Method Development: Micro Vacuum-distillation Experiments (µVDE)

NWMO-TR-2017-12

July 2017

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University of Ottawa

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This report has been prepared under contract to NWMO. The report has been reviewed by NWMO,
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ABSTRACT

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Abstract

The University of Ottawa was contracted by the NWMO to optimize the high-temperature vacuum-distillation extraction (VDE) technique for porewater characterization of low permeability rock, and to further assess the reliability of the method. As a part of this work program, a modified micro sampling technique (µVDE) was developed to optimize the vacuum-distillation method for analysis of smaller samples of low water content. Optimization was achieved by undertaking complete closed-system sample crushing in stainless steel containers fitted with high-temperature silicone septa – in order to facilitate transfer of water vapour directly to the extraction vial under dynamic vacuum while heating the sample. An extraction temperature of 150˚C was determined experimentally to be the optimum for extraction of porewater. A dual transfer line was also developed to accommodate ultra-low water content samples.

The µVDE method has several key advantages over the previous VDE method, including less potential for evaporative loss during sample crushing and loading, reduced extraction times, smaller sample size – enabling precision sampling of heterogeneities – and potential for reliable analysis by isotope ratio infrared laser spectroscopy (IRIS), provided there is no interference from residual hydrocarbons. The µVDE methodology was bench-tested with a series of control tests (using lab water of known isotopic concentration within a known matrix), including testing of porewater extracted from preserved core samples. Initial µVDE testing was completed on archived core material (DGR-6), which showed some evidence of evaporation due to repeated exposure/sampling and/or larger headspace in the extraction vial. Test waters extracted by closed-system high-temperature vacuum distillation (µVDE) to a smaller extraction vial show good reproducibility (±2.0‰ for δD and ±0.5‰ for $\delta^{18}O$; within the analytical uncertainty of isotope analysis by IRIS).

The new method also was further demonstrated using freshly-drilled core from DGR-8, which showed good agreement with previous DGR1-6 results obtained by VDE. The results of the µVDE testing demonstrates that it is an appropriate method for characterization of the ultra-low permeability, low water content and high salinity porewaters in the sedimentary rocks underlying southern Ontario.

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1. INTRODUCTION

In the context of the long-term management and isolation of nuclear waste in a deep geologic repository, geochemical knowledge of the groundwater and porewater systems is essential to assess water-rock interaction processes, groundwater/porewater origin and evolution, and solute residence times. Geochemical studies are focused on improving our knowledge of such attributes, as they are relevant from a variety of perspectives (e.g., engineering, safety assessment and geoscience) when considering the long-term behaviour of deep groundwater systems and the potential suitability of a rock mass to safely contain radioactive waste from the surface environment. The extensive characterization program at the site for Ontario Power Generation’s proposed Deep Geologic Repository (DGR) for low- and intermediate-level waste has yielded insight into the deep aquiclude system within the Paleozoic sedimentary sequence. Measured hydraulic conductivities for the proposed host rock (Cobourg Formation) were as low as 10^{-15} m/s and volumetric water contents ranged from 2% to 0.5% (Intera Engineering Ltd. 2011). Characterizing the pore fluids from such ultra-low permeability carbonates and shales presents a challenge, requiring new and innovative techniques, and pushing the boundaries of conventional methods.

During the NWMO DGR Site Characterization Program, vacuum-distillation, to extract porewaters from rock core samples, was demonstrated to produce reliable results for the low-porosity, ultra-low permeability Silurian and Ordovician shales and carbonates (Intera Engineering Ltd. 2008a). The experimental parameters of the vacuum-distillation experiments are critical to ensure all porewaters are extracted from the sample to avoid the risk of inherent fractionation. Low extraction temperatures typically yield low water recoveries and, as a consequence, more isotopically-depleted waters as a result of partial/incomplete extraction of water vapour (NEA 2000). Testing at the University of Ottawa on partially crushed cores (2-4 mm grain size) demonstrated that high-temperature vacuum-distillation at 150°C for 6 hours to extract porewaters, coupled with aqueous leaching of the dehydrated rock, offered the most reliable approach for the determination of stable water isotopes ($\delta^{18}O$ and δD) and major ion chemistry of the pore fluids (Intera Engineering Ltd. 2008b; 2008c; 2008d & 2010b).

In rocks with very high clay content and very low water content, the potential for partial extraction of strongly bound water is of concern (NEA 2000). However, interlayer and crystallization water is considered negligible for certain rock types, including crystalline rocks, carbonates and illite-dominated shales, where contributions from clay interlayer waters (i.e., smectites) are minimal. The Ordovician shale units at the Bruce Nuclear Site are dominated by illite and this was an important consideration when developing these vacuum-distillation techniques. Furthermore, fluid inclusions are not characteristic of the rock matrix in these sedimentary units and it can be reasonably assumed that the water present in the pore spaces is open to diffusive exchange.

Within the framework of Adaptive Phased Management (APM), the Nuclear Waste Management Organization (NWMO) supports on-going research at the University of Ottawa investigating methods for improving the extraction and analysis of pore fluids from low-permeability sedimentary rocks, and the development of new, innovative methods for crystalline rocks. This report outlines novel approaches developed at the University of Ottawa to optimize the vacuum-distillation technique for application to sedimentary rocks, including closed-system crushing and extraction of water vapour from smaller core samples, and direct transfer of water vapour into sample vials in order to minimize the potential for evaporative loss.

2. METHODOLOGY

A vacuum-distillation extraction (VDE) method was developed for sedimentary rocks in southern Ontario and applied to core from the first six boreholes (DGR1-6) at the proposed L&ILW DGR site near Tiverton, ON. Given the success of the VDE technique for characterizing hyper-saline pore fluids from low-permeability sedimentary rocks, the University of Ottawa has continued research to optimize porewater extractions from rock cores, with the following objectives:

1) Develop closed system extractions to minimize evaporative interferences during sample preparation.
2) Reduce sample size, as this could allow for examination of sample heterogeneity at the cm scale.
3) Reduce sample analysis time.
4) Adapt the method for rapid $\delta^{18}O$ and δD analysis by isotope ratio infrared laser spectroscopy - IRIS (provided there is an absence of hydrocarbons from the extracted porewaters).

With these objectives in mind, a micro vacuum-distillation technique (µVDE) was developed at the University of Ottawa. This report summarizes method development and testing, including: a) comparison of VDE and µVDE methods using waters of known isotopic composition; and b) testing conducted on preserved core from DGR-8.

2.1 VACUUM-DISTILLATION EXPERIMENTS (VDE) APPLIED TO DGR1-6 CORES

The vacuum-distillation method involves heating partially-crushed rock cores under vacuum, and water recovery with an on-line liquid nitrogen trap, followed by dry-rock leaching to reconstruct porewater chemistry. Upon receipt at the University of Ottawa, core samples were unpacked and approximately 20 mm of the exposed outer core was removed mechanically with a chisel to avoid any drill fluid contamination. The inner portion of the cores was crushed and sieved to collect a grain size fraction between 2.88 and 4.69 mm in diameter (Ricard 1993; Moreau-Le Golvan et al. 1997). Approximately 40 g sample aliquots were placed in 50 mL pre-weighed Erlenmeyer flasks and mounted onto the heater side of the individual vapour-transfer line. A pre-weighed 12 mL Labco exetainer, with a septum cap fitted to the line, was placed on the water vapour-recovery side of the line (Figure 1). A total of eight individual extraction lines were connected to the vacuum manifold, along with an Edwards E2M18 two-stage vacuum pump.

Prior to heating, the loaded sample flasks were submerged in liquid nitrogen to freeze the sample and were individually evacuated to 30 mTorr. The exetainer and porewater vapour transfer line were also evacuated during this step. Once a vacuum of 30 mTorr was reached in the system, the transfer line was isolated from the vacuum pump, the liquid nitrogen bath was removed from the crushed-rock flasks, and the bottom 3 cm of the exetainers were immersed in a liquid nitrogen bath. Two insulated resistance ovens, fitted to enclose four Erlenmeyer flasks, were put into place and the temperature of the rock samples was slowly raised over a period of one hour to 150˚C, which was maintained with periodic checks over a period of 6 hours. During this time, water vapour released from the rock diffused through the transfer line and was trapped cryogenically in the exetainer at liquid-nitrogen temperatures under static vacuum (see Intera Engineering Ltd. 2010b for detailed testing of this protocol).

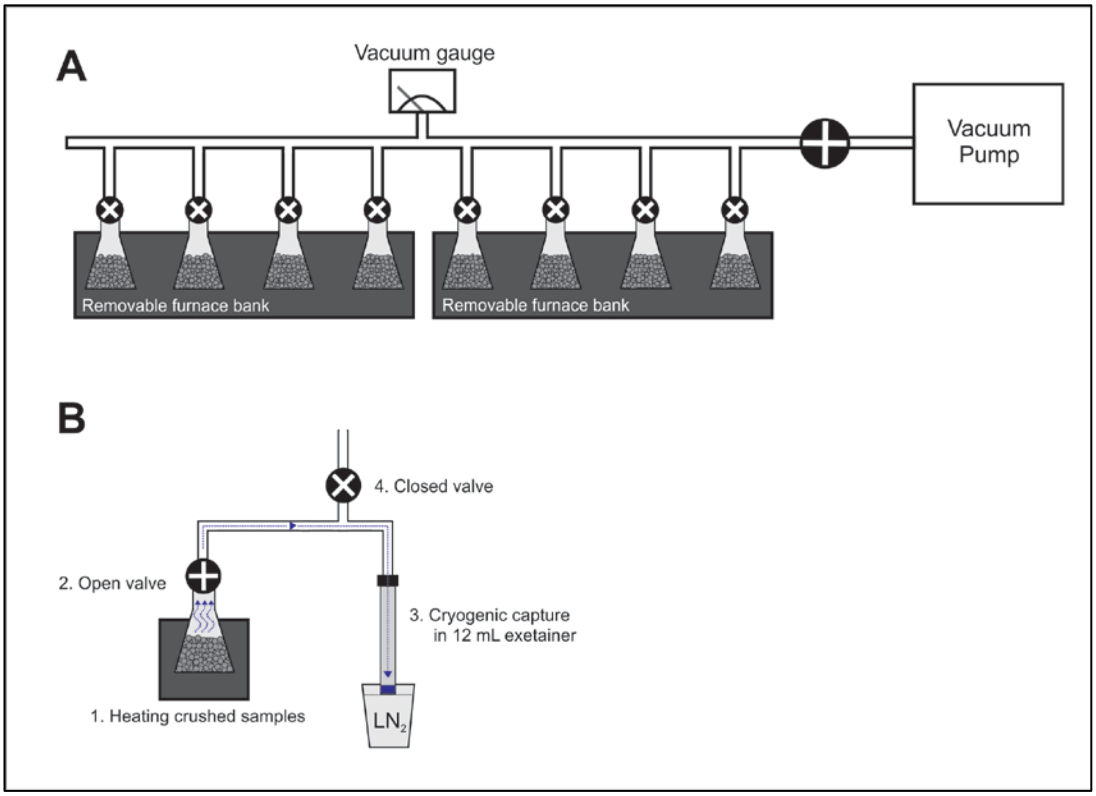

Figure 1: Schematic Diagram of Vacuum-distillation Extraction Line (VDE): A) VDE Line with 8 Sample Ports Connected to a Vacuum Manifold; B) Individual Transfer Line in Cross-section, Displaying the Transfer of Water Vapour from the Partially Crushed Core

