

DGR-8 Pore Fluid and Gas Analysis

NWMO-TR-2017-11

July 2017

Sarah Murseli, Ian Clark, Gilles St-Jean, Ratan Mohapatra, Dalal Hanna, David Zuliani, Morgan McLellan, François Lagacé, Max Genest and Laurianne Bouchard

University of Ottawa

nwmo

NUCLEAR WASTE
MANAGEMENT
ORGANIZATION

SOCIÉTÉ DE GESTION
DES DÉCHETS
NUCLÉAIRES

Nuclear Waste Management Organization
22 St. Clair Avenue East, 6th Floor
Toronto, Ontario
M4T 2S3
Canada

Tel: 416-934-9814
Web: www.nwmo.ca

DGR-8 Pore Fluid and Gas Analysis

NWMO-TR-2017-11

July 2017

**Sarah Murseli, Ian Clark, Gilles St-Jean, Ratan
Mohapatra, Dalal Hanna, David Zuliani, Morgan McLellan,
François Lagacé, Max Genest and Laurianne Bouchard**
University of Ottawa

This report has been prepared under contract to NWMO. The report has been reviewed by NWMO, but the views and conclusions are those of the authors and do not necessarily represent those of the NWMO.

All copyright and intellectual property rights belong to NWMO.

Document History

Title:	DGR-8 Pore Fluid and Gas Analysis		
Report Number:	NWMO-TR-2017-11		
Revision:	R000	Date:	July 2017
Author Company(s)			
Authored by:	Sarah Murseli, Ian Clark, Gilles St-Jean, Ratan Mohapatra, Dalal Hanna, David Zuliani, Morgan McLellan, François Lagacé, Max Genest and Laurianne Bouchard		
Approved by:	Ian Clark		
Nuclear Waste Management Organization			
Reviewed by:	Laura Kennell, Monique Hobbs		
Accepted by:	Mark Jensen		

ABSTRACT

Title: DGR-8 Pore Fluid and Gas Analysis
Report No.: NWMO-TR-2017-11
Author(s): Sarah Murseli, Ian Clark, Gilles St-Jean, Ratan Mohapatra, Dalal Hanna, David Zuliani, Morgan McLellan, François Lagacé, Max Genest and Laurianne Bouchard
Company: University of Ottawa
Date: July 2017

Abstract

DGR-8 porewater characterization was completed at the University of Ottawa over the summer of 2012. DGR-8 porewaters were extracted from the cores using the new μ VDE (micro vacuum-distillation experiment) method, and pore fluid geochemistry was reconstructed via post-distilled leaching of the dried rock powders. DGR-8 μ VDE volumetric water contents and stable isotopes agree well with DGR1-6 DGSM data (previous VDE method). Good reproducibility is observed between core replicates ($\pm 0.5\%$ for $\delta^{18}\text{O}$, and $\pm 2.0\%$ for δD , and volumetric water contents mostly within $\pm 0.5\%$), with heterogeneities at the sub-core scale although still within the natural variability observed within these formations. Geochemistry results reveal inconsistencies, in particular with the divalent ions as well as SO_4^{2-} and K^+ (10x higher than previously reported), which is likely the result of leaching of illite interlayer and sulphate minerals due to powdering the rock matrix. These artefacts can be remediated coupling the μ VDE method with a granulated crush and leach technique on contiguous subsamples within the same core length or interbed unit. DGR-8 CH_4 and CO_2 concentration and isotope profiles produced by a newer out-diffusion technique (Isojars[®]) are also consistent with DGSM data (via Wheaton[®] bottles/exetainers), demonstrating good benchmarking.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT.....	iii
1. INTRODUCTION	1
2. BACKGROUND	1
3. METHODOLOGY	1
3.1 μVDE SAMPLE PREPARATION	2
3.1.1 MICRO VACUUM-DISTILLATION (μ VDE) AND STABLE ISOTOPE ANALYSIS OF POREWATERS	3
3.2 SOLUTE LEACHING FOLLOWING MICRO VACUUM-DISTILLATION	4
3.3 PORE GAS ANALYSIS	4
4. RESULTS & DISCUSSION	5
4.1 VOLUMETRIC WATER CONTENT AND STABLE ISOTOPES OF POREWATERS	5
4.2 POREWATER GEOCHEMISTRY	7
4.3 PORE GASES (CONCENTRATIONS AND ISOTOPES).....	11
5. CONCLUSIONS	13
ACKNOWLEDGEMENTS.....	15
REFERENCES	16
APPENDIX A: SUPPLEMENTAL DATA.....	17

LIST OF FIGURES

	<u>Page</u>
Figure 1: Schematic Diagram of μ VDE Porewater Extraction Line.....	2
Figure 2: DGR-8 Versus DGSM Volumetric Porewater Content and Stable Isotope Composition	6
Figure 3: DGR-8 Versus DGSM Porewater Geochemistry	8
Figure 4: Na:Cl and Ca:Mg Ratios from DGR-8 Versus DGSM Leachate	9
Figure 5: DGR-8 Versus DGSM Porewater Trace Element Geochemistry (DGSM data only available for Br)	10
Figure 6: DGR-8 Versus DGSM Pore Gas CH ₄ , CH ₂ H ₆ , C ₃ H ₈ Concentrations and Isotopes	12
Figure 7: DGR-8 (upper) Versus DGSM (lower) Pore Gas CO ₂ Concentrations and Isotopes ..	13

1. INTRODUCTION

The NWMO has been carrying out in-depth geoscientific investigations for the OPG's proposed development of a DGR at the Bruce site, near Kincardine, ON for long-term management of low- and intermediate-level waste (L&ILW). As a part of the NWMO's mandate, a shaft investigation drilling program was completed in 2011 with the drilling of two new boreholes (DGR-7 and DGR-8) to conduct geoscientific investigations near the proposed DGR vent and main shafts to support the design and construction planning for the DGR, and to confirm the results of the DGSM at the shaft locations. This report summarizes results from DGR-8 core pore fluid analysis, using the new micro vacuum-distillation method (μ VDE) developed to optimize pore fluid extraction and analysis from sedimentary rock (Murseli et al. 2017; as NWMO-TR-2017-12), including an out-diffusion technique for characterization of pore gases.

Work described in this Technical Report is within the framework of the NWMO's Adaptive Phase Management Program (APM), which supports ongoing research at the University of Ottawa aimed at investigating methods for improving pore fluid characterization (extraction and analysis) from sedimentary and crystalline rocks. All work was completed in accordance with Test Plan TP-11-04 (DGR-8 core sampling for porewater, microbiology and petrophysical analysis).

2. BACKGROUND

Over the past six years, the University of Ottawa has played a key role in geoscientific investigations at the proposed DGR site for L&ILW, specifically relating to pore fluid characterization methods of low permeability sedimentary formations using high-temperature vacuum-distillation. Other characterization methods have not been consistently successful due to the low porosity and low permeability of the formations of interest. The University of Ottawa's porewater characterization vacuum-distillation line has evolved and improved over the years, and has developed into a robust method able to produce reliable results for the unique shales and carbonates that underlie southern Ontario (Intera Engineering Ltd. 2010a). During the shaft investigation drilling program of the DGR-7 and DGR-8 boreholes, drill core samples were collected for analysis of pore fluid and pore gases, with the objective to confirm the results of the DGSM at the shaft drilling locations as well as for use in design and construction planning near the shaft locations.

3. METHODOLOGY

During the 2011-2012 drilling program, rock cuttings samples from each core length were emplaced in gas-tight Isojars[®] in the field for gas analysis in order to minimize loss from degassing. The remaining core lengths were preserved using the standard method of double vacuum-sealing in N₂-flushed polyethylene followed by aluminum/plastic sleeves, and kept in cold storage at the University of Ottawa until ready to be analyzed. DGR-8 porewaters were analyzed using the new closed-system μ VDE (NWMO-TR-2017-12) method over the summer of 2012. The method involves closed-system crushing and heating of small rock samples (~10 g). A total of 4 to 6 replicates were completed per core to observe sample heterogeneity.

3.1 μ VDE SAMPLE PREPARATION

Cores are prepared for sampling by removing a puck-sized disk from the central region of the core so that only freshly exposed samples are used for analysis. The outer exposed edge of the disk is chipped away to avoid drill fluid contamination, and the remaining portion is broken into several pieces (~8-10 g). These sub-samples are immediately weighed, placed into individual stainless-steel sample holders with a ½" stainless steel ball for crushing, and sealed with a high-temperature silicone septum.

The sample holders containing the rock samples are placed on a Retch MM 200 ball mill, and shaken until crushed to a fine powder (<100 μ m) for approximately 10-15 minutes. Following milling, the sample holders are mounted into individual temperature-controlled block heaters and connected to individual vacuum extraction lines via a 1/16" custom double side-holed needle, fitted with a 20 μ m VCR filter to prevent rock dust from getting into the vacuum transfer during evacuation. Each line is paired with a pre-weighed septum-sealed high recovery 1.2 mL vial on the water vapour recovery side of the line, completing the closed-system extraction. A schematic diagram of the porewater extraction line is depicted in Figure 1.

