 Unit. However, two samples from DGR-6 with low water contents (lower permeability) close to the Salina Upper A1 Unit groundwater have depleted values and are considered to be representative of porewater values. Porewater samples considered to be affected by drill fluid contamination are highlighted in Appendix A.

4.2.2 Guelph Formation Permeable Horizon

The profiles for both $\delta^{18}\text{O}$ and δD through the Guelph to Gasport formations become more enriched with depth (Figure 2). The porewater results in the Guelph Formation are more depleted than those for the Guelph groundwaters (from DGR-3 and DGR-4). This is accompanied by a trend to high water content in the Guelph Formation core samples (Figure 1). A comparison of the DGR-5 and DGR-6 water isotope results with the drilling fluid chemistry (TR-09-02, Geofirma Engineering Ltd., 2011a) suggests drill water contamination may be a factor for the porewater results in the Guelph Formation (Appendix A). Due to the permeability of the Guelph Formation, porewater results cannot be considered to be free of drill fluid contamination.

4.2.3 Gasport Formation to Cabot Head Formation

The downward enrichment trend in this lower Silurian section shows a clear reversal at the base of the Gasport Formation, with isotopic depletion through the Cabot Head and Manitoulin formation dolostones to the top of the Queenston Formation shales. This reversal is observed in DGR-5 and even more clearly in DGR-6 (Figure 2). This reversal is largely coincident with a zone of higher water content (up to 10%) found over the contact between the Gasport Formation and the underlying Cabot Head Formation.

No groundwater inflows or elevated hydraulic conductivity have been previously identified in this interval. Drilling fluid contamination in these samples can be ruled out as this is a positive trend, with no excursions to more negative values which would signify drilling fluid present in the porewaters. Below this feature, both isotopes and water content decrease to the base of the Silurian section and the contact with the Upper Ordovician shales. At this contact, the stable isotope values of porewaters are near those measured in the upper Queenston porewaters.

4.2.4 Cobourg – Sherman Fall Formation Contact

Analysis of isotopes of methane and helium in DGR-2, DGR- 3 and DGR-4 core porewater (TR-07-21, Intera Engineering Ltd., 2010i; TR-08-19, Intera Engineering Ltd., 2010g) indicated the presence of a barrier to gas migration at the top of the Sherman Fall Formation limestone based on measured steep concentration gradients in this area. This area has further been suggested to be an interface between in-situ biogenic CH_4 and He production in the Upper Ordovician shales and allochthonous thermocatalytic CH_4 and regional He that has moved into the Black River and lower Trenton groups via the Cambrian sandstone.

The trends for $\delta^{18}\text{O}$ and δD in DGR-5 and DGR-6 core samples near the Cobourg –Sherman Fall contact are shown in Figure 2. For the DGR-6 core, $\delta^{18}\text{O}$ begins a depletion trend starting at the base of the Cobourg Formation towards the low values measured in the Gull River Formation. For DGR-5 core the $\delta^{18}\text{O}$ depletion trend starts deeper near the bottom of the Sherman Fall Formation. At these approximate depths δD begins an enrichment trend that decouples it from ^{18}O . Geochemical profiles (below) show a trend towards lower concentrations beginning approximately at the Cobourg/Sherman Fall formation contact.

The available gas, major ion and isotope profiles all indicate a significant interface at this approximate depth that impedes solute and gas transport. This transport barrier is likely related to very low hydraulic conductivities measured in the Sherman Fall and underlying Kirkfield formations from field straddle-testing. The lowest hydraulic conductivities at the DGR site were recorded in these formations, approximating 10^{-16} to 10^{-15} m/s (TR-

08-32, Geofirma Engineering Ltd., 2011b).

4.2.5 Coboconk Formation

From the isotope profiles in Figure 2, three samples from DGR-6 (DGR-5 was completed short of the Coboconk Formation) show enrichments in $\delta^{18}\text{O}$ and δD near the Kirkfield-Coboconk contact. This observation is consistent with enrichments observed for porewater isotopes at this depth in the DGR-3 and DGR-4 cores. The isotope enrichments in DGR-3 and DGR-4 cores were also accompanied by enrichments in Cl^- , which is also found in these three DGR-6 samples (Section 4.3.1 below).

The high water content (approximately 12%) recorded in the upper part of the Coboconk Formation is the ash bed (Figure 1). This sample, however, has an isotopic and geochemical signature that indicates contamination with drilling fluid and so does not represent formation water in this interval.

4.2.6 Deuterium Excess

Figure 3 presents the depth profile of deuterium excess, d , determined as the enrichment of D relative to ^{18}O where (Dansgaard, 1964):

$$d = \delta\text{D} - (8 \times \delta^{18}\text{O}) \quad [2]$$

Deuterium excess is a useful parameter with insights into meteoric and non-meteoric processes responsible for partitioning D differently than ^{18}O and expresses the deviation of D from the Global Meteoric Water Line (GMWL) relationship.

As observed in the DGR-2, DGR-3 and DGR-4 profiles, the deuterium excess in DGR-5 and DGR-6 porewater shows a strong shift from near-meteoric values in the Silurian section near the Salina Upper A1 Unit interval, towards deuterium depletion in the Ordovician shales, characteristic of basin brines. The DGR-5 and DGR-6 deuterium excess values then increase down-section through the Middle Ordovician limestones to the bottom of the core in the Coboconk Formation (Figure 3). This downward enrichment trend in deuterium enrichment was first observed in the DGR-2 core and attributed to contributions of water from the underlying crystalline Shield underlying the sedimentary units. Shield brines have a characteristically depleted $\delta^{18}\text{O}$ value with enrichment in δD due to hydrolysis reactions on feldspars (Pearson, 1987).