Once the extraction period was complete, the flasked containing the crushed rock were isolated from the transfer line, the ovens were removed, and the rock samples were allowed to cool. The liquid nitrogen dewars were removed and the exetainers were detached from the line, closed with a septum cap and allowed to warm to room temperature. When the rock flasks and exetainers reached room temperature, they were weighed to determine water loss in the flasks and water gain in the exetainers, which allows for the calculation of the dry-rock mass. These mass measurements (m) were used to calculate gravimetric water loss, which was normalized to the percent of volumetric freshwater content using an average mineral density of 2.7 g/cm^3 across all formations (Koroleva et al. 2009) and a density of 1 g/cm^3 for water according to equation 1:

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

2.1.1 Stable $\delta^{18}O$ & δD Analysis of Extracted Porewater

The porewaters recovered in the exetainers by vacuum-distillation were analyzed for stable O-H isotopes by gas-source continuous flow isotope ratio mass spectrometry (CF-IRMS), on a Thermo Delta Plus XP interfaced with a Gasbench II. Prior to analysis, charcoal grains were added to each sample exetainer containing the extracted porewaters to remove any condensed hydrocarbons (suspected from the petriliferous odour detected during core preparation), and allowed to interact for a period of 24 hours. For analysis, 0.2 mL of extracted water was transferred to a clean exetainer and an approximately 10 mg Cu strip was added to each exetainer 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% CO_2 in He gas and allowed to equilibrate for 24 hours to allow exchange of ^{18}O between CO_2 and H_2O (Epstein and Mayeda 1953). Following CO_2 analysis on the mass spectrometer, a platinum bead catalyst was added to the same exetainers containing the 0.2 mL sample aliquots. The exetainers were re-flushed with a mixture of 2% H_2 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 $\delta^{18}O$ and δD to calibrate the measured ratios to the international reference water VSMOW (Vienna Standard Mean Ocean Water). These procedures were applied to all samples, standards and laboratory blanks (Intera Engineering Ltd. 2010b). Results are given in per mil differences between the isotope ratio, R ($^{18}O/^{16}O$ or $D/^{1}H$), of the sample versus the isotopic ratio of the reference standard and is expressed by Equation 2:

$$\delta D \text{ or } \delta^{18}O = [R_{SAMPLE}/R_{VSMOW}) - 1] \qquad \text{(Equation 2)}$$

2.1.2 CO_2 Sampling and Analysis

The on-line trapping of porewater as vapour during vacuum-distillation allows the recovery of CO_2 in the rock. This is important for measurements of both CO_2 concentration and $\delta^{13}C$. Although the analysis of ^{18}O of recovered CO_2 is of no value for porewater analysis, equilibrium between the ^{18}O of CO_2 and ^{18}O of the porewaters would have existed under in-situ conditions, followed by subsequent re-equilibration with the porewater at the extraction temperature. As a result, the ^{18}O of CO_2 may have the potential to be used as a qualitative check to ensure that the isotopic composition of the ^{18}O of CO_2 was indeed collected under equilibrium conditions – i.e., constant temperature and closed-system conditions.

For the vacuum-distillation experiments carried out as part of site characterization activities (DGR-1 through DGR-6 cores), CO_2 was routinely recovered in the sample exetainer with the porewater. After thawing, the samples were initially analyzed for CO_2 concentration and $\delta^{13}C$ by injection into a gas chromatograph, interfaced with a continuous-flow isotope ratio mass spectrometer. The use of calibration standards for volume allowed quantification of sample CO_2 concentration, which was normalized to both porewater mass and rock mass (Intera Engineering Ltd. 2010a, 2010b).

2.1.3 Solute Leaching Following Vacuum-distillation

Pore fluid chemistry was reconstructed by leaching of the post-distilled dehydrated partially-crushed core samples (Intera Engineering Ltd. 2011). Aqueous leaching was completed in an anaerobic chamber to minimize the oxidation of sulphate-bearing minerals and the associated artifacts of elevated SO_4 concentrations by dissolution of these minerals during leaching. Once cooled and weighed, the desiccated rock samples, from which the porewater was extracted, were emptied into a pre-weighed polypropylene graduated centrifuge tube (falcon tube) and the flasks were rinsed several times with approximately 50 mL of deoxygenated doubly-deionized water (Deox-DDIW) for solute leaching in order to ensure recovery of all salts originally present in the sample flasks. The falcon tube was then re-weighed to determine the total mass of Deox-DDIW. The crushed rock samples were left to leach for an 8-week period with periodic shaking. The leachate is then filtered with a 0.45 µm syringe filter and analyzed for major anions (Cl^-, SO_4^{2-}, and NO_3^-) by routine liquid chromatography (Dionex® DX-100 coupled to a Dionex® AS40 auto sampler), major cations (Ca^{2+}, Mg^{2+}, Na^+, K^+, B^{3+}, Sr^{2+}) by atomic emission spectroscopy in an inductively coupled argon plasma (ICP-AES), and Br^- by ICP-MS. All samples were run with a set of internal standards. Analytical reproducibility of the analyses was less than 5% relative to standard deviation (RSD). The total molar amount of each ion leached from the dried rock was normalized to the gravimetric water loss yielded by vacuum-distillation, giving molal concentrations for the original porewaters.

2.2 CLOSED-SYSTEM MICRO VACUUM-DISTILLATION EXPERIMENTS (µVDE)

The micro vacuum-distillation method involves closed-system crushing and heating of small rock samples (~8-10 g). Complete closed-system extractions are attained by crushing rock samples inside individual stainless-steel ball-mills, which have been retrofitted with a septum cap that allows subsequent connection to the vacuum transfer line for water vapour extraction (see Appendix A for pictures of equipment). A refurbishment of the existing vacuum-distillation line was required to accomplish these objectives, which included re-designing and re-building the glass transfer lines and re-design of sample holders and heating units (see Appendix A, Figure A.3.

Precautions are taken to avoid contamination from drilling fluid by removing the outer part of the core, with solute ratios and isotopic/geochemical signatures used as tracers for contamination, all of which has been well documented in previous technical reports (i.e., NaFl & ^3H field tracers; Intera Engineering Ltd 2011; 2011a; 2011b). Similar to the VDE method, core samples are prepared for sampling by removing the outer exposed edge (~20 mm) to eliminate drilling fluid contamination. The inner part of the core, containing only freshly exposed surfaces, is used in the analysis (Figure 2; detailed methodology depicted in Appendix A, Figure A.1). A puck-sized disc is broken into several sub-samples, which are immediately weighed and placed into each of 4 stainless-steel ball mills with a 1/2” stainless steel ball and sealed with a high-temperature silicone septum. The sample holders containing the rock samples are placed on a Retsch MM 200 ball mill and shaken for approximately 10-15 minutes until crushed to a fine powder (<100 um). The sample holders do warm slightly (increase of 10 – 20˚C) during milling, but not to the same extent to which they are heated during the extraction (150˚C). The septa and O-ring on the sample holder are designed to accommodate heating to these temperatures so that the vacuum seal will not be lost. 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 µm filter to prevent rock dust from being drawn up into the vacuum transfer line during evacuation. Each line is paired with a pre-weighed septum-sealed vial on the water vapour recovery side of the line (Figure 3), completing the closed-system extraction. Phase 1 of the µVDE testing included 12 mL Labco exetainer vials used for the VDE methodology (Figure 1). Phase 2 of µVDE testing included a modified glass line, with 1.2 mL high-recovery[1] micro-vials (HRµV) fitted to the transfer line with a septum cap (Figure 3) in order to reduce headspace volumes (see Section 2.2.2).

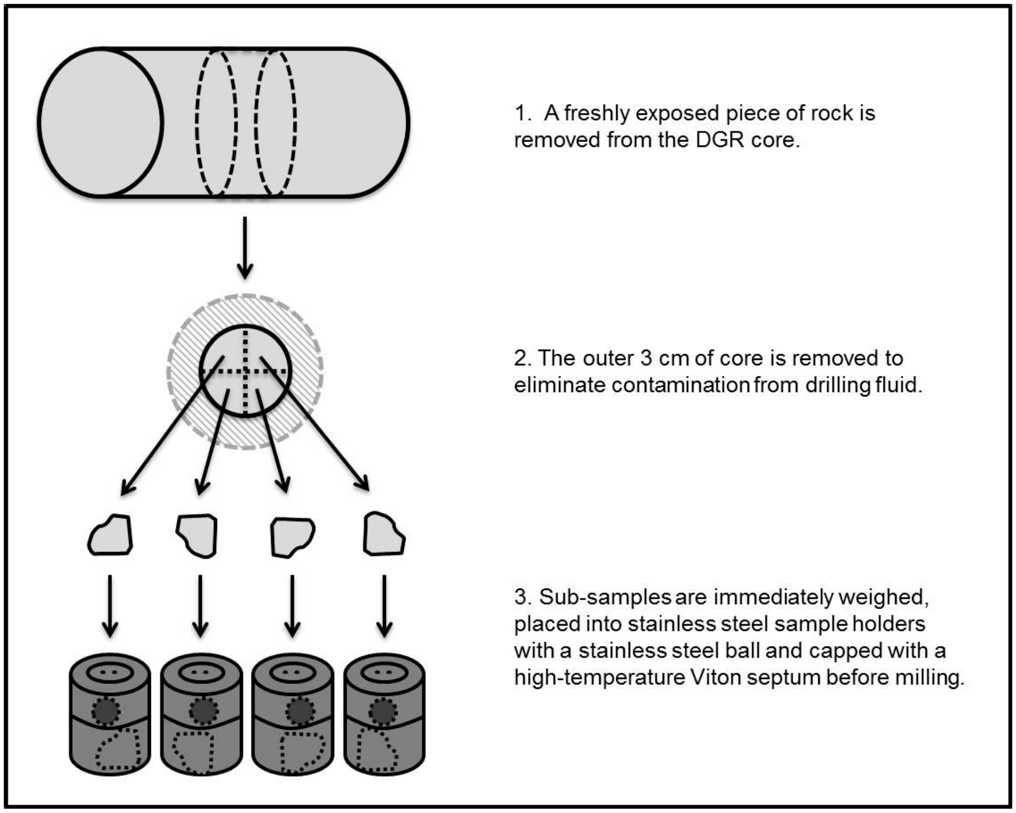

Figure 2: Protocol for µVDE Core Sample Preparation

The µVDE methodology involves two extraction stages: (I) primary transfer of water vapour during heating by dynamic[2] vacuum; and (II) secondary transfer directly to a septum-sealed vial under static[3] vacuum. 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

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[1] High-recovery vials include a tapered bottom to maximize retrieval of contents containing valuable samples via autosampler syringe in order to limit dead volumes.