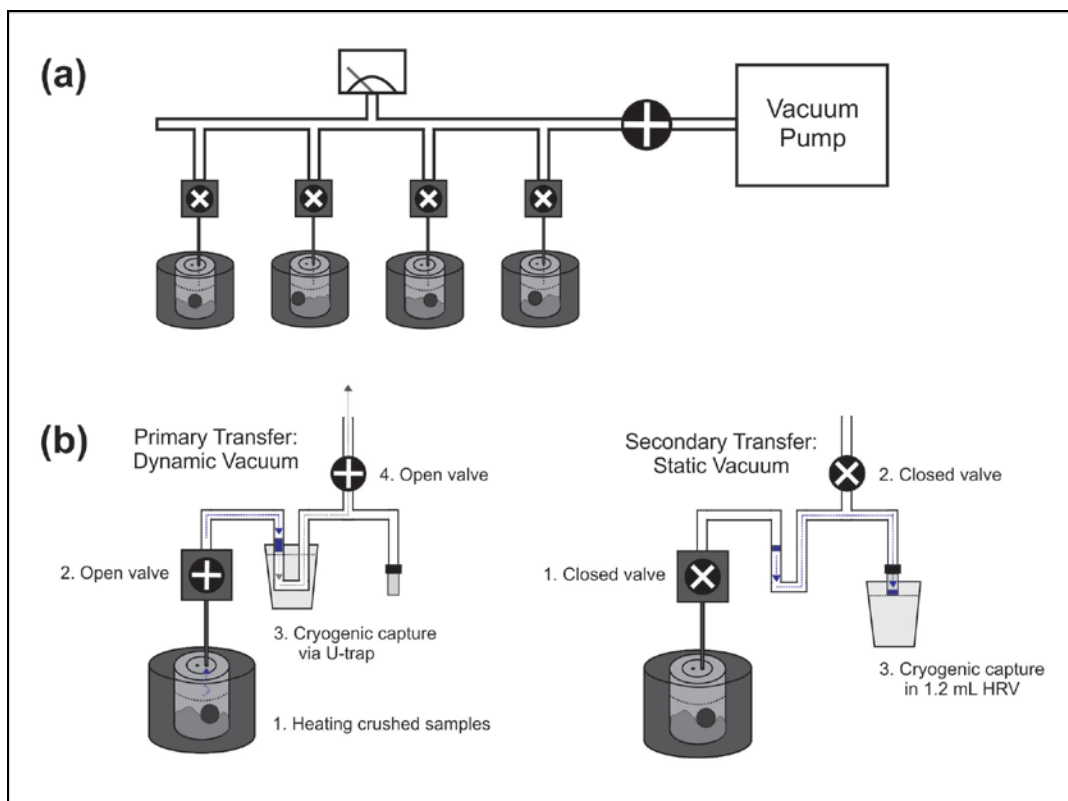


Figure 1: Schematic Diagram of μ VDE Porewater Extraction Line

3.1.1 MICRO VACUUM-DISTILLATION (μ VDE) AND STABLE ISOTOPE ANALYSIS OF POREWATERS

Porewater extraction via the μ VDE methodology involves two stages: 1) primary transfer of water vapour during heating by dynamic vacuum; and 2) secondary transfer directly to a septum-sealed vial under static vacuum (see Figure 1). During primary transfer, the transfer lines are individually evacuated to 30 mTorr, and a built-in U-trap is placed in a liquid nitrogen bath. With the U-trap at liquid nitrogen temperature, the sample valve is slowly opened, and water vapour is frozen in the U-trap under dynamic vacuum over the duration of the extraction period, allowing the vacuum on the transfer line to be maintained. At the same time, the block heaters are turned on, and the temperature is slowly raised to the target temperature, at a ramping speed of 2-3°C/min, and held for the desired heating period. Once the heating/extraction period is complete and the rock sample has been entirely desiccated, the transfer line is isolated from the vacuum pump and sample holder, and the water vapour is transferred from the U-trap directly into a HRV with a heat gun under static vacuum (secondary transfer). Once the extraction process is complete, the vacuum is gently released from the transfer line and the sample is brought to 0°C before it is removed from the line and capped with a silicone/PTFE septum cap. The pre-weighed vials are weighed again to determine the mass of porewater recovered, which is used to calculate the percent of volumetric freshwater content (Equation 1), assuming an average mineral density of 2.7 g/cm³ (Koroleva et al. 2009) and as density of 1 g/cm³ for water.

$$\text{Volumetric water content, WC}_{\text{vol}} (\%) = \frac{m_{\text{wetrock}} - m_{\text{dryrock}}}{m_{\text{dryrock}} / 2.7} \cdot 100 \quad (\text{Equation 1})$$

Sample volume within the individual stainless steel sample holders is limited (approx. 10-12 g maximum, depending on rock density), and overloading the holders can result in poorly crushed samples and incomplete recoveries as a result. In order to accommodate the larger sample volume required to extract sufficient volumes of water for isotopic analysis (>100 μ l), a dual extraction line was developed for the ultra-low water content samples (WC_{vol} <2%). The dual line combines extracted porewaters from two sample holders to one central collection vial, effectively increasing sample volume capacity.

Due to the presence of hydrocarbon contaminants in the recovered porewaters, stable isotope analysis could not be completed by direct injection methods (i.e., cavity ring-down spectroscopy, such as a LGR liquid water stable isotope analyzer) as the hydrocarbons would create spectral interferences. For this reason, $\delta^{18}\text{O}$ and δD of the recovered porewaters were analysed by continuous flow isotope ratio mass spectrometry (CF-IRMS), with an analytical reproducibility of $\pm 0.2\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 2.0\text{‰}$ for δD . The average of the four replicates is reported for each core, and values are expressed as ‰ relative to Vienna Standard Mean Ocean Water (VSMOW).

The porewaters recovered from the DGR-8 cores were analyzed for stable O-H isotopes by CO₂/H₂ equilibration via gas-source continuous flow stable isotope ratio mass spectrometry (CF-IRMS) on a Thermo Delta Plus XP interfaced with a Gasbench II. Samples were analyzed in 3 separate batches, depending on volumes recovered (i.e., 50 μ L, 100 μ L and 200 μ L batches). Samples were prepped for analysis by transferring aliquots to a clean 12 mL exetainer, and adding charcoal grains to each sample exetainer to remove any condensed hydrocarbons, as well as a small amount of Cu to remove any S-containing compounds that

may have condensed from the heated rock, in order to prevent S-sorption and subsequent catalyst poisoning. The exetainers containing the sample were then flushed and filled with a mixture of 2% CO₂ in He gas, and allowed to equilibrate for 24 hours to allow exchange of ¹⁸O between CO₂ and H₂O (Epstein and Mayeda 1953). Following CO₂ analysis on the mass spectrometer, a platinum bead catalyst was added to the same exetainers with the sample aliquots. The exetainers were re-flushed with a mixture of 2% H₂ in He and left to equilibrate with the water prior to mass spectrometer analysis (Coplen et al. 1991). Three laboratory water standards were run sequentially with samples for both δ¹⁸O and δD to calibrate the measured ratios to the international reference water VSMOW. Results are given in per mil differences between the isotope ratio, R(¹⁸O/¹⁶O or D/¹H) of the sample versus the isotopic ratio of the reference standard. Periodic quality control duplicates (QCD) were run on select samples, volume permitting.

3.2 SOLUTE LEACHING FOLLOWING MICRO VACUUM-DISTILLATION

Porewater geochemistry is reconstructed by leaching of porewater solutes from the dry (post-distilled) powdered rock matrix. Following the μVDE procedure, the stainless steel sample holders are transferred to an anaerobic chamber for aqueous leaching in order to minimize the oxidation of sulfate-bearing minerals. The dried rock powder from which the porewater was extracted is transferred into a pre-weighed polypropylene graduated centrifuge tube (falcon tube) and the sample holder is rinsed several times with approximately 40 mL of de-oxygenated doubly deionized water (Deox-DDIW) to ensure recovery of all salts/powders originally present in the sample holder. The powdered rock sample is left to leach in the falcon tube with the Deox-DDIW for a period of 24 hours, after which time the falcon tube is removed from the anaerobic chamber and re-weighed to determine total mass of leach water used. The leachate is promptly filtered out with a 0.45 μm syringe filter, and analyzed for major anions (Cl⁻, SO₄²⁻ and NO₃⁻) by routine liquid chromatography (Dionex® DX-100 coupled to a Dionex® AS40 auto sampler), major cations (Ca²⁺, Mg²⁺, Na⁺, K⁺, B⁺ and Sr²⁺) by atomic emission spectroscopy in an inductively coupled argon plasma (ICP-AES), and trace elements (Br, I, Rb, U and Li) by ICP-MS. All samples were run with a set of internal standards. Analytical reproducibility is better than 5% relative to standard deviation. The total molar amount of each ion leached from the dried powdered rock was normalized to the gravimetric water loss yielded by vacuum-distillation, and presented as molal concentrations for the original porewaters (mmol/kgw).

3.3 PORE GAS ANALYSIS

DGR-8 pore gases are characterized using an out-gassing procedure. Approximately 500 g of fresh bulk core fragments (>3cm) from each core sample were individually sealed in 660 mL gas-tight Isojars® fitted with silicone septa on the lid to enable gas sampling. This step was completed in the field to minimizing loss by degassing. Gases present in the core were left to outgas into the headspace of the Isojar® containers until the concentrations stabilized. Periodic sampling of the CH₄, C₂H₆ and C₃H₈ present in the headspace in the Isojar® found that gas concentrations plateaued after approximately 60 days. Duplicate testing was carried out on select samples to confirm reproducibility.