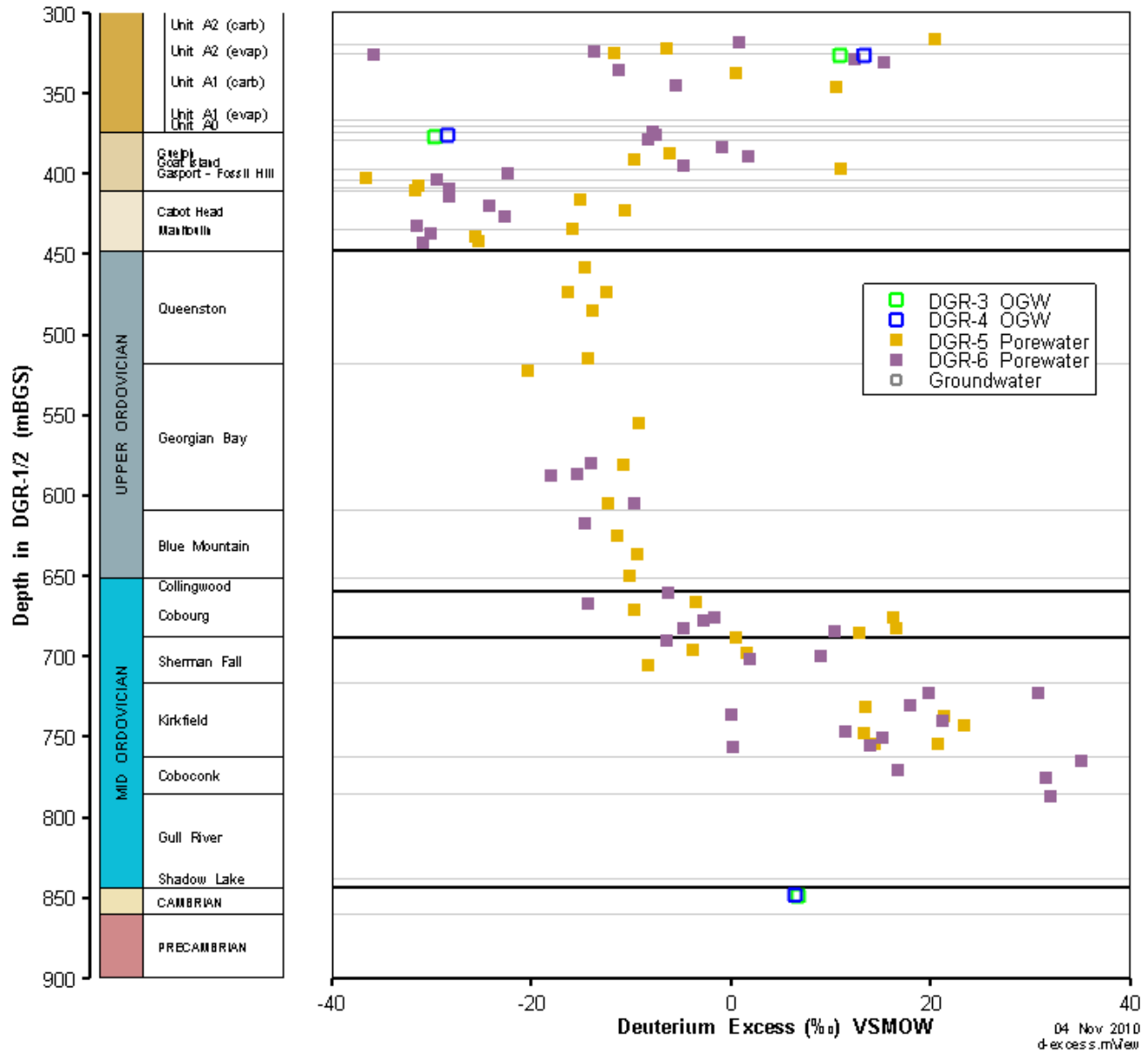


Figure 3 Profiles of Deuterium Excess, d , for DGR-5 and DGR-6 Porewaters, with Data from DGR-3 and DGR-4 Groundwaters for Comparison

4.2.7 Water Isotope Comparison – All DGR Boreholes

Porewater $\delta^{18}\text{O}$ and δD values are plotted together in Figure 4 for all samples from DGR boreholes and from DGR- and US-series groundwater samples. This diagram emphasizes the isotope groupings observed in DGR-2 to DGR-6, including a broad range for the shallow Devonian to Silurian waters which are influenced by various degrees of mixing between the basin brines (Guelph water-bearing zone), shallow meteoric waters and glacial meltwaters. The Ordovician shales cluster in the region typical for basin brines, while the deeper porewaters from the Ordovician limestones follow the downward trend discussed above to more $\delta^{18}\text{O}$ depleted values with an increasing excess in deuterium (δD enrichment).

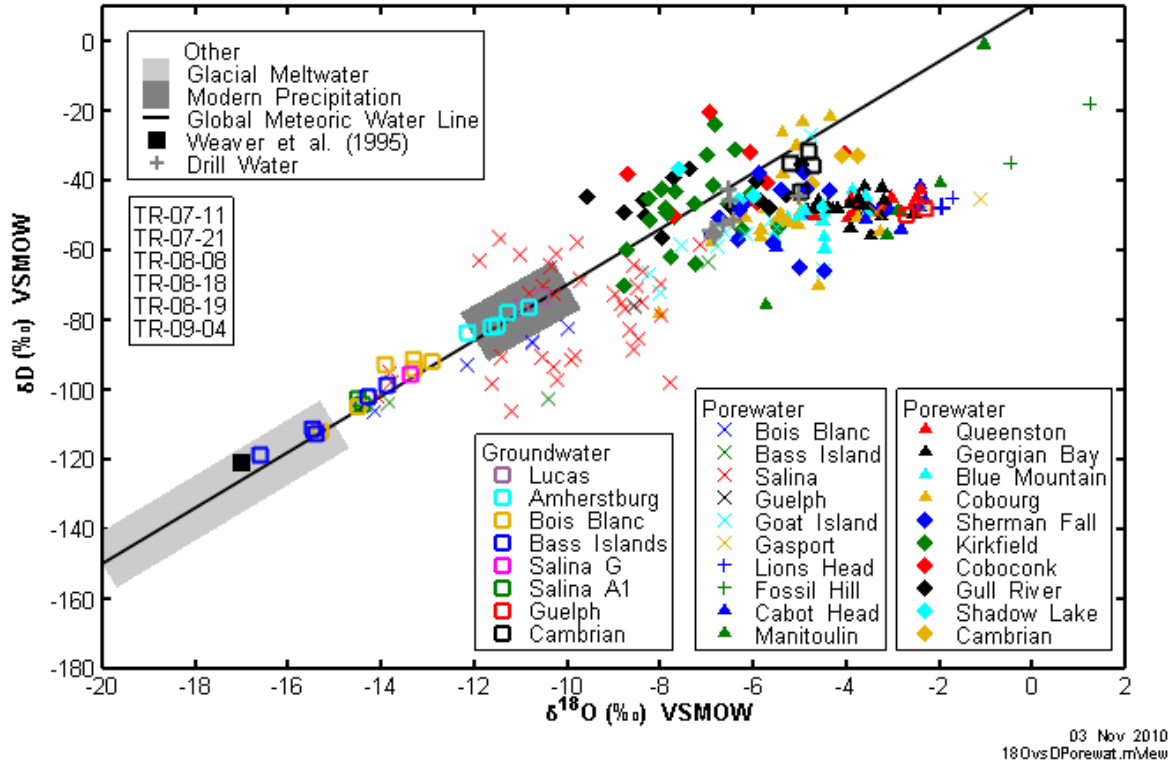


Figure 4 Plot of $\delta^{18}\text{O}$ vs δD for Porewater and Groundwater Samples from All DGR Boreholes and US-series Wells

4.3 Porewater Geochemistry

Porewater data are expressed in molal units as determined from porewater extraction analyses. Groundwater geochemical data from DGR-3 and DGR-4 are from TR-08-18 (Intera Engineering Ltd., 2010c) and are converted from molar concentrations to molal concentrations considering the TDS and density of the groundwaters (Intera Engineering Ltd., 2011).

Porewater geochemistry trends determined for DGR-5 and DGR-6 cores follow those observed in the DGR-1 through DGR-4 drill cores. The Cl^- trends are similar to the $\delta^{18}\text{O}$ profile, featuring values increasing down-section through the Silurian dolostones to values near 6000 mmol/kgw. This high salinity is maintained through the Ordovician shales. Cl^- concentrations remain high or higher in the Cobourg formation then follow a general trend to lower concentrations in the Middle Ordovician limestones (Figure 5).

4.3.1 Na-Cl Salinity

The groundwater contamination observed for the Salina Upper A1 Unit and Guelph Formation permeable horizons prevents detailed interpretation of solute concentrations from these samples as well. However, that contamination notwithstanding, Na^+ and Cl^- concentrations are observed to increase below the Salina Upper A1 Unit to the Guelph Formation.

Below the Guelph Formation permeable unit, Na^+ concentrations decrease and Cl^- concentrations remain relatively unchanged, resulting in a steady decrease in the Na/Cl ratio through the Gasport and Cabot Head/Manitoulin formations with depth toward the top of the Upper Ordovician shales. This appears to be a transition from a halite-dominated salinity source in the Silurian strata to a brine source that is dissimilar to the

Na-Ca-Cl type Guelph Formation brine and closer to the Ca-Na-Cl type brine observed in the Cambrian rocks (Figure 5). Below the Queenston Formation, this facies trends back through the balance of the Upper Ordovician shales and Middle Ordovician limestones towards the Na-Ca-Cl facies observed in the Guelph Formation.