[2] Continuous evacuation of vacuum line (open port)

[3] Baseline vacuum is obtained, then sample port is isolated from vacuum pump (closed port)

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 of 150˚C, at a ramping speed of 5-10˚C/min, and held for the desired heating period.

Recovery tests have shown that the rock sample is entirely desiccated after 30 minutes of heating under vacuum, and all the water has been extracted to the U-trap (discussed below). Once this heating/extraction period is complete, 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 HRµV 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 (to reduce the effect of condensing atmospheric moisture into the vial at liquid nitrogen temperatures) and capped with a silicone/PTFE septum cap. The pre-weighted vials are weighed again to determine water recovery, and volumetric water content is calculated based on the mass of porewater recovered (following Equation 1). The new system has the capability of directly and simultaneously analyzing δ^{18}O and δD of the recovered waters by IRIS on a DLT-100 Los Gatos Research (LGR) liquid water stable isotope analyzer, with an analytical reproducibility of ±0.3‰ for δ^{18}O and ±2.0‰ for δD (IAEA, 2009), providing there is no contamination from hydrocarbons in the extracted porewaters (spectral interferences). Most core samples processed at the University of Ottawa by vacuum-distillation show trace amounts of polyaromatic hydrocarbon compounds and other aliphatic species to be present in the extracted porewaters (confirmed by GC-MS). In the case of hydrocarbon contamination, the extracted waters can be analyzed by CF-IRMS (see Section 2.1.1). The δ^{18}O and δD values are expressed as ‰ relative to VSMOW.

Sample volume is limited within the individual sample holders (~10-12 g maximum, depending on rock density) and overloading can result in poorly crushed samples, as well as incomplete recovery. This may present a problem for water yield within the ultra-low porosity sedimentary units, such as the Ordovician limestones (WC_{vol} < 1%). To accommodate the larger sample volume required to extract sufficient volumes of water for isotopic analysis (> 100 µL), a dual extraction line was developed to increase sample volume capacity (Appendix A, Figure A.6).

Porewater geochemistry is reconstructed by leaching of porewater solutes from the dry powdered rock matrix at ambient temperatures (as outlined in Section 2.1.3). Leaching time is reduced to only 24 hours, as powdering of the rock samples directly exposes porosity to the leach water.

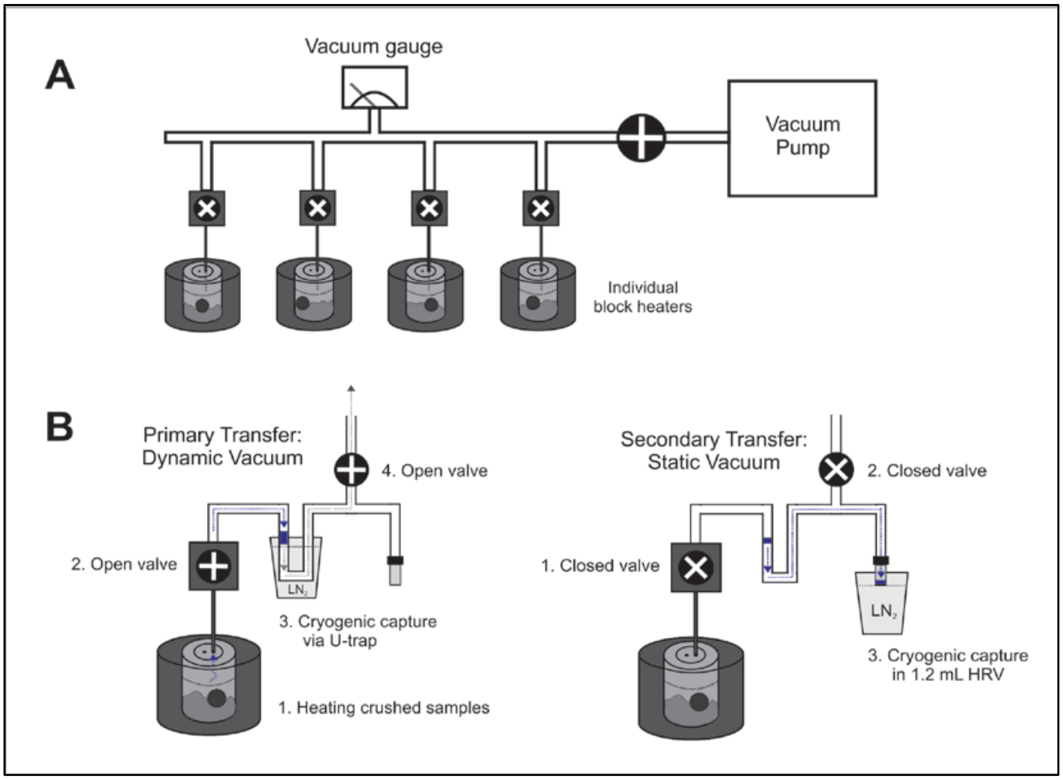

Figure 3: Schematic Diagram of Micro Vacuum-distillation Extraction Line (µVDE): A) µVDE Line with 8 Sample Ports Connected to a Vacuum Manifold in a Completely Closed System; B) Individual Transfer Line in Cross-section, Displaying the Transfer of Water Vapour from the Crushed Core During Primary Transfer (left) and Secondary Transfer (right)

2.2.1 Phase 1 µVDE Method Testing: Rock Core Tests (12 mL vials)

Several experiments were designed to test the efficacy and reproducibility of the new µVDE methodology using the mill jars to crush the sample to a powder. The testing phase was carried out over the latter half of 2011 (Phase 1), continuing into 2012 (Phase 2, Section 2.2.2). Phase 1 testing included extracting water vapour into 12 mL exetainers, followed by transferring recovered water via pipette to 2 mL micro-vials for δ^{18}O and δD analysis by IRIS on a DLT-100 Los Gatos Research (LGR) liquid water stable isotope analyzer. The experimental approach of this testing phase was designed to test the effects of extraction time and temperature on vacuum-distillation. Samples were heated at various temperature steps and held for varying periods of time to observe: 1) when the extraction procedure reached completion (i.e., when all porewater has been extracted from the rock sample), as well as 2) any isotopic effects and experimental artifacts related to variations in the heating regimes.

For the purpose of testing, cores within the Lower Silurian and Upper Ordovician shales from the DGR-6 borehole were chosen for primary testing under the new experimental method due to their intrinsically-high water content (to ensure adequate water recovery). These represent the

DGR core most-recently tested using the VDE method and the VDE results were used as a reference against which the new method was compared.

In initial trials, it was found that some rock samples were not completely crushed after milling, leaving behind small, sub-rounded, pebble-sized fragments. Uncrushed samples may result in incomplete porewater extractions, with inconsistencies in the isotope and leaching data as a consequence. This was remediated by experimenting with various sizes and quantities of stainless steel balls in the sample holder, with the best results for complete crushing observed using a single ½" diameter stainless steel ball.

µVDE experiments were carried out at various hold times and temperatures (i.e., the experimental parameters were maintained at a consistent temperature for a specified period of time) on several cores (Figure 4), including high temperatures (120-150˚C) and low temperatures (<100˚C). The results show a trend of relative $\delta^{18}O$ and δD enrichment compared to the expected values from the data generated using the previous VDE method, particularly for the experiments carried out at higher temperatures with longer hold times. Both sets of experiments also reveal significant variability within $\delta^{18}O$ (ranges of up to ~6‰) and δD (ranges of ~25‰). It was postulated that the enrichments may be an artefact of oxygen exchange with the matrix (slopes on $\delta^{18}O$ versus δD close to 0) or a product of evaporation effects (slopes closer to 5); however, the results vary from core sample to core sample.

While a concerted effort was made to ensure the integrity of the rock samples, it is important to note that the cores are more than 2 years old and have been subject to repeated sampling and exposure (i.e., opening and re-sealing), and so re-sampling using the new µVDE technique may not be a fair assessment of the method. It remains difficult to postulate the effect of long-term storage and repeated exposure of cores, but these factors may have influenced the isotopic values of the porewaters via evaporation, and may explain some of the deviations observed when comparing re-sampling by µVDE to the original expected values by VDE. In addition, some of the observed variability may also, in part, be related to the increased precision of the new technique. The previous method involved sampling a larger aliquot (~40 g) from bulk core that has been partially crushed and sieved, whereas the new µVDE method allows for focused sampling using ~10 g bulk rock samples, which may then sample heterogeneities within the core. This being said, the smaller sample size equates to smaller water yields and larger headspace volumes in the 12 mL exetainers and sampling vials. These artefacts were not observed with direct extraction into smaller vials (Phase 2 testing, discussed below). Together with secondary transfer via pipette into 2 mL vials, it is expected that these potential artifacts may explain the differences in the µVDE tests, as well as the evaporative slopes observed from the δD versus $\delta^{18}O$ plots ($m<5$).

Some of the dehydrated rock powder from the crushed core experiments was rehydrated by re-injecting a known amount of lab water (DDIW; $\delta^{18}O = -10.38 \pm 0.21$, $\delta D = -78.72 \pm 1.23$) and performing a secondary extraction to observe any matrix-related effects (Figure 5). The isotopic composition of the water recovered from the re-injections on the crushed shale deviated slightly from the initial DDIW values, trending toward compositions more enriched in $\delta^{18}O$ and δD. This trend is less pronounced for δD, where determined values are closer to expected. Slopes on the $\delta^{18}O$ versus δD plot are closer to 5, which may be suggestive of evaporation. The effect of evaporation, as suggested by the slope of the $\delta^{18}O$-δD plots, is consistent with the greater variability measured for the $\delta^{18}O$ data than for the δD data.