CH₄, C₂H₆ and C₃H₈ (C₁-C₂-C₃) concentrations were measured using an SRI 8610c Gas Chromatograph and PeakSimple Gas Chromatography software. After the 60-day outgassing period, 35 μL of headspace gas was sampled from each Isojar® with a gas-tight micro-syringe

and injected into the GC for determination of the concentration of all three hydrocarbons present in the Isojar®. A calibration curve was generated using three internal standards to calculate the C₁-C₂-C₃ concentrations for each sample gas. CO₂ concentrations were measured using 50-1000 µL gas aliquots (dependent on sample concentration) run in continuous flow via a GasBench peripheral (Thermo Finnigan) interfaced to an Isotope Ratio Mass Spectrometer Delta XP (Thermo Finnigan). A calibration curve was created using the same internal standards. Final gas measurements from the Isojar® samples were normalized to rock mass and reported as mmol/g_{rock}. Analytical precision is ± 2%.

Stable isotopes of CH₄ (¹³C & ²H) and CO₂ (¹³C & ¹⁸O) were analyzed on a continuous flow Isotope Ratio Mass Spectrometer Delta XP (Thermo Finnigan) interfaced with a Gasbench peripheral. Approximately 50-1000 µL were used for each sample injection, depending on the concentration of target gas of each sample. A calibration curve was created with internal carbonate standards. Analytical precision is reported at ± 0.1‰.

4. RESULTS & DISCUSSION

4.1 VOLUMETRIC WATER CONTENT AND STABLE ISOTOPES OF POREWATERS

The volumetric water content and stable isotopic composition of the recovered DGR-8 porewaters by the new µVDE method are plotted in Figure 2 (see Appendix A for tabulated data). These data are presented with the DGSM data by the VDE method (DGR1-6, previous method) for comparison purposes. Each black dot on the composite profiles represents the average of four replicate measures on one single core (DGR1-6, VDE method). DGR-8 µVDE porewater results (average of 4-6 core replicates) are superimposed on these profiles in large red circles. Larger light blue disks represent groundwater values obtained by opportunistic groundwater sampling (Intera Engineering Ltd. 2010b).

The µVDE DGR-8 volumetric water content and stable isotope profiles align well with previous VDE DGR porewater results, with good correlation between porewaters and groundwaters (large blue circles). The new method also shows good reproducibility between replicates, where most samples are within +/- 0.5‰ for δ¹⁸O, and +/-2.0 ‰ for δD, with volumetric water contents mostly within ±0.5% (see Supplemental data in Appendix A). Heterogeneities can be observed at the sub-core scale. For example, the high standard deviations reported within some of the interbedded zones (i.e., Georgian Bay – shale and limestone) are not an artefact of the method, but rather are a reflection of the heterogeneities within each rock core. Sub-sampling within the Georgian Bay (DGR8-530.81) revealed two very different volumetric water contents within the same core length (~1.3% within the limestone and ~7.2% within the shale interbeds), and different pore fluid compositions (see Figure 3, Section 4.2), resulting in higher standard deviations of the reported averages.

There are some disparities, particularly with δ¹⁸O, in the Blue Mountain through the Trenton Group formations, where we observe δ¹⁸O enrichments up to 2-3‰, but still within the natural variability observed in the DGSM DGR1-6 porewater data. Although there are some deviations on δD in the same region, the effect is not as pronounced as δ¹⁸O. Hydrocarbon contamination of extracted porewaters was considerable for the Blue Mountain, however, this is not suspected to have any effect on δ¹⁸O or δD, as the waters were analysed by equilibration on a gas-bench CF-IRMS. The low water-content samples within the Trenton Group (1-2% by weight) required

pushing the limits of conventional analysis, as volumes were limited (as low as 50 μL ; traditionally 200 μL is required). Reliable isotopic measurements by CO_2/H_2 equilibration methods require a minimum of 100 μL of water (Paul Middlestead, personal communication; 2012); however, efforts were made to analyze the very small volumes (50 μL) by avoiding contact time with the atmosphere during transfer, reduced flushing time/intensity, using a smaller amount of activated charcoal (to mitigate the effects of hydrocarbons), and periodic checks with blind standards. In some cases, there were insufficient volumes for analysis (<50 μL), in which case volumes were combined where at all possible via a second distillation to combine aliquots. It is important to note that extracted porewaters had to be transferred from 1.2 mL micro-vials to 12 mL exetainer vials for analysis of δD and $\delta^{18}\text{O}$ by equilibration. Despite best efforts, the unconventional approaches for analyzing extremely small volumes are pushing the boundaries of analytical methods, and ultimately these smaller volume samples are susceptible to evaporative effects.

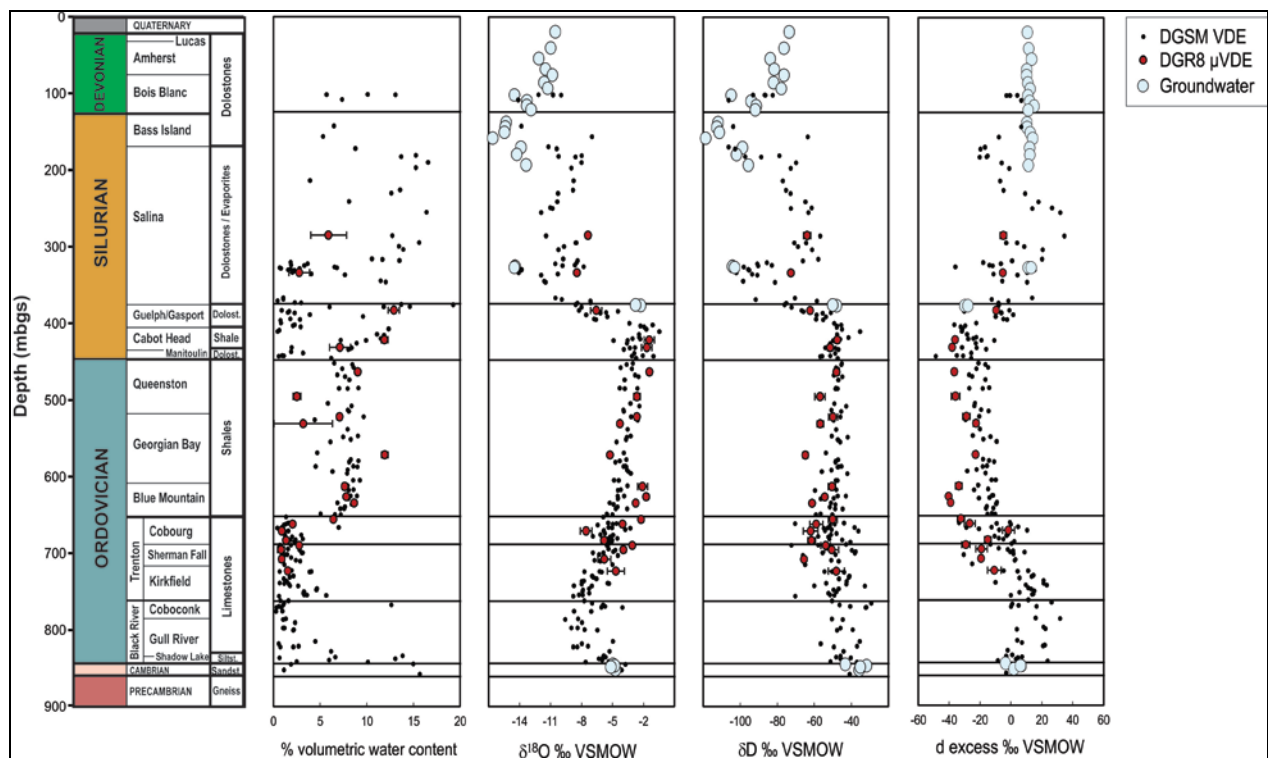


Figure 2: DGR-8 Versus DGSM Volumetric Porewater Content and Stable Isotope Composition

4.2 POREWATER GEOCHEMISTRY

Porewater geochemistry reconstructed from the post-distilled crushed core powders are presented in Figures 3 (major anions & cations), 4 (ratios) and 5 (trace elements). Data is also compiled in Appendix A. DGSM DGR1-6 data (granulated leach; black dots) are also presented for comparison with the DGR-8 data obtained by μ VDE (larger red circles). μ VDE and VDE data is expressed as the average of all replicates on one core length. Groundwater values are also presented where available (large light blue disks).

Subsequent leaching of the post-extraction sample powder provides robust reconstruction of conservative solutes, including Cl^- , Br^- and Na^+ , with generally good agreement between DGR-8 (μ VDE) and DGSM (VDE) data, although solutes with higher ion-exchange potentials are non-conservative during leaching of the powders. Crushing the cores to a fine powder via the μ VDE method greatly increases the exposed surface area and may increase the potential for cation exchange, which can result in the underestimation of reported cations from leaching of the dried powders. Some of the divalent cations (Ca^{2+} and Mg^{2+}) appear to be underestimated in this regard, potentially associated with sorption processes. Sr^{2+} also appears to be underestimated. Nevertheless, cation ratios seem to be preserved (Figure 4), as Na:Cl and Ca:Mg ratios appear to be consistent with results obtained under the VDE method (DGSM data). Elevated K^+ concentrations also are observed for the μ VDE samples (upward of 10x compared to DGSM data), which may be attributable to interlayer leaching of the illite clays. In addition, we also observe more variable SO_4^{2-} concentrations (some data off-scale in Figure 3, see Appendix A), which may suggest dissolution of gypsum or other sulphate minerals, particularly in the Salina Formation, or minor oxidation of the finely disseminated pyrite in these rocks when exposed by powdering. The variable SO_4^{2-} concentrations are, therefore, not considered to be reflective of pore fluid compositions.