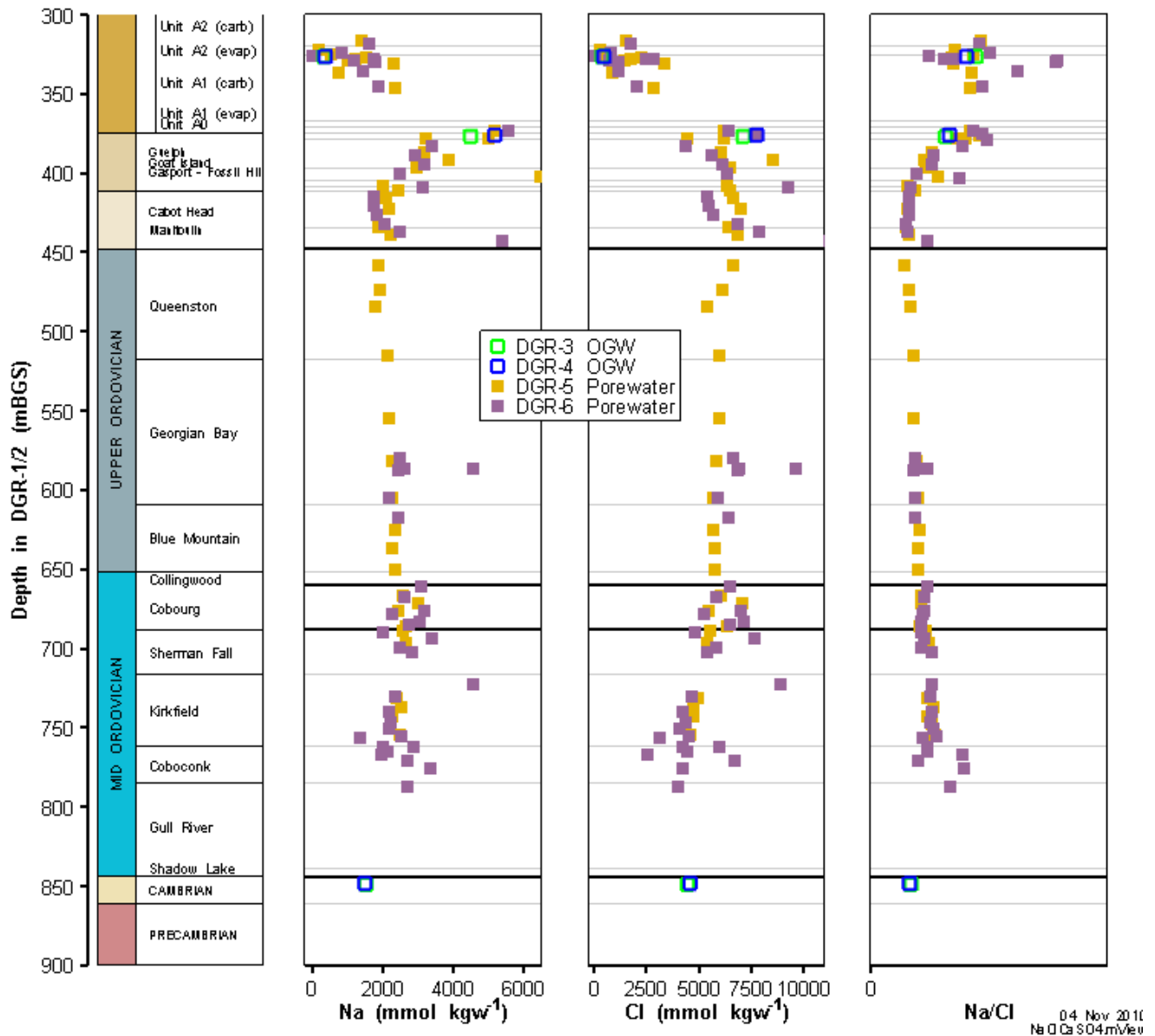


Figure 5 Concentration Profiles for Na^+ and Cl^- with Na/Cl Molal Ratio for DGR-5 and DGR-6; Groundwater Values from DGR-3 and DGR-4

Cl^- concentrations are relatively constant through the Upper Ordovician shales, while Na^+ concentrations increase from 1860 to 2300 mmol/kgw. One sample at 578 mBGS reference depth in DGR-1/2 (DGR6-658.83) shows anomalously high concentrations of both Na^+ and Cl^- , and a jump in Na/Cl , indicating dissolution of halite during sample leaching in the laboratory. A second sample with excess Na^+ and Cl^- leached from halite in the laboratory is seen at the top of the Collingwood at 652 mBGS (DGR6-747.54). These samples should not be used for geochemical interpretation due to the possible effects of halite dissolution. All DGR-5 and DGR-6 core samples affected by halite dissolution are highlighted in Appendix A.

The Na/Cl ratio continues to increase through the Cobourg Formation, accompanied by variable but increasing solute concentrations. Higher uncertainty in these measurements may reflect poorer precision associated with the much lower water contents in these low porosity rocks. Cl^- concentrations begin to decrease at the Cobourg/Sherman Fall contact, coincident with an increase in the Na/Cl ratio.

Similar Na^+ and Cl^- trends to those observed in DGR-2, DGR-3 and DGR-4 are seen in the DGR-5 and DGR-6 Middle Ordovician limestones from the Sherman Fall through to the Coboconk formations. Here Cl^- concentrations decrease from values near 6000 mmol/kgw to less than 4000 mmol/kgw, with a minimum value of less than 3000 mmol/kgw. Over the same interval, Na^+ remains near 2000 to 2500 mmol/kgw. This trend towards lower Cl^- with relatively unchanging Na^+ is reflected by the Na/Cl ratio which increases through this section. High variability for both Cl^- and Na^+ in the Kirkfield Formation makes this trend less discernable.

The variability observed in the lower Kirkfield Formation at the top of the Coboconk Formation is partially attributable to the anomalies observed near the ash bed at this depth. The relatively higher porosity, and likely permeability, of the ash bed suggests drill fluid has contaminated the porewater samples, preventing these samples from being considered representative and further interpreted. Two of the three samples with enriched $\delta^{18}\text{O}$ values associated with this ash bed also have elevated Cl^- values. Neither, however, has elevated concentrations of Na^+ , and so halite dissolution is not responsible for this increase in Cl^- salinity.

4.3.2 Ca-SO₄ Salinity

Sources of Ca and SO₄ in the reconstructed DGR porewater geochemistry include the porewater itself, gypsum and anhydrite that may have been excessively leached from the crushed rock samples, and sulphide oxidation during the leach period. In the case of sulphide oxidation, the acidity the rock samples from this oxidation would likely contribute to the Ca^{2+} concentration in the leachates by dissolving carbonate minerals in the rock. The experimental protocol for the DGR-5 and DGR-6 core samples included the rinsing and storage of the rock samples for the leaching period in an anaerobic chamber. This was done for two replicates of most samples in the DGR-5 and DGR-6 program. Anaerobic rinsing and storage was not performed on all samples and replicates, however, due to restrictions on the space available in the anaerobic chamber.

The leaching of samples under anaerobic conditions inhibits sulphide oxidation, but does not prevent dissolution of other minerals such as gypsum and anhydrite. The calculated porewater concentrations for Ca^{2+} and SO_4^{2-} are shown in Figure 6.