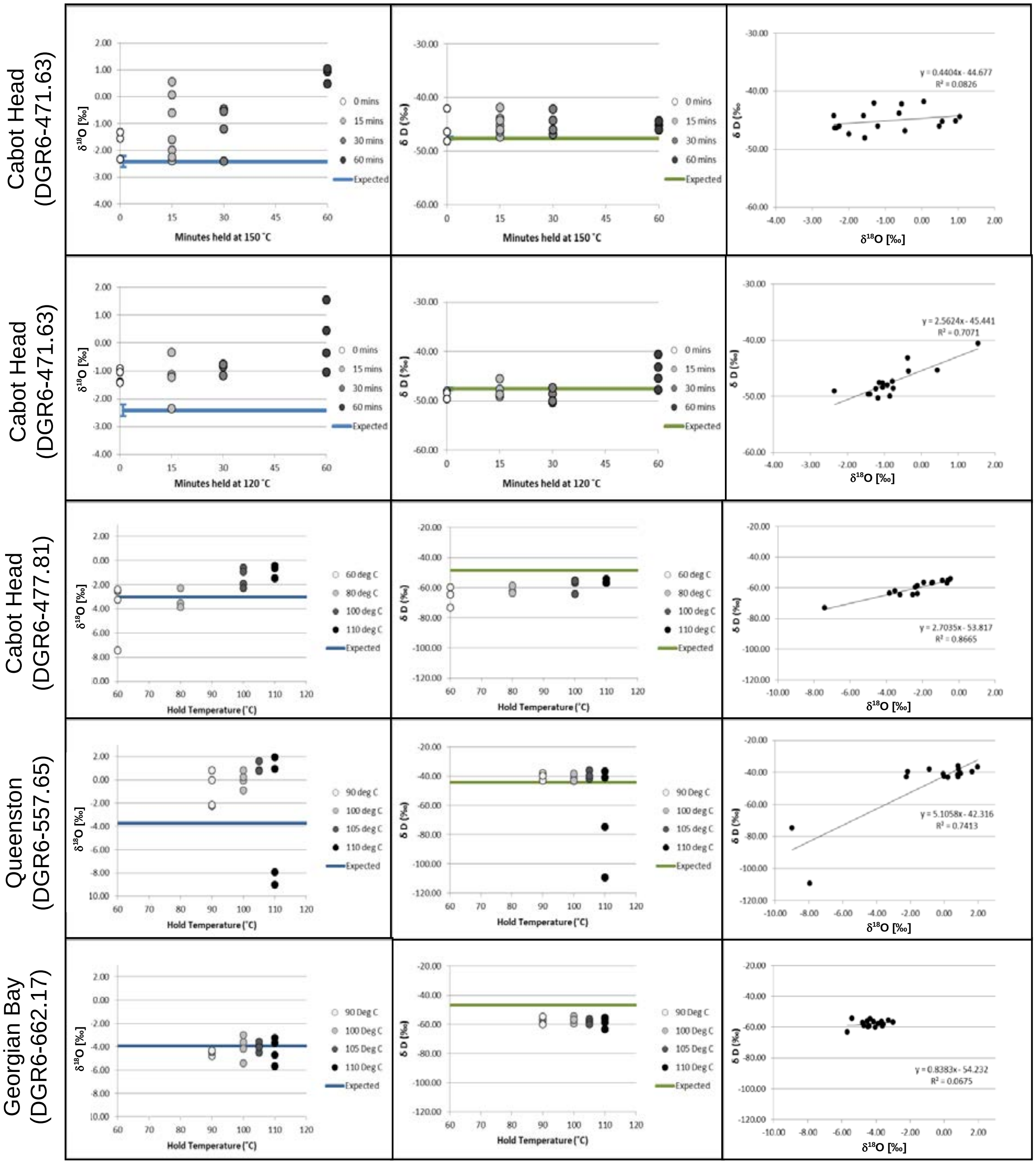

Figure 4: Phase 1 µVDE Testing on DGR-6 Core at Different Temperatures and Hold Times of 15 and 30 minutes (not distinguished due to lack of significance between 15 and 30 minute hold time results; Table B.1)

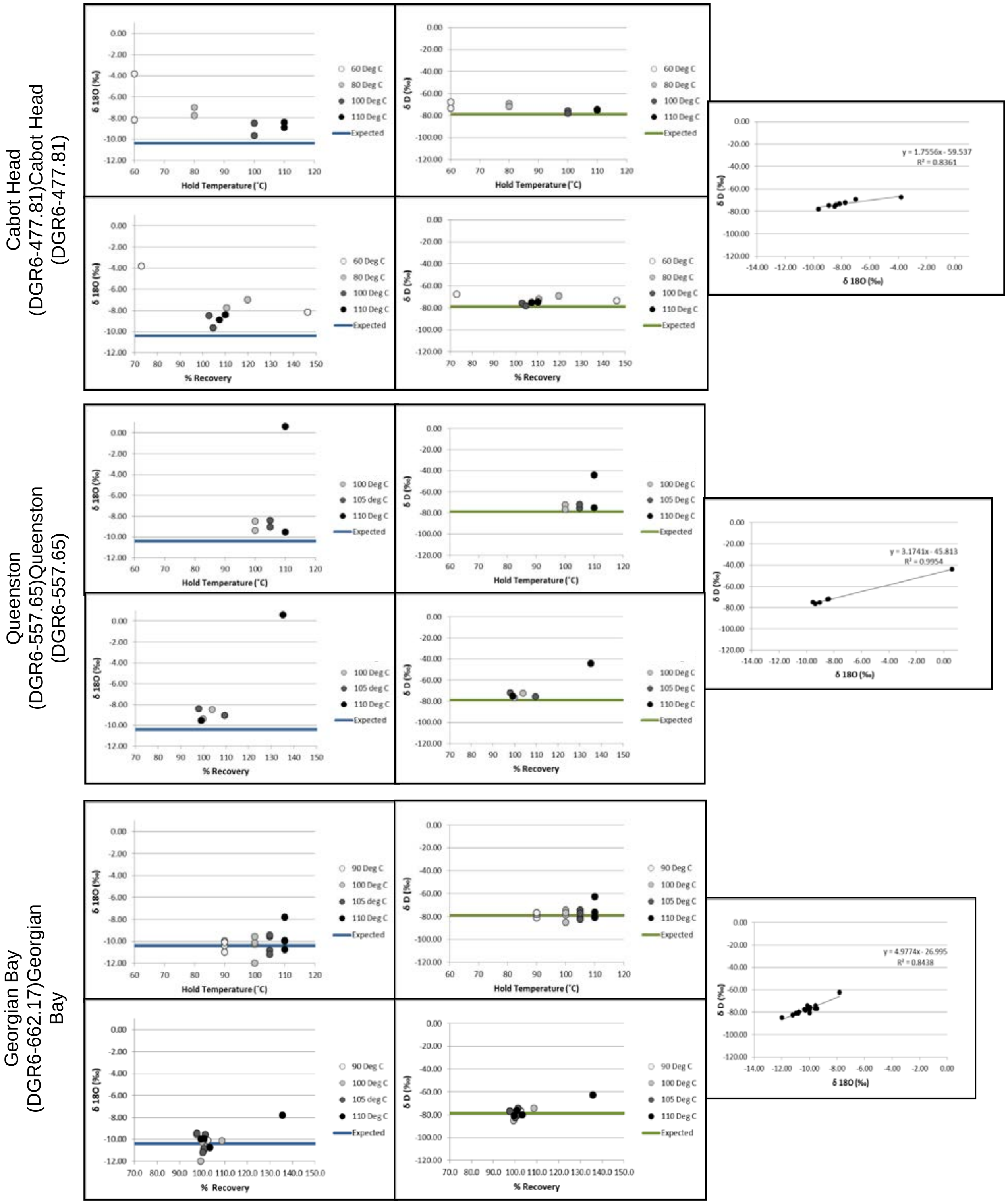

Figure 5: Phase 1 μVDE Re-injection Tests on DGR-6 Cores

2.2.1.1 Aqueous Leaching of Crushed Powders

Once cooled to room temperature, the stainless steel sample holders, along with the transfer needle/valve unit, were brought to an anaerobic chamber to minimize the oxidation of sulfide-bearing minerals and the associated artifacts of elevated concentrations of SO_4 by dissolution of these minerals during leaching. The sample containers were then opened and the powdered sample was rinsed several times from the holder into a pre-weighed 50 mL centrifuge tube using approximately 50 mL of de-oxygenated doubly-deionized water (Deox-DDIW) to ensure recovery of all salts originally present in the sample holder.

The aqueous leaching method is similar to that described in Section 2.1.3; however, the solution was allowed to leach in the anaerobic chamber for a period of 24 hours at room temperature. After this 24-hour period, the tubes containing the transferred samples and leachate were removed from the chamber, weighed to determine the total mass of Deox-DDIW, and promptly filtered into 15 mL centrifuge tubes using a 0.45 µm syringe filter for ion analysis. Major anions ($Cl^–$, $SO_4^{2–}$, Br^- and NO_3^-) were analyzed by routine liquid chromatography on a Dionex® DX-100 coupled to a Dionex® AS40 auto sampler, and major cations by atomic emission spectroscopy in an inductively coupled argon plasma (ICP-AES) at the University of Ottawa. Porewater solute concentrations (mol/kg rock) were determined by normalization of the mass of solutes leached from the dried rock powder to the mass of recovered water, assuming all major ions leached are from the porewater

Leaching experiments were completed over the summer of 2011 to determine the length of time required for aqueous leaching of powdered rock cores, including the conditions required for successful leaching (i.e., oxic/anoxic). Two cores from the DGR-5/6 series were selected for testing, one from the Blue Mountain Formation shale and one from the Cobourg Lower Member Formation limestone. Approximately 10 g of these rock tailings (i.e., < 2.88 mm diameter grain size) from the original VDE experiments were crushed to a powder using the ball mill and leached according to the method outlined in Section 2.1.3. Separate aliquots of the same bulk rock sample were allowed to leach for varying time periods (i.e., from 3 hours to 21 days) and under different conditions (i.e., oxic/anoxic leaching and filtering, and leaching the tube upright or sideways). Leaching the dehydrated rock powder for 24 hours in an anaerobic chamber in the horizontal position was demonstrated to be the most effective leaching method. Horizontal leaching maximizes the surface area of the powder in contact with the leach water, ultimately speeding up the process. These experiments were conducted to examine whether or not the dissolution of sulphate minerals – such as gypsum ($CaSO_4 \bullet 2H_2O$), anhydrite ($CaSO_4$) and celestite ($SrSO_4$) – and oxidation of sulphide minerals (e.g. pyrite - FeS_2) occurred during leaching, resulting in elevated concentrations of Ca, Sr, SO_4 and Fe. The experiments were carried out under oxic conditions and anoxic conditions (i.e., leaching in an oxygen-free glove box) to observe these effects. Volumetric water equivalents of the bulk rock sample were calculated based on data from the original VDE experiments (e.g., Intera 2008c, 2008d) and anions (Cl^- and SO_4^{2-}) are expressed as mmol/kgw. Cl^- concentrations versus leaching time are presented in Figures 6 and 7.