Trace element geochemistry is presented in Figure 5 (see also Appendix A). DGR-8 Br concentrations compare well with DGR1-6 data. Other trace elemental results (Li, I, Rb & U) are presented (DGR1-6 data not available for comparison). Increased variability within core replicates is observed at depth (namely within the Trenton group).

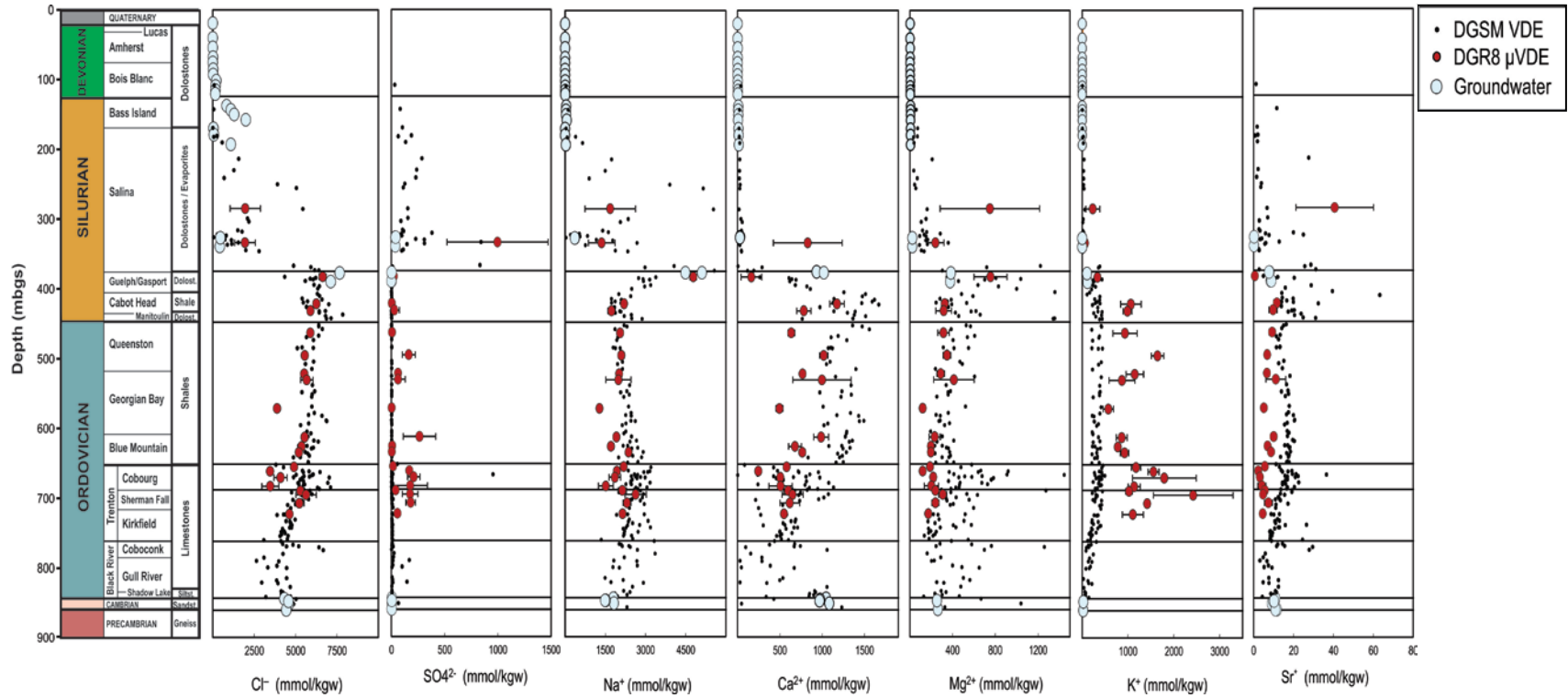


Figure 3: DGR-8 Versus DGSM Porewater Geochemistry

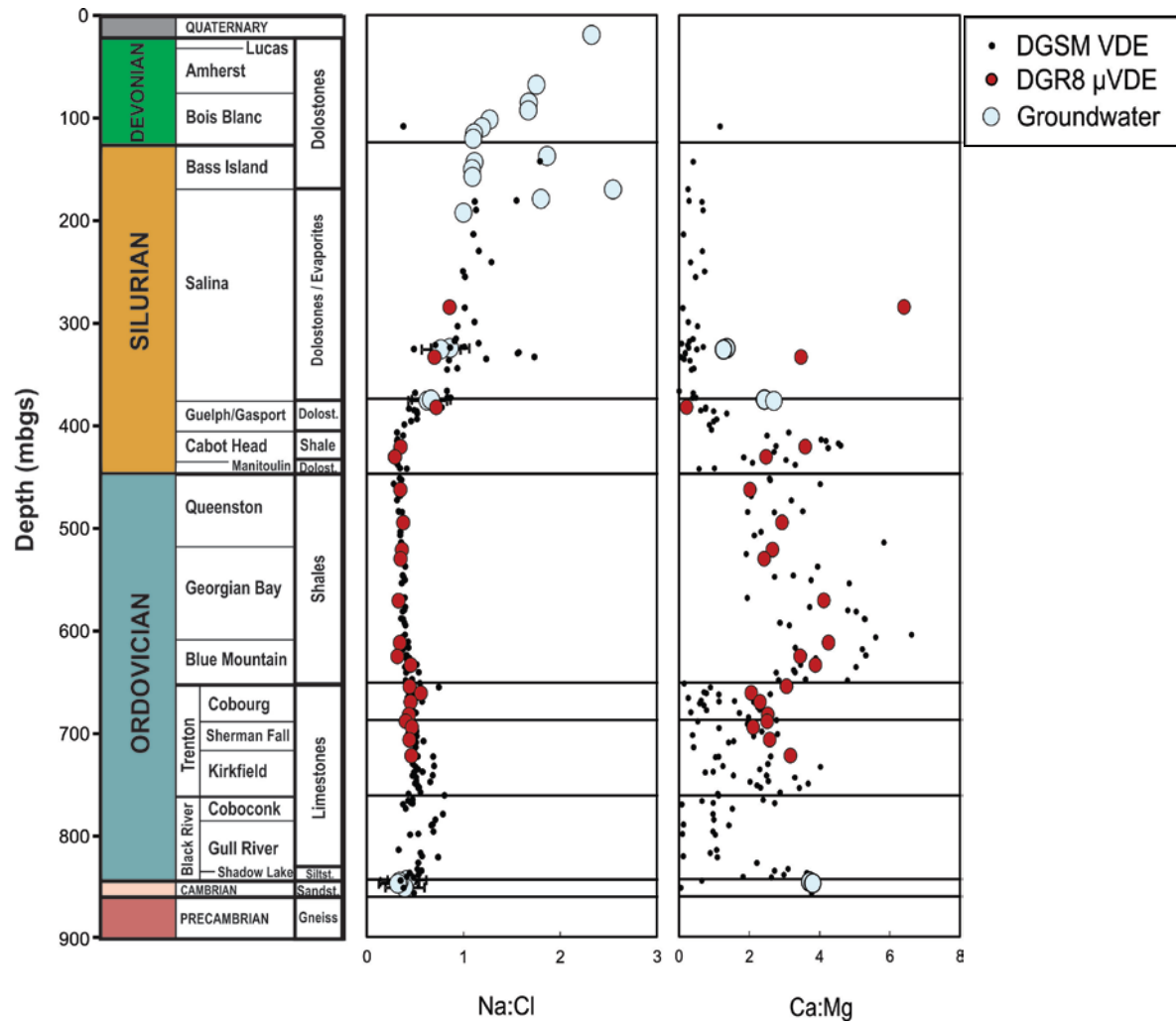


Figure 4: Na:Cl and Ca:Mg Ratios from DGR-8 Versus DGSM Leachate

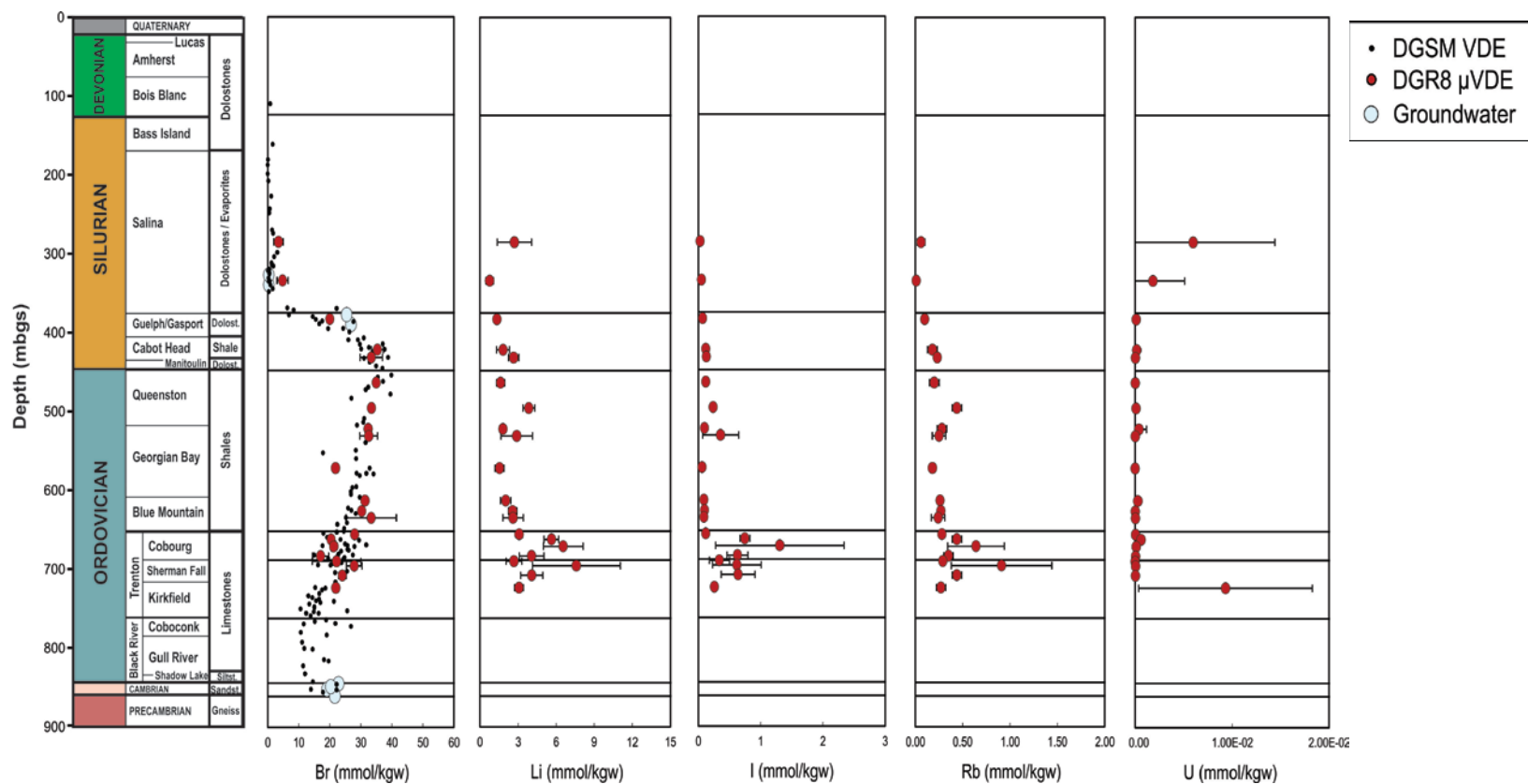


Figure 5: DGR-8 Versus DGSM Porewater Trace Element Geochemistry (DGSM data only available for Br)

4.3 PORE GASES (CONCENTRATIONS AND ISOTOPES)

DGR-8 pore gas concentrations and isotopes are plotted in Figures 6 (CH_4 , C_2H_6 , C_3H_8) and Figure 7 (CO_2), with the complete data set presented in Appendix A. DGSM (DGR1-6) pore gas concentrations and isotopes (CH_4 and CO_2 only) also are presented on these profiles for comparison (black dots). The DGR-8 CH_4 and CO_2 concentration profiles are consistent with the DGSM data (via