Three anaerobically-treated samples in the Salina section have elevated SO_4^{2-} , and $\text{SO}_4^{2-}/\text{Ca}^{2+}$ ratios, but low Ca, which suggests minor gypsum/anhydrite dissolution has occurred. Others in this section, treated aerobically, show enrichments in both Ca^{2+} and SO_4^{2-} , indicating that sulphide oxidation and/or gypsum/anhydrite dissolution has likely occurred in these porewater leachates. The groundwaters from the Salina Upper A1 Unit and Guelph Formation (TR-08-18, Intera Engineering Ltd., 2010c) have much lower SO_4^{2-} than the reconstructed porewaters in this section, and so all porewaters in this section appear to have been affected by mineral interaction as an artefact of the leaching protocol.

The Upper Ordovician shales have low baseline SO_4^{2-} concentrations of less than 10 mmol/kgw, with occasional anomalous concentrations that coincide with increased Ca^{2+} concentrations. Assuming the baseline concentration is correct, the porewater concentrations significantly greater than 10 mmol/kgw suggest anhydrite dissolution during sample leaching. Ca^{2+} baseline concentrations in the shales are approximately 1200 mmol/kg, which on an equivalence basis (2400 meq/kgw) is greater than the Na concentrations in this section (2000 meq/kg).

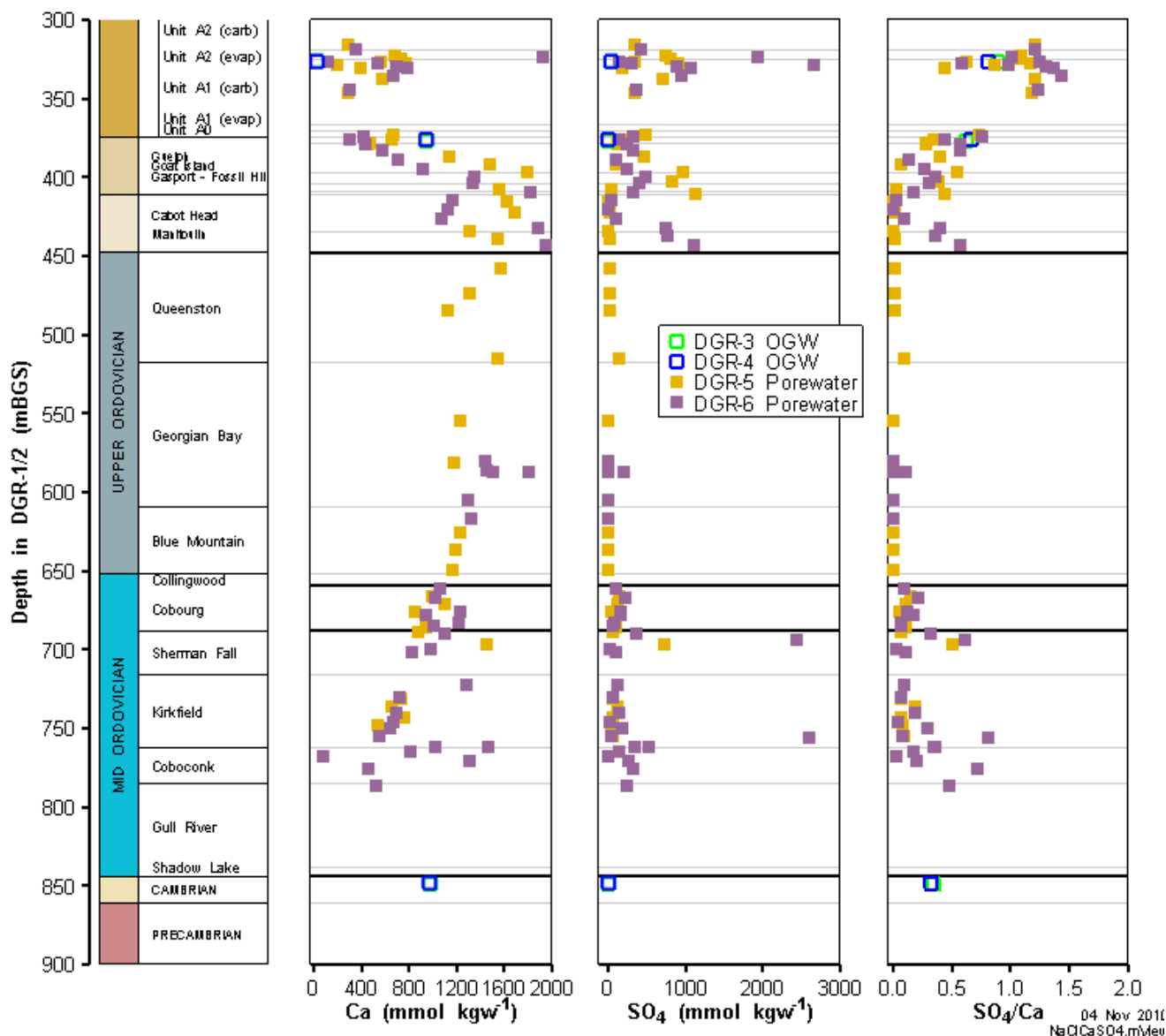


Figure 6 Concentration Profiles for Ca^{2+} and SO_4^{2-} and the Ca/SO_4 Molal Ratio for DGR-5 and DGR-6; Groundwater Values are from DGR-3 and DGR-4

SO_4^{2-} concentrations increase in the Cobourg Formation, along with increases in the $\text{SO}_4^{2-}/\text{Ca}^{2+}$ ratio, suggesting dissolution of anhydrite during leaching in the laboratory. This is not the case for all samples in this section, as Ca^{2+} shows anomalous increases in only a few samples. Ca^{2+} concentrations in the Cobourg Formation follow a baseline trend from a concentration near 1000 mmol/kgw at the top of the Cobourg Formation to <700 mmol/kgw at the base of the Cobourg. Ca^{2+} concentrations decrease in the Kirkfield Formation but are variable in the Coboconk Formation. The variable concentration in the Coboconk Formation are coincident with increases in both SO_4^{2-} and the $\text{SO}_4^{2-}/\text{Ca}^{2+}$ ratio, and are attributed to anhydrite dissolution during leaching.

5 Data Quality and Use

DGR-5 and DGR-6 core porewater chemistry, and isotope data, presented in this Technical Report were generated using vacuum distillation methods previously used for DGR-1, DGR-2, DGR-3 and DGR-4 core samples (Intera Engineering Ltd., 2010g; 2010h). One difference in the testing of DGR-5 and DGR-6 was that the mass of water recovered on the vacuum distillation line was used to determine porewater concentrations, rather than the mass of water lost from the crushed rock core, as was done in previous analyses.

The data presented in this report follow the basic distribution trends as those observed in earlier drill cores (DGR-1 through DGR-4). Further, these results show higher reproducibility, with better resolution, and in many sections, smoother trends, than observed in the previous porewater results. This is believed to be, in part, due to improvements in the vapour transfer during vacuum distillation that were possible because CO₂ sampling was not undertaken for DGR-5 and DGR-6 samples.

Based on 1) the similarity of DGR-5/6 data with DGR-1/2 and DGR-3/4 results, 2) an assessment of confidence in the vacuum distillation results from DGR-1/2 testing (Intera Engineering Ltd., 2010h), and 3) a laboratory evaluation of vacuum distillation methods (Intera Engineering Ltd., 2010d), the major ion and isotope results presented in this Technical Report are believed to be reliable and representative of raw porewater chemistry and isotopic contents from leached cores. The Ca²⁺ and SO₄²⁻ results are shown for some samples to have been affected by mineral dissolution. Samples with significant impact can be identified by the SO₄/Ca ratio. All others can be considered to be representative of raw porewater from the leached cores. Samples with high volumetric water contents (>~10%) across the Salina Upper A1 Unit and Guelph Formation intervals were affected by drilling fluid and are not presented. Drilling fluid contamination also occurred in fluid samples from the Coboconk Formation ash bed for DGR-6.