Initial experiments show that the conservative solute concentrations appear to plateau after a period 24 hours and, therefore, subsequent tests were ended after a period of 3 days. The Cl^- leach time curve appears to plateau near 4000 mmol/kgw for the Blue Mountain shale, and closer to 7000 mmol/kgw for the Cobourg Formation limestone (after a period of 24 hours), when leaching the samples sideways in the anaerobic chamber (maximizing surface area in contact with the leach water) and then promptly filtering outside the chamber (anoxic leach/oxic filter). The spikes for Cl^- in the first aliquots of the Cobourg sample (days 1 to 4) are attributed to halite contributions. SO_4^{2-} stabilized around 220 mmol/kgw for the Blue Mountain, and closer to 450 mmol/kgw for the Cobourg, under the same conditions. There is no obvious effect on the SO_4 concentrations associated with the dissolution of gypsum or anhydrite, as assessed by excursions towards higher concentrations of both sulphate and calcium with a molar ratio near 1 and by gypsum oversaturation in the solute-normalized porewater. Although oxidation of pyrite will be insignificant in an anaerobic environment, the dissolution of trace amounts of anhydrite or gypsum cannot be ruled out.

Select sub-samples from the DGR-5/6 cores used for the porewater experiments were leached for pore fluid solutes following the method outlined above. Figure 8 illustrates the Cl^-, SO_4^{2-} and Na^+ pore fluid concentrations in mmol/kgw for two cores within the Cabot Head shale (DGR6-471.63 and DGR6-477.81). Variability can be observed between sub-samples extracted repeatedly at 120˚C and 150˚C, where lower water yields are generally consistent with lower temperature extractions. More detailed temperature sampling on adjacent core revealed that lower extraction temperatures yield lower water contents, which in turn forces higher reported pore fluid concentrations (and vice versa) because the data are normalized to the porewater volumes (kgw).

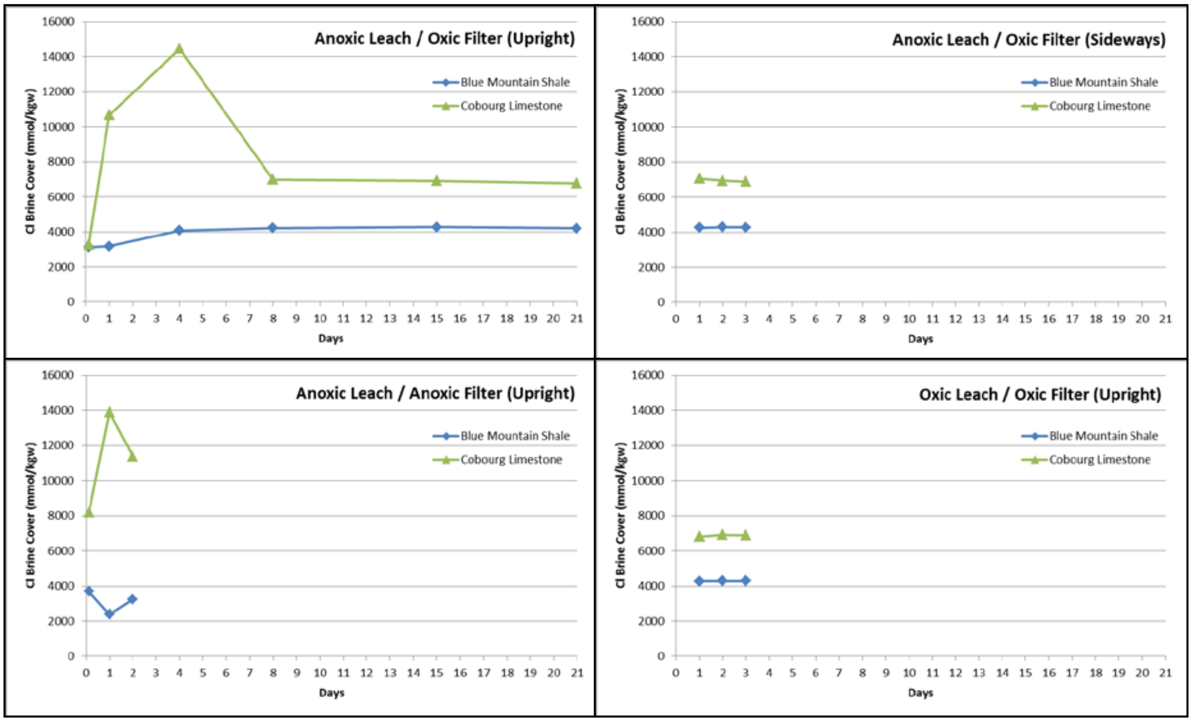

Figure 6: Cl^- Versus Leach Time

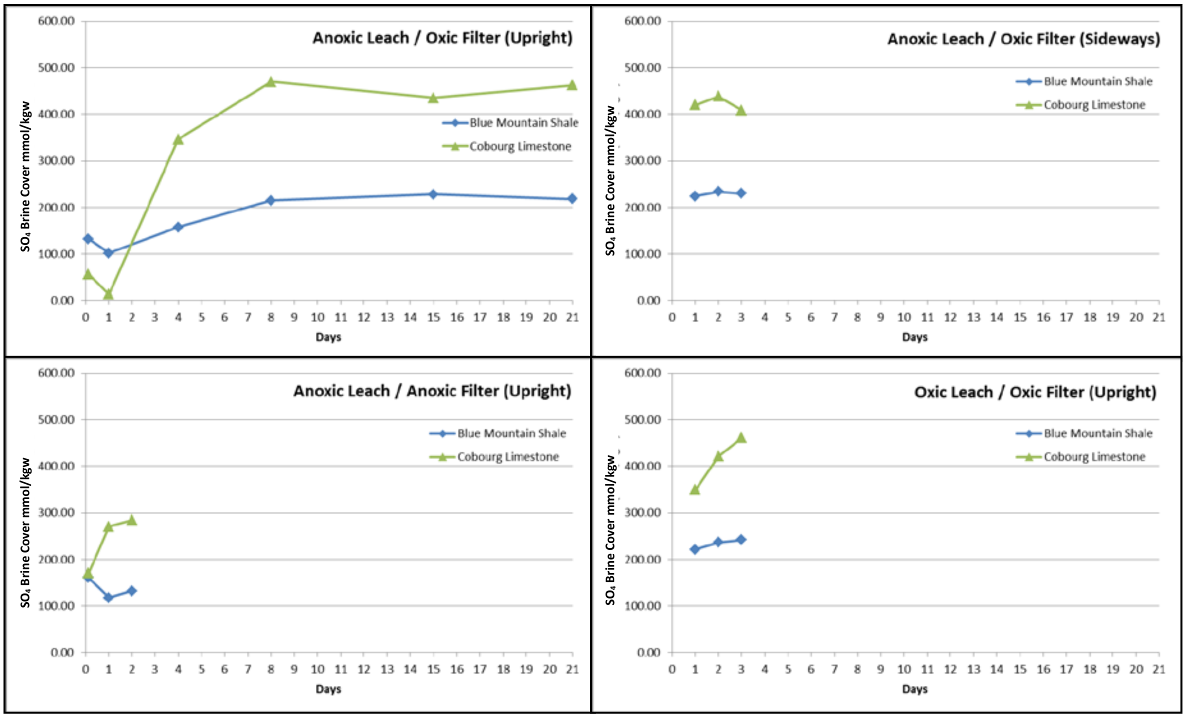

Figure 7: SO_4^{2-} Versus Leach Time

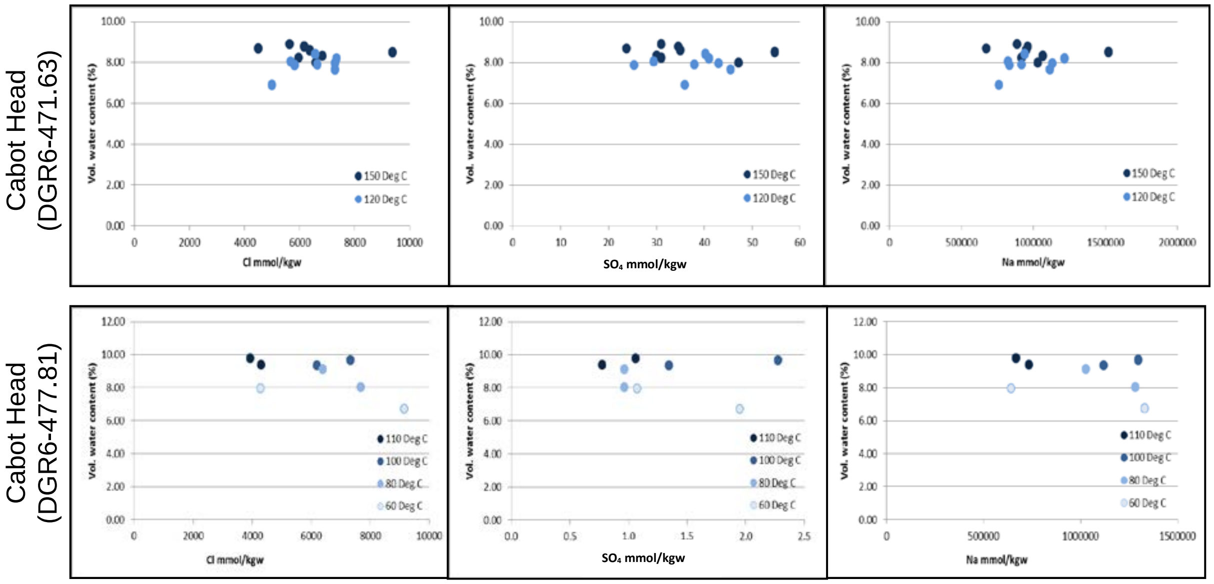

Figure 8: Pore Fluid Geochemistry of Crushed DGR-6 Core Illustrating Higher Variability at Lower Extraction Temperatures

2.2.2 Phase 2 µVDE Method Testing: Control Tests (1.2 mL vials)

In order to address the issue of evaporative effects seen from the first phase of µVDE testing, further refinements were made during Phase 2 of testing to develop a fully-closed water transfer system with direct transfer to 2 mL micro-vials. To accomplish this, the system was refurbished to have water transfer directly to 1.2 mL HRVs, which are used directly for LGR analysis by IRIS. This approach eliminated the need for post-extraction transfer via pipette, and significantly reduced the amount of headspace in the vial.