Wheaton[®] bottles or exetainers), exhibiting higher CH_4 concentrations in the Cobourg (also observed with DGSM data). Both DGR-8 CH_4 and CO_2 isotope profiles also show good agreement with the DGSM data, with one divergence in the Cobourg formation (^2H of CH_4 enriched, ^{13}C of CO_2 depleted) to which we may attribute this to instrumental error (encircled in red on Figures 6 and 7). We also observe a systematic enrichment in $\delta^{13}\text{C}$ and $\delta^2\text{H}$ of C_1 - C_2 - C_3 . These results were attained by utilizing a diffusive technique, whereby the gas was left to out-gas from the rock core into a gas-tight Isojar[®] container over a defined period. Adsorption is greater for the heavier gas molecules (C_2 - C_3) due to the differences in their vapour pressures, and this effect is more pronounced on organic-rich rocks (Cheng and Huang 2004); therefore, one must consider the underestimation of heavier hydrocarbons by diffusive methods as a result of these sorption effects.

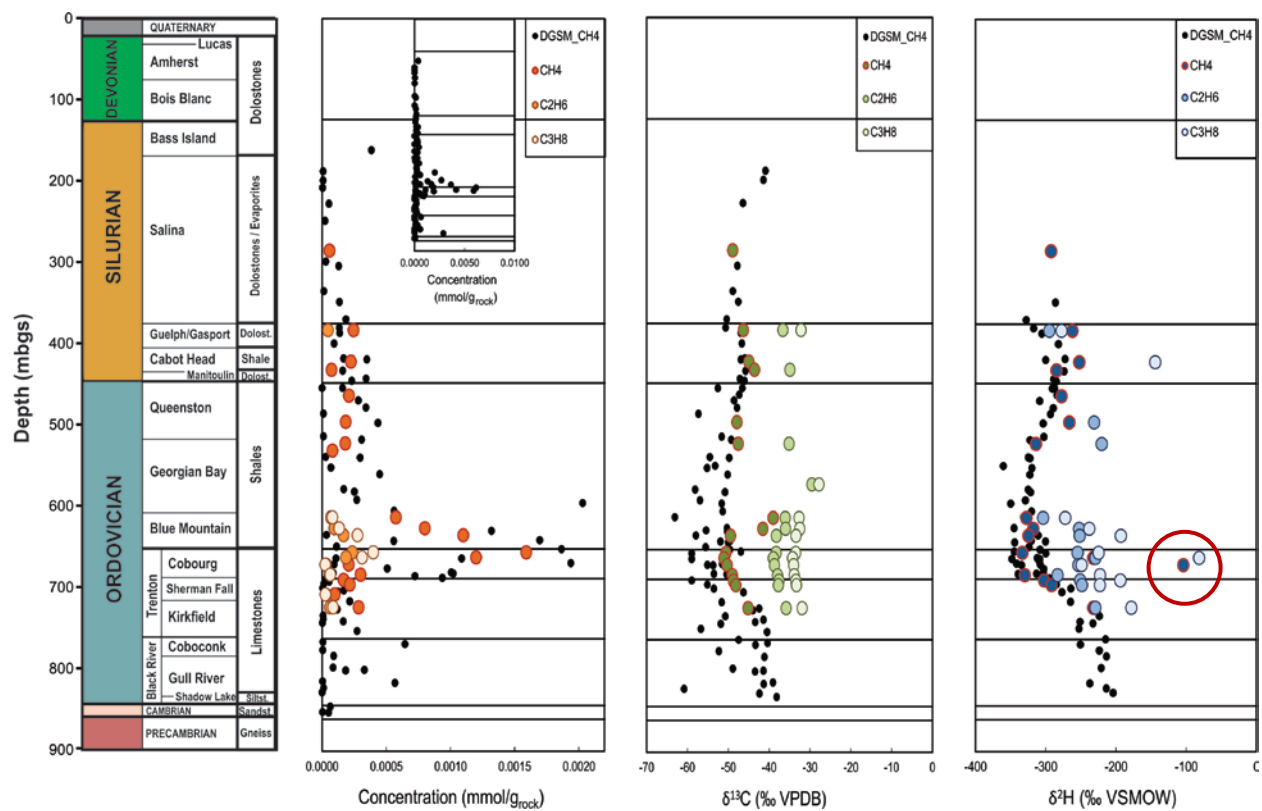


Figure 6: DGR-8 Versus DGSM Pore Gas CH₄, CH₂H₆, C₃H₈ Concentrations and Isotopes