The porewater ion chemistries presented in this Technical Report will be further evaluated and adjusted based on assessment of soluble mineral effects on core leachates (e.g., anhydrite and halite dissolution) and the influence of suspected anion exclusion on shale porewater chemistry. These evaluations and adjustments will be given in the Descriptive Geosphere Site Model Report (Intera Engineering Ltd., 2011). These adjusted porewater chemistries and isotopes profiles will then be suitable for use in developing descriptive hydrogeological models of the Bruce nuclear site.

6 Conclusions

Methods developed for the DGR-2, DGR-3 and –DGR-4 programs to extract porewaters, gases and solutes from the low porosity and low permeability rocks at the proposed Bruce Deep Geological Repository site have been refined and applied to two new angled cores – DGR-5 and DGR-6. Results for the new tracer profiles replicate the main features of the DGR-2, DGR-3 and DGR-4 profiles, as well as add detail and insights in some important transition sections.

- DGR-5 and DGR-6 porewater results from the Salina Upper A1 Unit, the Guelph Formation and the Coboconk ash layer appear to be, at least, moderately affected by drilling fluid, which prevents geochemical interpretation.
- DGR-5 and DGR-6 stable isotopes show similar trends to the DGR-1, DGR-2, DGR-3 and DGR-4 results. Additional samples in the lower Silurian showed enriched water isotope values. The Cobourg/Sherman Fall contact is characterized by the start of a depletion trend for ¹⁸O accompanied by an increase in the deuterium excess. The trends to lower Cl⁻ salinity and increased Na/Cl ratios also begin near this contact. This is consistent with the He and CH₄ isotope ratios which show marked shifts at this contact. Thus, the gas, solute, and isotope profiles all indicate a significant interface at this depth that impedes solute and gas transport.

- DGR-5 and DGR-6 porewaters adjacent to the Coboconk ash bed show stable isotope and salinity enrichments that support similar enrichments observed in the DGR-3 and DGR-4 cores. These porewaters also have a shift in geochemical facies from the Na-Ca-Cl observed in the Middle Ordovician limestones towards a Ca-Na-Cl brine.

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APPENDIX A

Water Content, Isotopes and Geochemistry of DGR-5 and DGR-6 Pore Fluids by Vacuum Distillation and

Deionized Water Leach

All concentration data in mmol/kgw

¹⁸O and D values relative to VSMOW

DGR-5

Sample ID	% vol.		D	d	B	Na	K	Mg	Ca	Sr	Cl	SO4	Br	charge balance
	WC	18O												
DGR5 345.44-5	10.43	-10.20	-63.9	17.7										
DGR5 345.44-6	10.37	-9.66	-53.1	24.2										
DGR5 345.44-7	10.69	-9.53	-56.3	20.0	12.1	1413	16.6	120	294	2.90	1511	350	1.39	1.0
DGR5 345.44-8	10.65	-9.67	-57.9	19.5	11.6	1387	15.1	116	292	2.57	1519	354	1.36	-0.2
DGR5 352.08-1	3.76	-10.35	-90.8	-8.0	23.7	198	4.05	118	622	5.57	266	675	0.30	2.0
DGR5 352.08-2	3.66	-10.37	-93.3	-10.3	25.0	202	4.41	123	623	5.51	284	680	0.33	1.6
DGR5 352.08-4	3.55	-10.88	-88.0	-1.0	25.9	186	3.97	122	596	5.29	264	659	0.31	1.4
DGR5 354.64-5	2.95				62.4	490	7.86	163	822	8.38	578	893	0.41	2.1
DGR5 354.64-6	3.13	-9.86	-84.9	-6.0	55.8	464	7.23	146	697	7.24	554	760	0.41	2.0
DGR5 354.64-7	3.59	-9.82	-116.6	-38.1	54.0	563	6.90	134	705	7.48	655	746	0.40	2.3
DGR5 354.64-8	3.21	-9.79	-69.5	8.8	67.8	700	8.93	158	731	7.99	776	788	0.48	2.8
DGR5 356.89-1	3.07	Cbnd			1.08	1571	18.6	152	634	5.91	2352	413	3.40	-0.3
DGR5 356.89-2	6.43	-8.14	-69.1	-4.0	0.88	1490	17.2	152	503	6.70	2104	308	3.06	1.7
DGR5 356.89-3	5.81	Cbnd			1.01	1679	19.4	163	595	6.54	2423	370	3.49	0.7
DGR5 356.89-4	6.67	-8.28	-66.4	-0.2	0.82	1463	16.7	143	499	5.93	2110	309	2.92	0.6

DGR5 358.01-5	0.67	-8.98	-66.5	5.4	1.56	1242	21.8	524	761	45.0	1712	880	2.11	4.9
DGR5 358.01-6	0.70		-67.3	-67.3	1.64	1248	22.7	530	794	36.1	1777	929	2.28	3.7
DGR5 358.01-7	0.70				1.60	1231	20.7	494	720	35.4	1752	839	2.11	3.5
DGR5 358.01-8	0.63				1.49	1210	21.6	527	803	37.0	1800	950	2.26	2.5
DGR5 358.99-1	2.83	-10.13	-79.1	1.9	0.57	973	11.6	187	195	19.6	1412	167	1.92	0.0
DGR5 358.99-2	2.85	-10.94		87.6	0.56	982	11.9	196	209	20.3	1436	182	1.92	0.0
DGR5 358.99-3	2.81	-10.61	-81.0	3.9	0.54	1000	11.8	193	202	20.0	1431	173	1.91	0.7
DGR5 358.99-4	2.84	-10.61	-79.3	5.6	0.54	1025	12.0	199	202	20.1	1435	180	1.91	1.1
DGR5 361.64-1	1.87	-7.96	-52.7	11.0	2.88	2274	27.3	129	377	44.1	3263	168	4.16	-4.2
DGR5 361.64-2	1.96	-7.92	-65.1	-1.7	3.97	2327	53.6	146	415	51.4	3363	182	4.97	-3.2
DGR5 361.64-3	1.71	-7.76	-64.1	-2.0										
DGR5 361.64-4	1.90	-8.19	-65.4	0.2										
DGR5 368.20-5	9.43		-92.1	-92.1	1.55	552	6.51	68	475	4.56	610	532	0.22	-0.8
DGR5 368.20-6	4.89	-12.57	-90.2	10.4	2.66	954	10.0	110	689	6.83	1157	874	0.44	-6.2
DGR5 368.20-7	4.61	-12.09	-90.4	6.3										
DGR5 368.20-8	7.26	-11.01	-90.3	-2.2										
DGR5-378.16 -1	11.94	-12.34	-85.3	13.5	2.02	2512	16.1	129	278	2.69	2826	327	1.66	-2.0
DGR5-378.16 -2	12.35	-11.67	-79.8	13.5	2.26	2163	16.4	136	302	2.92	2778	356	1.62	-6.7
DGR5-378.16 -3	12.64	-11.03	-79.7	8.6										
DGR5-378.16 -4	12.79	-10.81	-79.8	6.6										
DGR5 407.22-5	2.30	-6.84	-80.2	-25.5	10.9	5055	78.6	389	647	32.0	6114	429	8.49	1.6
DGR5 407.22-6	2.32	-6.70	-59.0	-5.4	11.5	5125	79.5	406	670	30.9	6236	503	8.37	0.7
DGR5 407.22-7	2.35	-7.45		59.6	11.3	5198	80.1	396	663	29.5	6159	490	8.35	1.7
DGR5 407.22-8	2.26	-7.43	-59.5	-0.1	11.4	5266	83.2	418	670	32.4	6174	503	8.33	2.3
DGR5 410.29-1	18.83	-7.23	-59.2	-1.3	2.40	12891	37.1	112	681	5.76	13146	237	7.67	3.1
DGR5 410.29-2	18.63	-7.21	-53.3	4.3	2.39	12612	35.9	107	682	5.70	13730	238	7.59	0.0
DGR5 410.29-3	18.73	-4.60	-49.6	-12.8	2.12	13082	32.1	94	621	5.12	14671	222	7.45	-1.9
DGR5 410.29-4	19.30	-5.01	-50.0	-9.9	2.31	10558	35.5	105	649	5.77	11785	214	7.32	-0.5