To examine the time and temperature needed for the extraction process to reach completion, experiments were conducted comparing gravimetric water loss at varying extraction times (t: 30-120 minutes) and temperatures (T: 50-200˚C) using standard doubly-deionized lab water (DDIW) of a known isotopic composition. The stable isotope compositions of the laboratory water used for these tests were characterized by IRIS to determine the instrumental uncertainty and acceptable range of error on δ^{18}O and δD values (Figure 9, shown in blue and green respectively; $\delta^{18}O = -9.76 \pm 0.21$, $\delta D = -79.11 \pm 1.09$). Extracted waters also were analyzed for δ^{18}O and δD by IRIS. Matrix-related effects were tested by spiking dried analytical grade SiO_2 and $CaCO_3$ powders with deionized lab water (t: 30-120 minutes; T: 120-150˚C). Water volumes used were typical of porewater recovery yields from rock samples (~200 µL).

Figure 9 illustrates the isotopic variations of distilled water samples on: A) no matrix, B) $CaCO_3$, and C) SiO_2 matrices at different extraction temperatures and hold times. Recovery yields (%) from the DDIW control tests (no matrix) at varying times and temperatures are shown in Figure 10. As expected, and consistent with the initial VDE tests, the µVDE tests show that low extraction temperatures (< 100˚C) typically yield poor water recoveries (< 76%) and lower isotopic compositions (up to –1.7‰ for δ^{18}O and -13.7‰ for δD) as a result of partial/incomplete extraction of water vapour, a phenomenon that tends to produce isotopically-depleted waters due to the inherent fractionation of ^{16}O and ^{18}O. Complete recoveries (i.e., 100% yields) are characteristic of higher extraction temperatures; however, a slight enrichment phenomenon can be observed at the upper temperature limit (i.e., 200 ˚C), which was also observed in the previous VDE experiments and may be attributable to isotopic exchange with the clay matrix (Intera Engineering Ltd 2010b; TR-08-37). Hold times for these tests were found to have little influence on recoveries and isotope values. Figure 9 also shows the range of data for different hold times at different temperatures. The distinction for hold times has, therefore, not been represented in the charts of isotope values with extraction temperature. Excellent water recoveries are observed for the experiments held at 150˚C for 45 minutes (shown in red), typically 100 ±2% (within acceptable experimental uncertainty for gravimetric comparisons), and the δ^{18}O and δD values of the same waters largely fall within the acceptable error range established for these tests. Experiments completed on $CaCO_3$ and SiO_2 matrices plot within the acceptable error range for recovered waters when held at 150˚C for 45 minutes.

It is important to note that most outliers can be identified as problematic extractions (encircled in grey on Figures 9 and 10), such as opening the sample holder or replacing the septum due to difficulties maintaining the vacuum. Evaporative processes (i.e., recovery loss or enriched values) are likely a consequence of such events. These deviations highlight the importance of complete closed-system extractions.

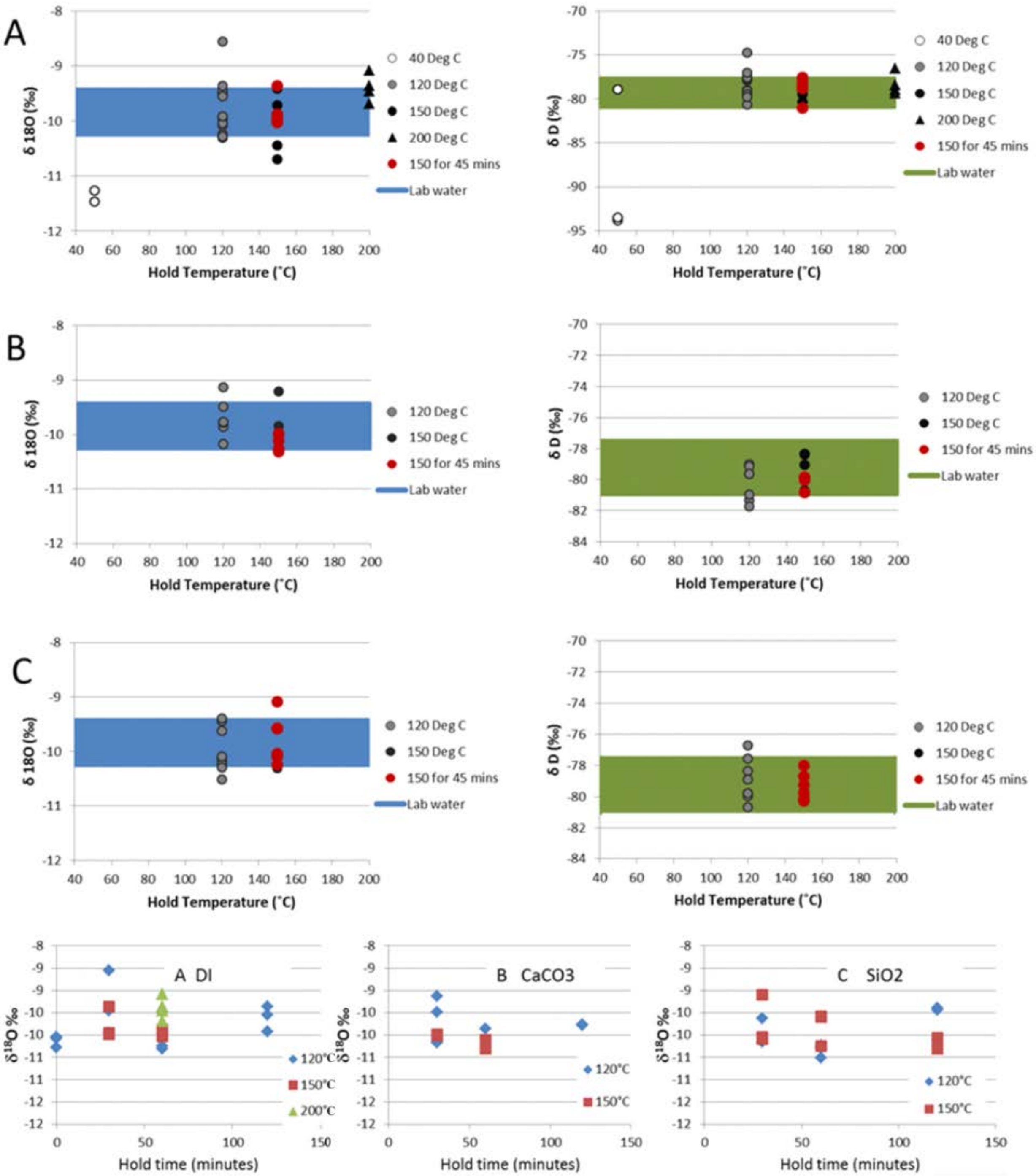

Figure 9: Phase 2 Closed-system μVDE Tests on: A) Laboratory Water – No Matrix, B) $CaCO_3$ and C) SiO_2 Matrices. Expected Values and Associated Error on $\delta^{18}O$ & δD are Displayed in Solid Blue and Green, Respectively; Optimal Extraction Time and Temperature is Highlighted in Red (150˚C for 45 minutes)

μVDE tests with direct and closed-system extraction to smaller vials (1.2 mL HRVs) show better agreement with expected values (Figure 11) when compared to tests using vials with larger volumes (12 mL exetainer vials), followed by pipette transfer (standard deviations <0.5‰ versus 2.0‰ for $\delta^{18}O$ and <1.5‰ versus 8.0‰ for δD). This difference can be attributed to the ten-fold reduction in headspace, which reduces evaporative effects. The new series of closed-system μVDE tests show good agreement with both recovery and expected isotope compositions (i.e., the volume and composition of the water that is put into the system is the same as that which comes out). Experimental results show improvement from previous experiments, and indicate that holding the crushed sample at 150˚C for 45 minutes is the optimal setting to extract all porewater from the low-permeability and low water-content Ordovician shales and limestones of the Michigan Basin. Experiments carried out at lower temperatures risk incomplete extraction of water vapour, resulting in isotopic depletion in the extracted water. This artifact of incomplete extraction is related to the fractionation that occurs between extracted water vapour (depleted) and the residual water (enriched) and the resulting Rayleigh-type distillation that occurs as water is extracted. Partial extraction produces water that is isotopically lighter than the original porewater composition, as the lighter isotopes would preferentially distill (Walker et al. 1994). Therefore, quantitative extraction of all the water from the connected pore spaces is required to avoid any isotopic fractionation of the sample. On the other end of the spectrum, over-heating (i.e., 200˚C) may result in isotopic exchange with the carbonate or clay matrix, which may explain the enrichment trend observed from some of the high-temperature experiments, although this phenomenon is barely pronounced at the experimental temperatures. The results from the experiments performed on $CaCO_3$ and SiO_2 suggest no matrix-related isotope effects.

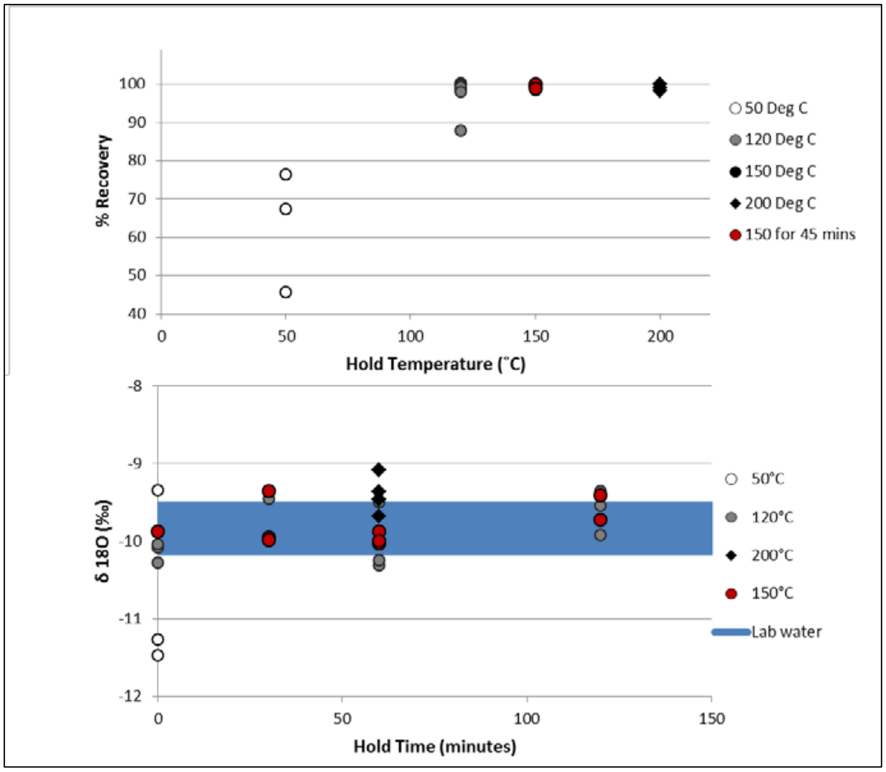

Figure 10: Phase 2 Recovery Yields for μVDE Tests at Different Extraction Temperatures (upper chart) Using Laboratory Water; and Hold Periods (lower chart).