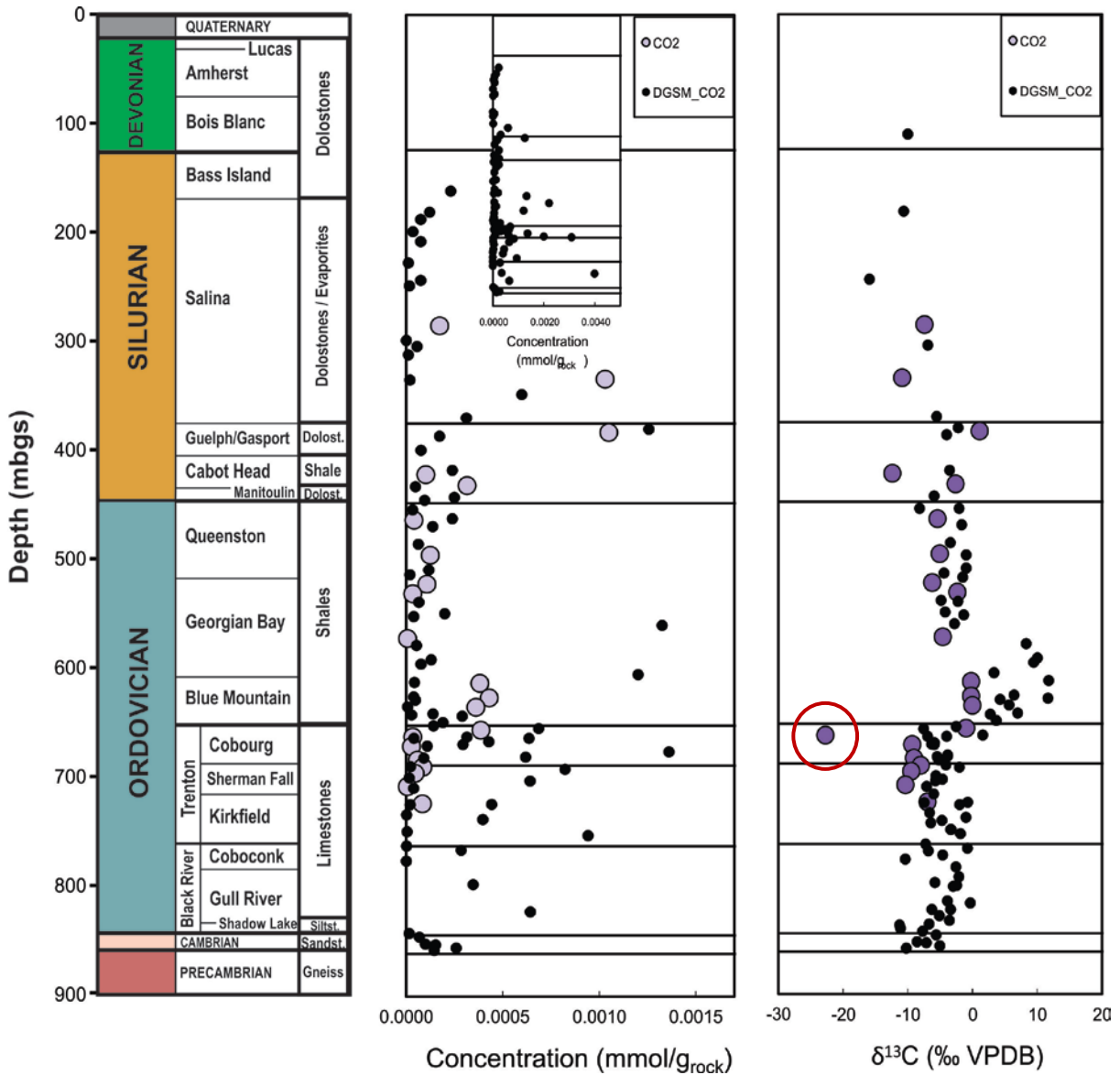


Figure 7: DGR-8 (upper) Versus DGSM (lower) Pore Gas CO₂ Concentrations and Isotopes

5. CONCLUSIONS

The DGR-8 porewater content and stable isotope results produced using the new μ VDE method show very good agreement with DGR1-6 data, replicating main features in the DGSM profiles, and fall within the variability observed within these formations for the DGR1-6 cores.

We also observe good reproducibility within μ VDE core replicates; moreover, we can distinguish heterogeneities at the sub-core scale due to the small sample mass required for analysis. Minor $\delta^{18}\text{O}$ enrichment (2 to 3‰) relative to DGR1-6 data is evident in the Blue Mountain through the Trenton formations, where hydrocarbon contaminants were observed at these depths, although increased variability is noted from previous results within the low water content Ordovician limestones, likely due to analytical artefacts relating to the small recovered porewater volumes. Moreover, organics remain a problem for analysis by direct injection (i.e., LGR); therefore, transferring very small volumes to larger exetainers for analysis by CO_2/H_2 equilibration remains delicate. Sample volume capacity is maximized for the current μ VDE system (~20 g: 10 g in each sample holder x 2 with use of dual line), which creates difficulty when analyzing the low water-content samples (<1%). Moving forward with the μ VDE technique, expansion of the current system to accommodate larger holders, in addition to developing a technique to separate hydrocarbons from the recovered waters, will facilitate the analysis of these exceptional samples. DGR-8 CH_4 and CO_2 concentration and isotope profiles produced using a newer out-diffusion technique (Isojars[®]) show essentially the same results reported from the DGR1-6 analysis (Wheaton[®] bottles and exetainers), which demonstrates good benchmarking.

Given the inconsistencies with the geochemistry results, in particular the divalent ions, as well as K^+ and SO_4^{2-} , coupling the μ VDE method with a granulated crush and leach technique on contiguous subsamples within the same core length or interbed unit will help to remediate the suspected artefact of leaching of illite interlayer clays and sulphate minerals due to powdering the rock matrix. Preliminary testing on analogous core samples from Southern Ontario show promising results from separate granular core leaching to reconstruct porewater geochemistry coupled with μ VDE for isotopic characterization, where the artefacts of divalent sorption issues and elevated K^+ & SO_4^{2-} are eliminated (data not shown).

ACKNOWLEDGEMENTS

We gratefully acknowledge the funding and support from the Nuclear Waste Management Organization. High quality core samples were provided by Geofirma Engineering Ltd. We thank the Machine Shop and Electronics Shop of the Faculty of Science at the University of Ottawa, who helped to execute the design of the new vacuum-distillation system. We also recognize the G.G. Hatch Stable Isotope Lab for their expertise and analysis of the porewater samples by Gasbench IRMS.

REFERENCES

- Cheng, A-L and W-L Huang. 2004. Selective adsorption of hydrocarbon gases on clays and organic matter. *Organic Geochemistry*, 35: 413-423.
- Coplen, T.B., J.D. Wildman and J. Chen. 1991. Improvements in the gaseous hydrogen-water equilibration technique for hydrogen isotope-ratio analysis. *Analytical Chemistry*, 63(9): 910-912.
- Epstein, S. and T. Mayeda. 1953. Variation of ^{18}O content of waters from natural sources. *Geochimica et Cosmochimica Acta*, 4: 213-224.
- Intera Engineering Ltd. 2010a. Vacuum-Distillation Experiments on DGR Core. Technical Report for the Nuclear Waste Management Organization, TR-08-37. Ottawa, Canada.
- Intera Engineering Ltd. 2010b. Opportunistic Groundwater Sampling in DGR-3 and DGR-4. Technical Report for the Nuclear Waste Management Organization, TR-08-18. Ottawa, Canada.
- Koroleva, M, A. De Haller, U. Mader, H.N. Waber and M. Mazurek. 2009. Borehole DGR-2 core: Pore-water investigations. Technical Report for the Nuclear Waste Management Organization, TR-08-06. Institute of Geological Sciences, University of Bern, Switzerland.
- Murseli, S, G. St.-Jean, D. Hanna and I. Clark. 2017. Method Development: Micro Vacuum-distillation Experiments (μVDE). Technical Report for the Nuclear Waste Management Organization, NWMO-TR-2017-12. Toronto, Canada.

APPENDIX A: SUPPLEMENTAL DATA

CONTENTS

	<u>Page</u>
A.1 DGR-8 SUPPLEMENTAL DATA	18

A.1 DGR-8 SUPPLEMENTAL DATA

Table 1: DGR-8 Pore Fluid Water Content and Stable Isotopes

Sample ID	Sub-sample ID	Vol _{wc} (%)	AVG Vol _{wc} (%)	σ Vol _{wc} (%)	δ ¹⁸ O (‰)	AVG δ ¹⁸ O (‰)	σ ₁₈₀ (‰)	δD (‰)	AVG δD (‰)	σ _D (‰)	d excess (‰)
DGR8-285.07	285.07-1	5.10	5.91	1.91	-7.35	-7.37	0.17	-62.20	-63.88	1.93	-4.89
	285.07-2	8.76			-7.67			-66.20			
	285.07-3	4.40			-7.24			-61.60			
	285.07-4	D			D			D			
	285.07-5	4.33			-7.33			-64.40			
	285.07-6	6.96			-7.28			-65.00			
DGR8-333.93	333.93-1	4.56	2.77	1.11	-8.44	-8.44	---	-72.70	-72.7	---	-5.18
	333.93-2	3.15			D			D			
	333.93-3	D			D			D			
	333.93-4	2.16			D			D			
	333.93-5	2.05			D			D			
	333.93-6	1.91			D			D			
DGR8-382.83	382.83-1	D	12.90	0.59	D	-6.58	0.54	D	-62.26	1.19	-9.59
	382.83-2	12.65			-6.09			-62.20			
	(382.83-2-QCD)	---			(-6.10)			(-60.30)			
	382.83-3	13.46			-7.47			-63.30			
	382.83-4	12.61			-6.23			-60.30			
	382.83-5	12.20			-6.51			-62.40			
	382.83-6	13.57			-6.62			-63.10			
DGR8-421.51	421.51-1	11.35	11.91	0.36	-1.22	-1.44	0.49	-45.40	-47.66	1.30	-36.14
	421.51-2	12.08			-2.00			-48.70			
	421.51-3	D			D			D			
	421.51-4	12.31			-1.93			-48.20			
	421.51-5	11.78			-1.01			-48.20			
	421.51-6	12.00			-1.04			-47.80			
DGR8-431.50	431.50-1	D	7.13	1.12	D	-1.69	0.50	D	-51.46	1.38	-37.94
	431.50-2	7.84			-2.26			-51.60			
	431.50-3	6.26			-0.92			-50.40			
	431.50-4	8.61			-1.55			-50.90			
	431.50-5	7.07			-1.90			-53.78			
	431.50-6	5.88			-1.82			-50.60			
DGR8-463.33	463.33-1	D	9.04	0.21	D	-1.42	0.21	D	-48.02	1.42	-36.66
	463.33-2	9.31			-1.26			-48.15			
	463.33-3	8.91			-1.22			-46.26			
	463.33-4	8.83			-1.56			-47.95			
	463.33-5	D			D			D			
	463.33-6	9.08			-1.64			-49.73			
DGR8-495.42	495.42-1	2.55	2.52	0.39	-2.16	-2.64	0.32	-54.2	-56.88	2.77	-35.79
	495.42-2	2.75			-2.87			-61.4			
	495.42-3	2.02			-2.90			-55.8			
	495.42-4	3.02			-2.47			-55.6			
	495.42-5	2.26			-2.78			-57.4			
	495.42-6	D			D			D			
DGR8-521.94	521.94-1	6.77	7.09	0.23	-2.45	-2.64	0.22	-47.11	-49.91	2.40	-28.78
	521.94-2	7.32			-3.03			-46.79			
	(521.94-2-QCD)	---			(-3.00)			(-46.21)			
	521.94-3	6.89			-2.70			-51.31			