DGR5 413.22-5	14.70	-5.50	-52.0	-8.0	3.19	3286	37.2	156	474	5.27	4420	133	7.20	-1.2
DGR5 413.22-6	14.56	-5.19	-50.6	-9.0	3.14	3168	36.7	153	466	5.29	4395	130	7.02	-2.4
DGR5 413.22-7	14.60	-5.14	-50.6	-9.5	3.34	3158	38.8	159	474	5.70	4421	128	7.03	-2.4
DGR5 413.22-8	14.52	-5.10	-50.1	-9.4	3.30	3271	39.5	163	475	5.73	4445	129	7.24	-1.3
DGR5 413.57-1	11.83	-6.84	-59.8	-5.1	7.11	4407	65.4	232	408	3.65	5597	121	9.8	-0.8
DGR5 413.57-2	11.77	-6.80	-60.0	-5.6	7.22	4588	67.0	232	405	3.70	5621	112	10.1	0.6
DGR5 413.57-3	8.31				10.7	6423	99.2	356	601	5.59	7957	165	14.3	0.8
DGR5 413.57-4	11.72	-6.91	-59.4	-4.1	7.26	4477	68.5	245	417	3.79	5659	127	9.7	-0.5
DGR5 422.14-5	1.94				47.2	3318	258	765	1237	11.8	6741	497	19.8	-1.1
DGR5 422.14-6	2.25	-5.87	-54.5	-7.5	42.3	3060	237	688	1086	10.6	5883	432	17.3	0.6
DGR5 422.14-7	2.27	-6.34	-56.7	-6.1	42.3	3051	235	670	1129	10.5	5787	451	16.6	1.3
DGR5 422.14-8	2.28	-6.28	-55.0	-4.7	42.5	3196	241	679	1120	10.7	5887	448	16.7	1.7
DGR5 426.96-1	9.42	-5.35	-53.1	-10.3	10.3	3742	200	661	1437	19.7	8452	92.5	30.6	-3.1
DGR5 426.96-2	9.46	-5.69	-53.4	-8.0	10.8	3949	202	672	1516	17.2	8650	95.4	31.2	-2.0
DGR5 426.96-3	9.61	-5.45	-55.0	-11.4	9.5	3830	195	632	1492	27.2	8510	106.1	30.9	-2.8
DGR5 426.96-4	9.59	-5.47	-53.2	-9.5	10.2	3854	192	643	1488	15.8	8493	90.2	30.5	-2.3
DGR5 432.17-5	0.89	cbnd			52.0	2913	282	793	1520	22.7	6393	698	19.5	0.1
DGR5 432.17-6	0.83	cbnd			53.7	2809	279	801	1805	30.9	6098	1041	18.6	0.6
DGR5 432.17-7	0.77	cbnd			58.5	3162	309	882	1791	34.7	6753	947	20.4	0.9
DGR5 432.17-8	0.79	-4.76	-27.1	11.0	55.1	2995	289	844	2051	27.2	6553	1218	19.5	0.4
DGR5 440.13-1	2.23	-2.01	-47.3	-31.2	10.8	6124	121	926	2042	25.6	11053	742	33.4	-1.6
DGR5 440.13-2	2.20	-0.92	-44.5	-37.1	11.3	6227	126	955	2068	27.1	11195	725	33.7	-1.1
DGR5 440.13-3	2.27	-0.57	-43.6	-39.1	11.7	6563	131	962	2323	27.6	11521	963	33.9	-0.8
DGR5 440.13-4	2.26	-0.92	-46.1	-38.8	10.1	6979	123	948	2259	27.7	11924	897	34.4	-0.9
DGR5 444.71-1	8.69				4.75	2030	108	496	1587	14.5	6275	53.7	31.4	-0.9
DGR5 444.71-2	12.32	-2.10	-45.1	-28.3	4.60	2030	107	479	1586	14.3	6222	45.7	31.0	-0.6
DGR5 444.71-3	12.37	-1.32	-44.1	-33.5	4.49	1949	103	465	1512	13.5	5979	42.3	30.1	-0.7
DGR5 444.71-4	12.06	-1.71	-45.9	-32.3	4.62	1997	109	496	1544	14.4	6855	45.6	31.5	-6.0

DGR5-799.17 -5	4.40	-7.82	-46.0	16.5	7.7	2117	165	188	518	8.01	4102	44.0	14.4	-6.5
DGR5-799.17 -6	3.83	-8.58	-54.9	13.8	9.5	2333	202	205	560	8.93	4561	51.2	15.6	-7.0
DGR5-799.17 -7	3.99	-7.76	-49.3	12.7										
DGR5-799.17 -8	4.42	-7.24	-47.8	10.1										
DGR5-805.80 - 1		-7.51	-49.1											
DGR5-805.80 - 2	1.43	-8.26	-52.7	13.4										
DGR5-805.80 - 3	1.22	-8.11	-50.8	14.1	10.0	3086	239	263	673	11.3	5658	66.7	18.3	-5.6
DGR5-805.80 - 4	1.46	-8.99	-52.9	19.1	6.2	1874	140	168	419	7.24	3458	37.9	11.4	-5.3