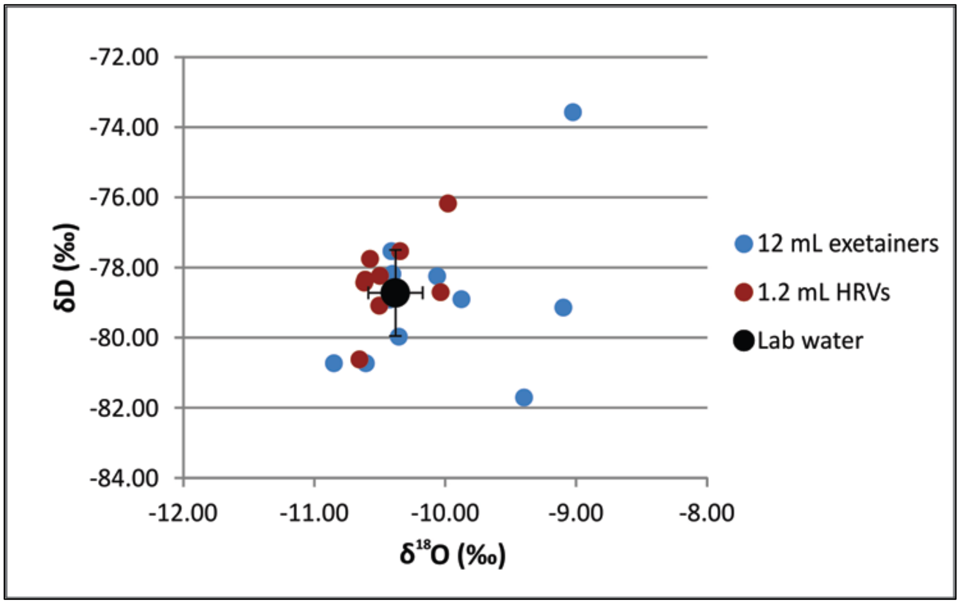

Figure 11: Comparison of Stable Isotope Compositions of Extracted Porewaters Under the µVDE Protocol Using 12 mL Extraction Vials (Phase 1 - blue) Versus 1.2 mL HRVs in a Closed System (Phase 2 - red) at 150˚C for 45 Minutes

3. PRELIMINARY RESULTS FROM DGR-8 CORES

Following testing of the new, closed-system µVDE method, porewaters from freshly-drilled DGR-8 cores (see Murseli et al. 2017; as NWMO-TR-2017-11) were extracted and analyzed for their stable isotopic compositions (δ^{18}O, δ^{2}H). Between 4 and 6 replicates were completed per core to observe sample heterogeneity over the sampled area (~5 cm). The stable isotope compositions of the extracted DGR-8 porewaters using the new µVDE method are presented in the composite profiles (Figure 12), with the average of the DGR-8 replicates presented with the DGR1-6 VDE results for comparison (see Supplemental data in Appendix B). Each black dot on the composite profiles represents the average of four replicate measures on one single core (DGR1-6, VDE only). The DGR-8 µVDE porewater values (average of 4-6 core replicates) are superimposed on these profiles in red. Larger light blue disks represent groundwater values (Intera Engineering Ltd. 2011). As the presence of hydrocarbons was suspected in some of the µVDE extracted porewaters (petroliferous odour during core preparation), the waters were analyzed by CF-IRMS. As such, these extracted porewaters were pipetted from the 1.2 µL high recovery vials to 12 mL exetainers for analysis of δD and δ^{18}O by equilibration.

The µVDE DGR-8 stable isotope profiles (Figure 12) 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 δ^{18}O, and +/-2.0 ‰ for δD (see Supplemental data). Heterogeneities can be observed at the sub-core scale.

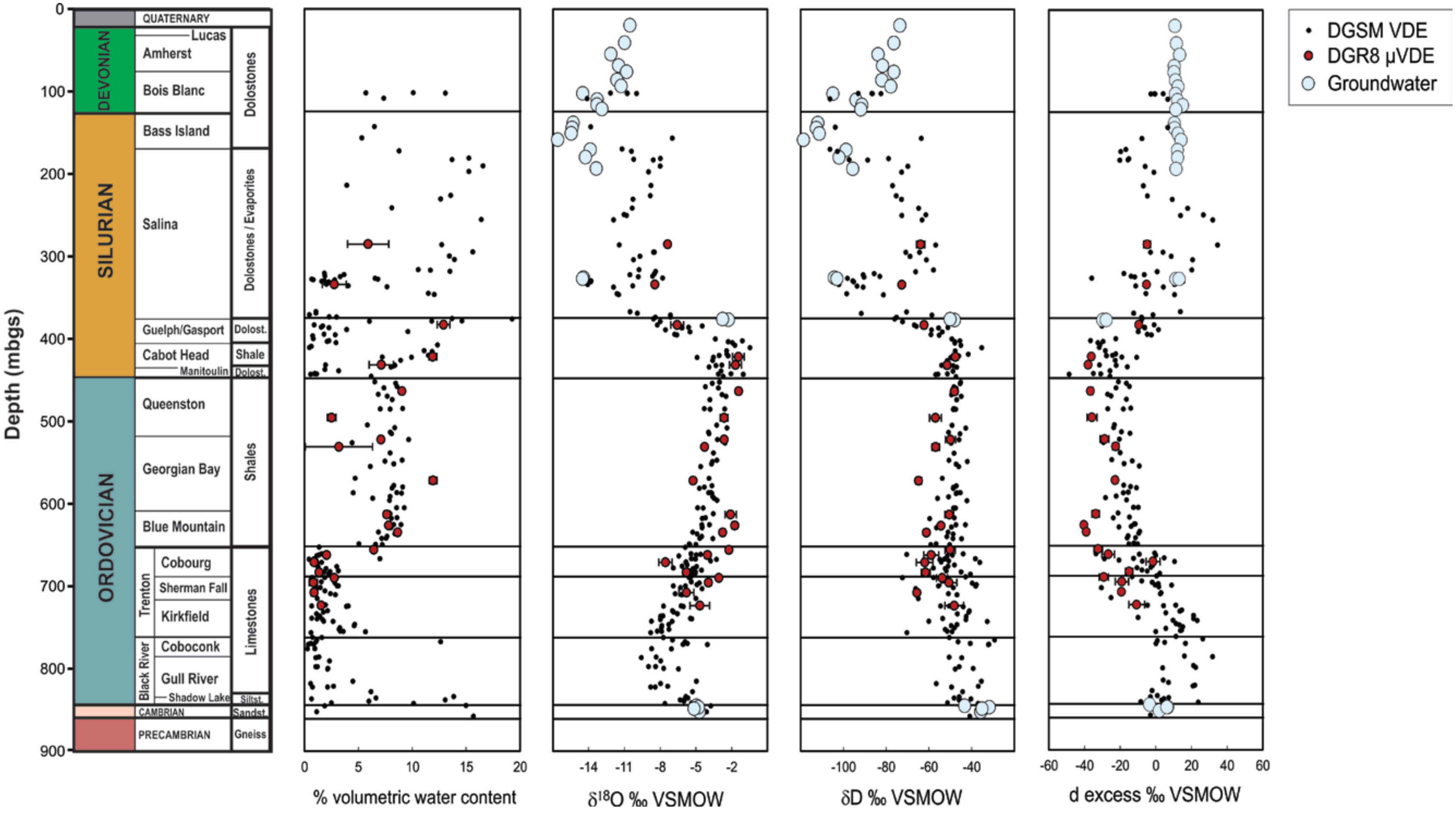

Figure 12: DGR Porewater Profiles: Volumetric Water Content and Stable Isotopes. Black Dots Represent the Average of Four Replicate Measurements on One Single Core (DGR1-6) Under the Previous VDE Method. μVDE DGR-8 Data is Superimposed in Red (average of replicates on one core). Groundwater Values are Displayed by the Large Blue Circles

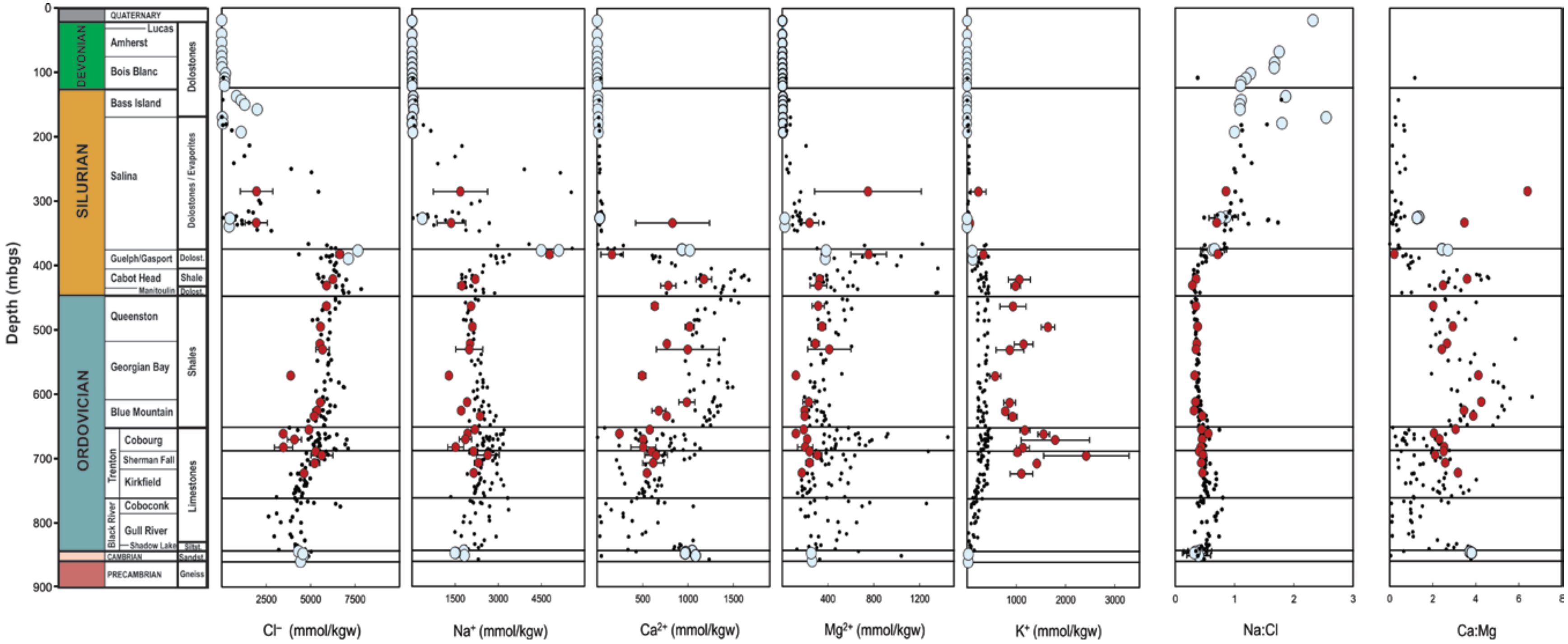

Figure 13: DGR Porewater Profiles: Major Ion Geochemistry. Black Dots Represent the Average of Four Replicate Measurements on One Single Core (DGR1-6) Under the Previous VDE Method. µVDE DGR-8 Data is Superimposed in Red (average of replicates on one core). Groundwater Values are Displayed by the Large Blue Circles

4. DISCUSSION

The evolution of the µVDE method has brought insights and improvements to optimizing porewater extractions from low-permeability sedimentary material. Preliminary µVDE testing (Phase 1) confirmed that δD was reproducible; however, there were some artifacts in measured $\delta^{18}O$ values. It was later confirmed, during Phase 2 of µVDE testing, that these discrepancies were likely linked to evaporative processes because the smaller volume yield from this technique results in larger headspaces in the transfer vial. The direct transfer method precludes opening of the larger exetainers and allowing the entry of air into the micro-vials following extraction, thus significantly reducing the headspace in the transfer vial (1.2 mL versus 12 mL) and eliminating any possibility of evaporation during transfer.