	521.94-4	7.07			-2.70			-52.59			
	521.94-5	7.14			-2.55			-50.36			
	521.94-6	7.37			-2.42			-51.30			
DGR8-530.81	530.81-1	1.35	3.20	3.13	D	-4.28	0.04	D	-56.79	1.73	-22.59
	530.81-2	1.27			D			D			
	530.81-3	7.46			-4.30			-58.01			
	530.81-4	6.99			-4.25			-55.56			
	(530.81-4-QCD)	---			(-4.21)			(-57.89)			
	530.81-5	1.04			D			D			
	530.81-6	1.06			D			D			
DGR8-571.68	571.68-1	12.18	11.94	0.34	-5.35	-5.24	0.19	-64.63	-64.80	1.36	-22.87
	571.68-2	12.15			-5.56			-65.10			
	571.68-3	11.48			-5.23			-64.33			
	571.68-4	12.03			-5.09			-62.56			
	571.68-5	12.25			-5.06			-65.60			
	571.68-6	11.56			-5.16			-66.59			
DGR8-612.82	612.82-1	7.73	7.65	0.26	-2.09	-2.09	0.48	-49.29	-50.45	2.05	-33.70
	612.82-2	7.81			-1.85			-49.99			
	612.82-3	7.47			-2.39			-47.50			
	612.82-4	7.28			-2.89			-51.42			
	612.82-5	8.00			-1.74			-50.92			
	612.82-6	7.60			-1.60			-53.56			
DGR8-626.22	626.22-1	7.84	7.82	0.11	-2.08	-1.75	0.23	-53.68	-54.34	0.76	-40.34
	626.22-2	7.95			-1.56			-54.10			
	626.22-3	D			D			D			
	626.22-4	7.69			-1.61			-54.14			
	626.22-5	7.78			-1.75			-55.43			
	626.22-6	D			D			D			
DGR8-634.64	634.64-1	8.84	8.64	0.19	-2.58	-2.76	0.20	-59.99	-61.15	1.04	-39.04
	634.64-2	8.58			-2.98			-61.46			
	634.64-3	8.74			-2.73			-62.00			
	634.64-4	D			D			D			
	634.64-5	D			D			D			
	634.64-6	8.40			D			D			
DGR8-655.63	655.63-1	6.52	6.43	0.13	-2.01	-2.23	0.22	-48.27	-50.06	2.35	-32.26
	655.63-2	6.48			-2.50			-49.97			
	655.63-3	6.37			-2.41			-50.87			
	655.63-4	6.55			-2.08			-48.01			
	655.63-5	6.48			-2.34			-48.91			
	655.63-6	6.20			-2.01			-54.32			
DGR8-662.01	662.01-1	2.10	2.06	0.05	-4.25	-4.03	0.20	-58.87	-58.93	3.50	-26.67
	662.01-2	2.08			-3.89			-54.52			
	662.01-3	1.99			-3.84			-59.25			
	662.01-4	2.07			-4.15			-63.08			
DGR8-670.80	670.80-1	1.04	0.89	0.19	-7.01	-7.55	0.56	-61.9	-61.97	3.90	-1.59
	670.80-2	0.70			-7.50			-58.1			
	670.80-3	0.74			D			D			
	670.80-4	1.07			-8.13			-65.9			
DGR8-683.08	683.08-1	1.08	1.35	0.26	D	-5.81	0.30	D	-61.50	2.10	-14.99
	683.08-2	1.64			-5.67			-60.0			
	683.08-3	1.20			-6.16			-60.6			
	683.08-4	1.48			-5.61			-63.9			
DGR8-689.68	689.68-1	2.89	2.76	0.16	-3.23	-3.08	0.16	-51.9	-53.82	2.61	-29.22
	689.68-2	2.60			-3.19			-57.6			
	689.68-3	2.65			-2.96			-53.6			
	689.68-4	2.91			-2.92			-52.3			

DGR8-695.36	695.36-1	1.36	0.82	0.38	-3.78	-3.95	0.24	-53.3	-50.65	3.75	-19.05
	695.36-2	0.47			-4.12			-48.0			
	695.36-3	0.75			D			D			
	695.36-4	0.69			D			D			
DGR8-707.56	707.56-1	0.89	0.90	0.30	-6.24	-5.80	0.63	-65.0	-65.60	0.85	-19.24
	707.56-2	0.61			D			D			
	707.56-3	D			D			D			
	707.56-4	1.20			-5.35			-66.2			
DGR8-723.29	723.29-1	1.69	1.54	0.15	-4.25	-4.67	0.82	-44.3	-48.13	4.38	-10.77
	723.29-2	1.38			D			D			
	723.29-3	1.46			-5.61			-52.9			
	723.29-4	1.65			-4.15			-47.2			
	(723.29-4-QCD)	---			(-4.14)			(-49.5)			

Notes:

*AVG is the average of 4 replicate measures on one core

D = discarded (experimental failure, etc.)

Table 2: DGR-8 Anion Pore Fluid Geochemistry (average of all replicates per core)

Sample ID	Cl mmol/kgw	σ_{Cl}	SO ₄ mmol/kgw	σ_{SO4}	NO ₃ mmol/kgw	σ_{NO3}
DGR8-285.07	1962.38	913.44	6333.76	2356.25	1.32	0.74
DGR8-333.93	1943.74	623.86	997.36	474.78	3.21	1.13
DGR8-382.83	6638.67	214.31	24.30	4.79	1.34	0.28
DGR8-421.51	6260.06	49.84	4.16	0.47	0.55	0.15
DGR8-431.50	5904.45	143.17	28.28	46.79	2.54	2.08
DGR8-463.33	5893.1	78.82	5.64	0.86	1.36	0.62
DGR8-495.42	5557.55	156.26	162.93	61.06	3.21	0.91
DGR8-521.94	5527.86	113.75	61.99	19.66	1.51	0.45
DGR8-530.81	5680.08	377.01	62.26	68.02	2.84	3.16
DGR8-571.68	3888.01	41.00	3.08	0.18	0.19	0.12
DGR8-612.82	5553.55	58.67	263.81	151.89	0.25	0.17
DGR8-626.22	5362.05	37.71	6.87	1.22	0.43	0.06
DGR8-634.64	5198.44	85.56	4.43	0.62	BD	n/a
DGR8-655.63	4909.99	103.55	16.08	2.01	0.33	---
DGR8-662.01	3463.63	59.75	169.06	9.20	0.61	---
DGR8-670.80	4093.12	399.38	210.48	58.38	BD	n/a
DGR8-683.08	3475.89	512.22	176.83	161.96	0.03	---
DGR8-689.68	5291.61	129.62	40.44	6.29	1.75	0.13
DGR8-695.36	5638.61	614.50	175.20	73.39	7.87	3.79
DGR8-707.56	5232.76	277.02	181.38	44.72	13.62	8.07
DGR8-723.29	4630.59	128.41	55.57	8.94	3.08	0.33

Notes:

BD = Below detection

Table 3: DGR-8 Cation Pore Fluid Geochemistry (average of all replicates per core)

Sample ID	B mmol/kgw	σ_B	Ca mmol/kgw	σ_{Ca}	K mmol/kgw	σ_K	Mg mmol/kgw	σ_{Mg}	Na mmol/kgw	σ_{Na}	Sr mmol/kgw	σ_{Sr}
DGR8-285.07	5.49	2.87	4798.54	1842.37	232.48	153.54	748.66	465.58	1682.73	942.28	40.67	19.44
DGR8-333.93	1.55	0.51	829.63	406.32	62.76	22.10	239.36	80.02	1362.46	494.51	394.14	146.52
DGR8-382.83	4.87	2.00	162.68	121.99	333.53	62.76	754.72	154.52	4785.82	122.33	0.62	0.85
DGR8-421.51	36.05	3.23	1175.02	84.74	1062.56	222.75	326.53	31.25	2201.98	17.75	11.69	1.52
DGR8-431.50	34.73	6.07	783.01	84.30	988.41	94.64	316.19	73.15	1732.61	135.51	9.74	2.02
DGR8-463.33	30.20	2.19	634.98	37.71	932.92	265.38	314.17	53.86	2054.64	60.67	9.28	1.42
DGR8-495.42	49.71	4.87	1017.98	49.37	1644.71	137.35	347.19	35.27	2100.74	107.68	6.79	0.43
DGR8-521.94	24.59	0.88	769.45	19.69	1149.36	190.51	289.40	34.83	2018.17	44.93	6.66	0.98
DGR8-530.81	25.07	9.44	997.74	345.18	869.89	280.77	411.56	189.95	1990.58	470.29	11.09	4.95
DGR8-571.68	17.58	0.94	494.87	40.46	572.40	111.18	119.78	13.58	1280.72	54.65	5.10	0.75
DGR8-612.82	23.65	2.48	988.36	87.94	862.82	119.74	232.43	51.93	1915.13	61.68	10.06	1.31
DGR8-626.22	23.21	0.94	679.22	74.63	777.31	57.35	196.68	12.45	1710.67	104.53	6.98	1.16
DGR8-634.64	24.55	1.86	765.10	31.92	925.95	90.03	196.80	12.60	2369.44	61.97	8.73	0.57
DGR8-655.63	27.89	1.20	579.29	19.32	1175.1	102.97	189.49	16.32	2184.97	32.59	5.62	0.42
DGR8-662.01	60.42	4.34	245.49	7.17	1554.71	118.94	119.21	6.02	1935.98	16.85	2.30	0.23
DGR8-670.80	45.43	7.30	506.13	26.89	1791.52	695.05	218.97	11.79	1855.54	212.06	3.14	0.78
DGR8-683.08	29.54	5.75	508.02	137.47	1134.61	130.74	201.40	67.24	1517.64	275.41	4.11	1.99
DGR8-689.68	26.14	1.84	599.82	53.04	1023.30	72.15	238.72	13.56	2138.08	150.07	5.62	0.90
DGR8-695.36	62.82	12.54	650.16	125.17	2421.56	868.99	307.58	38.47	2632.48	398.8	4.73	1.14
DGR8-707.56	46.84	3.21	617.55	115.54	1420.43	24.38	238.94	32.36	2310.46	144.21	7.40	1.97
DGR8-723.29	26.92	6.08	548.98	25.53	1105.40	229.51	173.18	14.00	2147.78	100.59	4.59	0.20