DGR-6

Sample ID	% vol. WC	18O	D	d	B	Na	K	Mg	Ca	Sr	Cl	SO4	Br	charge balance
DGR6 366.03-1	13.35				16.6	1638	32.3	157	361	3.23	1778	430	1.87	1.2
DGR6 366.03-2	13.77	-8.25	-63.2	2.8	15.9	1571	30.7	155	351	3.15	1737	427	1.84	0.4
DGR6 366.03-3	13.22	-8.35	-68.3	-1.5	15.8	1644	31.3	149	352	3.17	1779	421	1.93	1.0
DGR6 366.03-4	13.37	-8.51	-66.9	1.2	16.9	1601	32.7	164	370	3.30	1795	444	1.92	0.3
DGR6 370.70-5	1.77	-8.69	-83.5	-13.9	95.4	929	14.2	95	2069	27.6	934	2088	0.69	1.5
DGR6 370.70-6	1.95	-8.47	-82.0	-14.2	88.7	846	12.7	92	1849	23.6	807	1827	0.56	3.0
DGR6 370.70-7	2.07	-8.69	-83.3	-13.7	80.0	790	12.2	88	1947	24.8	750	1866	0.52	4.1
DGR6 370.70-8	1.84	-8.69	-82.8	-13.3	86.3	764	10.6	90	1845	24.0	802	1955	0.54	-0.7
DGR6 372.70-1	20.25	-7.64	-98.9	-37.8	0.04	24	0.6	48	120	1.06	52	149	0.08	1.6
DGR6 372.70-2	20.29	-7.73	-99.2	-37.4	0.04	68	1.0	51	128	1.14	131	147	0.21	0.0
DGR6 372.70-3	20.72	-7.85	-97.2	-34.4	0.08	12	0.4	50	128	1.17	26	164	0.05	2.2
DGR6 372.70-4	20.59	-7.91	-97.2	-33.9	0.02	11	0.4	46	111	0.97	25	147	0.05	1.4
DGR6 374.48-5	5.93	-6.42	-57.7	-6.4	0.63	1725	20.2	193	754	5.96	2713	553	4.52	-2.5
DGR6 374.48-6	7.67	-6.74	-59.6	-5.7	0.47	1766	19.6	167	367	11.5	2820	126	4.89	-3.8
DGR6 374.48-7	7.39	-6.54	-57.2	-4.9	0.47	1788	19.9	168	393	9.86	2890	152	4.96	-4.4
DGR6 374.48-8	6.25	-6.29	-56.3	-6.0	0.56	1736	20.3	180	629	6.63	2830	420	4.84	-4.3
DGR6 375.21-1	0.85	-6.42	-63.8	-12.5	1.14	1661	27.9	591	2672	25.5	2458	2757	4.05	1.5
DGR6 375.21-2	0.84	-6.01	-57.9	-9.8	1.05	1786	29.8	639	2954	27.8	2465	2835	4.10	5.0

DGR6 375.21-3	0.80	-5.98	-63.0	-15.1	1.14	1801	30.0	616	2637	26.9	2580	2611	4.23	3.3
DGR6 375.21-4	0.87	-5.84	-56.9	-10.2	0.98	1733	27.8	546	2511	23.7	2488	2443	4.01	3.3
DGR6 376.38-5	1.85	-14.01	-100.2	11.9	14.2	1126	31.2	158	649	3.12	723	861	0.58	6.2
DGR6 376.38-6	1.87	-13.93	-97.1	14.4	15.5	1179	34.3	157	624	3.14	736	772	0.60	9.8
DGR6 376.38-7	1.85	-13.59	-96.3	12.4	15.2	1198	35.0	172	725	5.13	743	898	0.61	8.8
DGR6 376.38-8	1.84	-13.58	-88.8	19.9	15.1	1153	33.9	177	761	5.21	757	1036	0.66	4.0
DGR6 377.48-1	1.72	-14.12	-89.8	23.1	19.5	1774	34.3	142	715	2.81	1109	975	0.54	7.0
DGR6 377.48-2	1.49	-13.87	-93.1	17.8	20.5	1809	38.4	157	866	3.25	1138	1176	0.58	5.5
DGR6 377.48-3	1.48	-13.75	-99.2	10.8	19.4	1761	35.1	148	760	3.02	1148	1040	0.59	5.6
DGR6 377.48-4	1.52	-13.47	-98.5	9.2	18.5	1758	36.7	151	799	3.86	1152	1087	0.55	5.2
DGR6 383.51-5	3.70	-10.28	-95.9	-13.7	11.3	1432	22.4	161	655	5.86	1139	905	0.27	2.3
DGR6 383.51-6	5.03				8.9	1057	17.6	121	519	4.79	819	700	0.21	2.9
DGR6 383.51-7	3.11	-10.34	-93.5	-10.8	13.9	1687	27.0	189	779	7.24	1330	1112	0.37	1.3
DGR6 383.51-8	3.13	-10.26	-91.3	-9.2	13.0	1559	33.7	183	710	6.55	1345	1100	0.33	-2.4
DGR6 393.76-1	11.44	-11.38	-93.6	-2.5	4.27	1851	12.9	103	272	2.47	1994	345	0.88	-1.3
DGR6 393.76-2	11.58	-11.23	-101.1	-11.2	4.29	1785	13.3	101	280	2.53	1935	345	0.85	-1.3
DGR6 393.76-3	11.03	-12.05	-104.6	-8.2	4.96	1988	14.3	111	317	2.87	2046	387	0.90	0.7
DGR6 393.76-4	11.22	-11.78	-94.3	0.0	4.72	1883	14.1	110	315	2.84	2024	381	0.88	-0.7
DGR6 426.51-1	3.12	-8.40	-84.6	-17.4	5.92	5616	55.2	291	386	2.61	6335	301	6.29	0.6
DGR6 426.51-2	2.87	-8.34	-73.1	-6.4	6.26	5665	58.6	307	415	2.91	6459	316	6.41	0.5
DGR6 426.51-3	2.88	-8.55	-73.6	-5.1	6.60	5492	60.6	311	438	2.94	6472	315	6.35	-0.4
DGR6 426.51-4	2.93	-8.26	-68.9	-2.8	6.45	5502	59.4	306	429	2.86	6390	327	6.27	-0.1
DGR6 428.53-5	13.76	-8.58	-76.5	-7.9	4.49	7571	48.7	156	314	2.05	8262	153	6.34	-0.1
DGR6 428.53-6	13.62	-8.53	-72.7	-4.4	5.38	7676	56.2	173	340	2.29	8133	146	6.67	1.9
DGR6 428.53-7	13.78	-8.54	-72.5	-4.1	4.60	7838	50.2	152	300	2.07	8070	126	6.21	2.7
DGR6 428.53-8	13.55	-8.58	-82.5	-13.8	4.41	6369	45.2	143	267	1.88	6831	118	5.73	1.1
DGR6 431.76-1	6.05	-8.04	-71.9	-7.6	6.68	21143	53.5	230	432	2.72	21425	248	6.85	1.3
DGR6 431.76-2	6.09	-7.94	-71.9	-8.3	6.47	22941	54.1	224	434	2.78	23234	241	7.29	1.2
DGR6 431.76-3	6.04	-8.04	-70.6	-6.3	6.73	23294	52.9	216	411	2.62	23686	239	7.38	0.9
DGR6 431.76-4	6.09	-7.94	-74.6	-11.1	6.66	21219	54.9	225	436	2.87	22227	243	7.29	-0.3
DGR6 436.54-5*	0.95	-8.05	-67.6	-3.2	39.1	3161	162	343	567	4.76	4073	334	6.74	4.0
DGR6 436.54-6*	0.93	-8.26	-71.3	-5.2	41.4	3455	173	363	605	5.12	4362	342	7.06	4.8
DGR6 436.54-7*	0.92	-8.32	-63.1	3.5	40.4	3687	172	363	617	5.10	4567	350	6.74	4.9