Table 4: DGR-8 Trace Element Geochemistry (average of all replicates per core)

Sample ID	Br mmol/kgw	σ_{Br}	I mmol/kgw	σ_I	Li mmol/kgw	σ_{Li}	Rb mmol/kgw	σ_{Rb}	U mmol/kgw	σ_U
DGR8-285.07	3.46	1.49	0.03	0.01	2.71	1.35	0.06	0.04	5.99E-03	8.42E-03
DGR8-333.93	4.74	1.78	0.05	0.02	0.76	0.29	0.01	0.01	1.83E-03	3.26E-03
DGR8-382.83	20.03	0.83	0.07	0.01	1.34	0.08	0.10	0.02	1.14E-04	1.70E-04
DGR8-421.51	35.28	1.93	0.12	0.01	1.82	0.51	0.18	0.05	1.56E-04	2.16E-04
DGR8-431.50	33.35	3.61	0.13	0.02	2.65	0.40	0.23	0.03	3.67E-05	4.08E-05
DGR8-463.33	34.92	0.63	0.12	0.01	1.63	0.32	0.20	0.05	1.62E-05	6.87E-06
DGR8-495.42	33.37	0.96	0.24	0.04	3.85	0.47	0.44	0.05	1.00E-04	8.16E-05
DGR8-521.94	32.34	0.73	0.10	0.01	1.81	0.24	0.28	0.05	3.83E-04	7.68E-04
DGR8-530.81	32.53	2.85	0.36	0.29	2.90	1.24	0.25	0.07	2.54E-05	2.94E-05
DGR8-571.68	21.85	0.31	0.06	0.01	1.54	0.35	0.18	0.03	1.30E-05	3.13E-06
DGR8-612.82	31.34	0.45	0.09	0.01	2.03	0.41	0.26	0.03	2.71E-04	2.10E-04
DGR8-626.22	30.30	0.84	0.10	0.01	2.57	0.32	0.27	0.03	2.12E-05	6.93E-06
DGR8-634.64	33.28	8.12	0.09	0.03	2.61	0.80	0.24	0.07	3.29E-05	2.03E-05
DGR8-655.63	28.02	0.69	0.12	0.01	3.09	0.26	0.28	0.02	6.04E-05	1.15E-05
DGR8-662.01	20.41	0.50	0.75	0.08	5.63	0.57	0.44	0.05	5.91E-04	6.42E-05
DGR8-670.80	21.29	1.02	1.31	1.03	6.56	1.55	0.64	0.30	1.14E-04	4.04E-05
DGR8-683.08	17.02	2.66	0.63	0.17	4.07	0.98	0.35	0.05	6.01E-05	1.19E-05
DGR8-689.68	22.16	7.88	0.34	0.16	2.68	0.61	0.29	0.02	9.54E-06	2.94E-06
DGR8-695.36	27.87	2.55	0.62	0.39	7.60	3.46	0.91	0.53	5.22E-05	1.45E-05
DGR8-707.56	23.96	1.24	0.64	0.27	4.08	0.88	0.44	0.05	3.25E-05	1.94E-05
DGR8-723.29	21.93	0.26	0.26	0.03	3.07	0.34	0.27	0.05	9.33E-03	8.95E-03

Table 5: DGR-8 Pore Gas Analysis by GC

Sample ID	CH ₄ (mmol/g _{rock})	C ₂ H ₆ (mmol/g _{rock})	C ₃ H ₈ (mmol/g _{rock})	CH ₄ / (C ₂ H ₆ +C ₃ H ₈)
DGR8-285.07	5.75E-05	NP	NP	n/a
DGR8-333.93	NP	NP	NP	n/a
DGR8-382.83	2.45E-04	4.68E-05	NP	n/a
DGR8-421.51	2.25E-04	NP	NP	n/a
DGR8-431.50	7.36E-05	NP	NP	n/a
DGR8-463.33	2.09E-04	NP	NP	n/a
DGR8-495.42	1.85E-04	NP	NP	n/a
DGR8-521.94	1.81E-04	NP	NP	n/a
DGR8-530.81	8.14E-05	NP	NP	n/a
DGR8-571.68	NP	NP	NP	n/a
DGR8-612.82	5.75E-04	6.93E-05	8.09E-05	3.83
DGR8-626.22	8.00E-04	9.63E-05	1.33E-04	3.49
DGR8-634.64	1.10E-03	1.67E-04	2.76E-04	2.48
DGR8-655.63	1.59E-03	2.35E-04	3.99E-04	2.50
DGR8-662.01	1.20E-03	1.87E-04	3.11E-04	2.41
DGR8-670.80	2.08E-04	3.15E-05	2.38E-05	3.76
DGR8-683.08	3.00E-04	5.97E-05	6.33E-05	2.44
DGR8-689.68	1.67E-04	NP	NP	n/a
DGR8-695.36	2.16E-04	NP	NP	n/a
DGR8-707.56	9.86E-05	2.76E-05	2.57E-05	1.85
DGR8-723.29	2.84E-04	6.15E-05	8.55E-05	1.93

Notes:

NP = No peak on gas chromatograph, below detection

Table 6: DGR-8 Pore Gas Analysis by GC-MS

Sample ID	² H _{CH4} (VSMOW)	¹³ C _{CH4} (VPDB)	² H _{C2H6} (VSMOW)	¹³ C _{C2H6} (VPDB)	² H _{C3H8} (VSMOW)	¹³ C _{C3H8} (VPDB)	¹³ C _{CO2} (VPDB)	[CO ₂] (mmol/g _{rock})
DGR8-285.07	-292.42	-48.93	NP	NP	NP	NP	-7.43	1.73E-04
DGR8-333.93	NP	NP	NP	NP	NP	NP	-10.89	1.03E-03
DGR8-382.83	-261.92	-46.32	-294.76	-36.62	-277.5	-32.18	1.11	1.05E-03
DGR8-421.51	-252.22	-44.94	-144.08	NP	-144.1	NP	-12.39	1.02E-04
DGR8-431.50	-284.60	-43.55	NP	-34.91	NP	NP	-2.63	3.15E-04
DGR8-463.33	-277.50	NP	NP	NP	NP	NP	-5.43	4.02E-05
DGR8-495.42	-266.25	-47.91	-231.02	NP	NP	NP	-5.08	1.24E-04
DGR8-521.94	-313.93	-47.58	-220.28	-35.11	NP	NP	-6.23	1.07E-04
DGR8-530.81	NP	NP	NP	NP	NP	NP	-2.35	3.35E-05
DGR8-571.68	NP	NP	NP	-29.51	NP	-27.77	-4.60	6.74E-06
DGR8-612.82	-327.46	-39.01	-303.70	-36.06	-272.2	-32.66	-0.21	3.82E-04
DGR8-626.22	-317.79	-41.52	-252.32	-35.97	-237.9	-32.47	-0.21	4.30E-04
DGR8-634.64	-324.60	-49.45	-251.60	-38.23	-193	-33.43	-0.04	3.61E-04
DGR8-655.63	-333.36	-50.56	-254.46	-38.26	-224.8	-33.48	-0.99	3.87E-04
DGR8-662.01	-232.22	-51.08	-229.25	-38.97	-81.54	-34.26	-22.73	3.46E-05
DGR8-670.80	-104.01	-50.29	-253.36	-38.71	-248.9	-34.02	-9.33	2.77E-05
DGR8-683.08	-329.70	-49.01	-283.21	-37.95	-222.7	-33.86	-9.05	5.78E-05
DGR8-689.68	-302.40	-48.76	-250.90	-37.61	-193.7	-33.46	-8.01	8.61E-05
DGR8-695.36	-291.70	-48.14	-248.50	-37.74	-222.8	-33.32	-9.49	4.64E-05
DGR8-707.56	NP	NP	NP	NP	NP	NP	-10.37	5.87E-06
DGR8-723.29	-232.2	-45.14	-229.30	-35.82	-178.2	-31.94	-6.97	8.45E-05

Notes:

NP = No peak on gas chromatograph, below detection