DGR6 436.54-8*	0.90	-8.30	-65.1	1.3	37.0	3238	159	325	523	4.64	4416	295	6.80	0.8
DGR6 442.96-1	3.95	-7.79	-59.8	2.6	19.1	2780	247	443	685	7.09	5536	84.3	15.3	-4.0
DGR6 442.96-2	3.99	-7.65	-53.0	8.2	21.0	3051	257	439	714	7.27	5553	82.9	15.2	-1.1
DGR6 442.96-3	3.89	-7.34	-61.8	-3.1	21.6	3001	250	467	698	7.22	5631	102.3	15.7	-2.3
DGR6 442.96-4	3.85	-7.39	-60.3	-1.1	21.7	2875	256	471	718	7.37	5671	97.1	15.7	-3.3
DGR6 449.08-5	1.81	-7.09	-63.9	-7.2	31.6	3070	223	621	879	9.06	6036	230	16.5	-1.7
DGR6 449.08-6	1.76	-6.67	-55.3	-1.9	34.5	3190	237	635	909	9.56	6070	235	16.5	-0.3
DGR6 449.08-7	1.70	-6.73	-55.4	-1.5	37.7	3216	241	641	942	9.65	6138	250	16.6	-0.2
DGR6 449.08-8	1.67	-6.60	-61.2	-8.4	36.2	3284	244	654	945	9.85	6251	243	16.8	-0.2
DGR6 455.65-1	0.84	-3.67	-53.0	-23.7	29.3	2649	219	1063	1505	16.5	6706	602	25.7	0.4
DGR6 455.65-2	0.79	-3.23	-46.1	-20.2	28.2	2651	215	1049	1383	17.4	6808	469	26.1	-0.3
DGR6 455.65-3	0.85	-3.12	-51.7	-26.8	27.5	2348	200	963	1311	15.7	6085	513	23.3	-0.3
DGR6 455.65-4	0.85	-3.37	-45.8	-18.8	26.1	2285	191	927	1194	14.1	5813	383	22.1	0.9
DGR6 460.10-5	2.15	-2.29	-46.2	-27.9	9.74	14743	114	870	1422	46.0	20250	396	29.6	-4.0
DGR6 460.10-6	2.14	-2.19	-43.5	-26.0	8.82	16533	109	849	1340	51.8	21985	384	29.3	-4.0
DGR6 460.10-7	2.09	-2.32	-50.9	-32.3	8.81	14715	104	818	1268	42.6	19774	391	28.4	-4.0
DGR6 460.10-8	2.09	-2.30	-50.1	-31.7	8.43	18039	106	845	1286	44.3	23992	428	29.9	-5.2
DGR6 465.67-1	0.44	0.40	-16.5	-19.7	30.0	3003	250	865	2233	22.7	8714	954	31.2	-6.0
DGR6 465.67-2	0.44	1.24	-16.8	-26.7	30.1	3189	264	841	1656	22.5	9298	99	34.4	-6.0
DGR6 465.67-3	0.43	1.34	-25.9	-36.6	33.6	3268	286	872	1686	23.4	9537	105	35.1	-6.0
DGR6 465.67-4	0.53	2.05	-13.4	-29.8	27.4	3138	265	874	1680	21.7	9407	135	35.2	-6.6
DGR6 471.63-5	10.45	-2.37	-38.6	-19.6	7.94	1782	270	278	1148	14.2	5431	33.4	29.2	-6.0
DGR6 471.63-6	10.31	-2.37	-44.4	-25.4	8.34	1767	285	292	1223	15.2	5594	35.2	30.1	-5.7
DGR6 471.63-7	10.29	-2.36	-48.8	-29.9	7.59	1805	281	291	1225	14.8	5585	36.2	30.0	-5.3
DGR6 471.63-8	13.41	-2.57	-58.7	-38.1	6.66	1565	255	268	1085	13.2	5021	29.1	27.0	-6.0
DGR6 477.81-1	11.47	-3.15	-46.7	-21.5	5.24	1616	272	239	1075	13.5	5200	2.25	28.1	-7.3
DGR6 477.81-2	11.40	-3.14	-50.4	-25.3	5.76	1811	294	253	1189	14.7	5706	2.44	31.0	-7.0
DGR6 477.81-3	11.53	-3.08	-50.2	-25.6	5.77	1724	289	244	1147	14.3	5554	2.42	30.2	-7.7
DGR6 477.81-4	11.48	-2.81	-46.8	-24.3	5.25	1781	278	245	1100	13.8	5439	2.30	29.5	-7.1
DGR6 484.51-5	8.90	-3.60	-49.0	-20.2	13.9	1888	353	368	1112	14.5	5742	112	30.5	-7.1
DGR6 484.51-6	8.86	-3.56	-51.6	-23.1	13.3	1840	341	356	1065	13.8	5619	105	29.9	-7.7
DGR6 484.51-7	8.86	-3.61	-51.6	-22.8	13.5	1847	337	361	1069	13.9	5723	109	30.4	-8.4

DGR6-861.96-5	3.59	-7.69	-47.5	14.0	5.74	2421	175	170	528	7.94	4357	41.3	14.4	-5.4
DGR6-861.96-6	3.32	-7.45	-47.7	11.9	6.11	2626	184	189	576	8.68	4680	45.7	15.6	-4.9
DGR6-861.96-7	3.41	-7.96	-49.5	14.2										
DGR6-861.96-8	3.50	-8.36	-51.5	15.3										
DGR6-863.65-5	0.61	-8.40	-71.2	-4.0	6.18	1342	118	540	3226	25.3	3177	2683	10.8	2.5
DGR6-863.65-6	0.62	-8.84	-68.8	1.9	6.52	1352	119	551	3154	23.8	3011	2515	10.4	4.9
DGR6-863.65-7	0.51	-8.93	-68.8	2.6										
DGR6-863.65-8	0.51	-8.99	-72.2	-0.3										
DGR6-870.44-7	0.47				8.16	1876	177	267	970	13.8	3932	341		
DGR6-870.44-8	0.41				8.97	2163	209	296	1061	15.3	4545	357	12.4	-1.8
DGR6-870.44-1					12.3	2594	203	441	1341	22.5	5318	506	14.6	0.1
DGR6-870.44-2	0.28	-6.72	-41.0	12.7	11.8	3186	252	544	1601	26.3	6640	543	18.3	-0.1
DGR6-870.44-3	0.28	-6.51	-38.6	13.5										
DGR6-870.44-4														
DGR6-874.28-1	0.80	-6.44	-33.6	17.9	10.5	2323	162	271	907	13.2	5065	161	15.9	-5.5
DGR6-874.28-2	1.02	-7.15	-24.8	32.5	8.86	1940	128	220	709	10.0	3850	131	11.7	-2.4
DGR6-874.28-3	0.83	-7.01												
DGR6-874.28-4	0.86	-7.21												
DGR6-876.74-1	11.99	-8.44	-47.2	20.3	4.57	2042	96	25	86	0.74	2533	1.78	8.56	-3.8
DGR6-876.74-2	12.09	-8.52	-46.1	22.1	4.57	1918	98	25	70	0.77	2541	1.75	8.58	-7.3
DGR6-876.74-3	12.19	-8.64	-45.8	23.4										
DGR6-876.74-4	12.37	-8.58	-45.5	23.1										
DGR6-880.40-1	0.56	-5.96	-24.4	23.2	2.28	2533	76	637	1247	30.2	6245	254	17.7	-3.0
DGR6-880.40-2	0.44	-6.16	-36.4	12.9	1.88	2861	89	757	1380	25.7	7122	263	19.9	-3.0
DGR6-880.40-3	0.57	-6.10	-34.9	13.9										
DGR6-886.53-5					29.0	3565	257	164	474	6.02	4415	343	12.1	-0.2
DGR6-886.53-6	0.66	-9.04	-49.6	22.7	23.7	3153	224	157	449	5.75	4085	318	11.2	-1.5
DGR6-886.53-7														
DGR6-886.53-8	0.78	-8.37	-26.7	40.2										
DGR6-899.14-5	0.52	-9.08	-42.5	30.1	24.1	3152	248	232	597	7.78	4673	285	12.5	-1.9
DGR6-899.14-6	0.70	-10.05	-46.7	33.7	17.1	2203	176	173	440	5.70	3322	206	8.9	-1.9

Notes: Samples highlighted in **Green** have drilling fluid contamination

Cells highlighted in **gold** include failed extractions due to poor recoveries on line (condensation) or poor reproducibility among replicates.

Cells highlighted in **blue** indicate sample leached in anaerobic chamber

Cbnd = water yields from different runs were combined to facilitate analysis.