Phase 2 of closed-system µVDE testing shows good agreement with both recovery and expected isotope values (i.e., the volume and isotopic value of the water that is put into the system is the same as that which comes out). Experimental results show improvement from Phase 1 experiments and indicate that holding a crushed sample at 150˚C for 45 minutes is the optimal setting to extract all water vapour from the sample. Experiments carried out at lower temperatures (i.e., 120˚C and less) risk partial or incomplete extraction of water vapour, resulting in lower recoveries and isotopic fractionation. All the water must be extracted to avoid this phenomena of isotopic depletion in the recovered porewaters due to the preferential distillation of lighter isotopes. On the other end of the spectrum, a slight enrichment trend is observed in higher-temperature experiments (i.e., 200˚C). Although the root cause of this trend is still unclear, it may be related to compromising the seal on the silicone septum by overheating or exchange with the matrix. The results from the experiments performed on $CaCO_3$ and SiO_2, however, suggest no matrix-related isotope effects.

Knowledge can also be gained from failed or problematic µVDE experiments, i.e., when there was difficulty experienced with obtaining a vacuum on the sample holders, either due to a damaged o-ring (likely during the milling process) or a leaky septum, prompting the temporary opening of the sample holders to replace the defective portion. Such effects are hypothesized to produce the outliers observed in the dataset – deviations from the expected value (typically, by enrichment) that are likely due to evaporative losses during brief exposure to atmosphere. We have learned that these samples must be discarded, which reaffirms the need for the closed-system extraction process. The variability observed with Phase 1 µVDE experiments can likely be attributed to similar evaporative effects associated with a partially opened extraction system, particularly when working with such small fluid volumes.

In general, the porewaters extracted from the DGR-8 cores by µVDE agree well with the results from VDE, with some notable observations discussed here. Sub-sampling within the Georgian Bay revealed two very different volumetric water contents (~1.3% within the limestone and ~7.2% within the shale interbeds) and different pore fluid compositions (Figure 13), resulting in higher standard deviations of the reported averages. High standard deviations reported within some of the interbedded zones (i.e., Georgian Bay – shale and limestone) are likely not an artefact of the method, but rather are a reflection of the heterogeneities within the rock related to the higher precision sampling of the µVDE method. There are some disparities, particularly with $\delta^{18}O$, in the Blue Mountain through the Trenton Group formations, where we observe $\delta^{18}O$ enrichments up to 2-3‰ compared to VDE data from DGR1-6. Although there are some deviations of δD in the same region, the effect is not as pronounced with the δD. Hydrocarbon contamination of extracted porewaters was considerable for the Blue Mountain Formation; however, this is not suspected to have any effect on $\delta^{18}O$ or δD, as the waters were analyzed by equilibration on a gas-bench CF-IRMS. The very 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). The variations observed in $\delta^{18}O$ or δD compositions of the extracted waters from DGR-8 by µVDE compared to the DGR1-6 data obtained by VDE are likely related to the smaller sample size, to allow for better precision of sampled heterogeneities. From the original VDE data (DGR1-6), variability is observed with changes in the lithology and water content across the profile, but these heterogeneities are likely sampled on a different scale with the µVDE method (DGR-8) due to the reduced sample size, which may explain some of the variability observed between the VDE and µVDE data.

Although powdered leaching requires less time for the ions to be leached into solution when compared to granulated crush and leach (24 hrs versus 7 days), crushing the cores to a fine powder (<100 µm) under the µVDE method greatly increases the exposed surface area and may increase the potential for cation exchange – resulting in the potential underestimation of cations concentrations from leaching of these dried powders when compared to granulated leaching (2-4 mm) by VDE. Some of the divalent cations (Ca^{2+} and Mg^{2+}) appear to be underestimated (compared to leaching of DGR-6 cores after VDE), but cation ratios appear to be preserved. For example, Na:Cl and Ca:Mg ratios appear to be consistent with results obtained using the previous method (DGR1-6 cores). In addition, SO_4^{2-} concentrations are somewhat more variable, which may suggest dissolution of gypsum or other sulphate minerals (particularly in the Salina units) or minor oxidation of the finely disseminated pyrite in these rocks when exposed by powdering. Therefore, these values would not be reflective of pore fluid compositions. As such, solutes with higher ion-exchange potentials (divalent cations and K+) are non-conservative during leaching of the powders, which may be linked to leaching of the clay interlayer or other accessory minerals of the crushed samples. Therefore, only conservative ions (Cl^-, Br^- and Na^+) may be representative of porewater compositions, provided no halite is present.

5. CONCLUSIONS

Vacuum-distillation is routinely used to extract porewaters for isotope analysis from soils and other high-permeability materials, and this method has been successfully adapted for the more challenging low-permeability and low water-content shales and limestones of the Ordovician stratigraphy of the Michigan Basin. High temperature vacuum-distillation to extract pure water for stable isotope analysis, coupled with aqueous leaching of dried rock matrix to reconstitute conservative ions, is an appropriate method to extract and analyze high-salinity pore fluids from shales and limestones with hydraulic conductivities as low as 10^{-15} m/s and water contents as low as 0.5%. The risk of isotopic fractionation as a result of incomplete porewater extraction (imparting an isotopic depletion on the extracted water) is reduced at elevated extraction temperatures. The good reproducibility achieved with vacuum-distillation at temperatures of 150˚C was previously reported by a similar study on the Tournemire argillite (Altinier et al. 2007). The convergence of the $\delta^{18}O$ and δD values from porewater analysis of the Cambrian formation with the measured Cambrian groundwater values at the base of the sedimentary sequence at the Bruce Nuclear Site demonstrates that the data are appropriate representations of in-situ porewater values. This method is appropriate for illitic clays and low water-content samples, where sorbed H_2O onto the clays are a negligible fraction of the total water content. Applications in other rock matrices would need to be fully tested before implementation, i.e., this method would be less appropriate for smectites, which have a hydrated interlayer, in particular at higher extraction temperatures.

The new closed-system µVDE method offers several advantages by optimizing the vacuum-distillation technique for extraction of low permeability rock with ultra-low water contents:

i. Closed-system isolated crushing and extraction eliminates the potential for evaporative loss, with direct water-vapour collection into septum-sealed sample vials rather than a transient capture container. In addition, a ten-fold reduction in headspace in the recovery vials (from 12 mL to 1.2 mL) reduces potential fractionation effects of very small volumes of water (typically <200 µL) by evaporation in the headspace or post-transfer (via pipetting). The transition to a fully closed-system extraction system improves precision for the low water-content (<2 %) Ordovician limestones.
ii. Crushing the rock to a fine powder significantly reduces the amount of heating time required to extract all porewaters (from 6 hours to less than 1 hour), and even heating distribution ensures that extraction conditions are consistent throughout the sample.
iii. Smaller sample volume (10 g for µVDE versus 40 g for VDE) allows for: i) improved transfer, with less H_2O loss in the transfer line; 2) precision sampling of heterogeneities away from key features such as fractures and bioclastic zones; and, 3) sub-sampling within interbeds.
iv. Reduced heating time, combined with rapid analysis by IRIS, allows for increased turn-around time and duplicate sampling.
v. A dual-extraction line facilitates the analysis of low-porosity rocks.

Subsequent leaching of the post-extracted sample powder provides robust reconstruction of conservative solutes, including Cl^-, Br^- and Na^+ (provided no halite is present), although solutes with higher ion-exchange potentials (divalent cations and K^+) are non-conservative during leaching of the powders, which may be linked to leaching of the clay interlayer or dissolution of other accessory minerals in the crushed samples. For these, leaching of intact core subsamples and normalization using Cl^- may resolve this issue, although further study of the crush and leach procedure may be required. It is recommended, therefore, that the µVDE technique be coupled with a gentle crush (2.88~4.69 mm diameter grain size) and leach on a separate core sample, within the same core length or interbed unit.

A significant problem with high temperature vacuum-distillation is the complication brought to isotope analyses by hydrocarbon contents in the core, which are released by heating and recovered with the water in the liquid nitrogen trap. Developing online hydrocarbon separation techniques will be important moving forward, so that extracted porewaters can be readily analyzed by IRIS. Until these methods can be developed, careful measurement of the stable isotope composition of these contaminated porewaters by CF-IRMS is more than adequate, as demonstrated for porewaters extracted from DGR-8 core.

Analysis of $\delta^{18}O$ and δD on very low-water content samples (<2%) remains difficult, as it pushes the limits of conventional sample size for gas bench CF-IRMS. This, of course, can be rectified by increasing sample size and subsequent volume of recovered porewaters. Another option is to analyse the waters by pyrolysis (TC/EA coupled with IRMS). The pyrolysis method, also known as high temperature conversion, involves reducing oxygen and hydrogen present in a compound to CO and H_2 respectively, at high temperatures (>1400˚C). The reactor consists of a glassy carbon tube with a glassy carbon filling, ensuring that neither sample, nor reaction gas, comes in contact with oxygen-containing surfaces at high temperatures. The reaction gases can then be separated in an isothermal gas chromatograph, reporting $\delta^{18}O$ and δD simultaneously. Typical sample amounts for water are <0.5 µL. The caveat of this method is that waters must be pure (i.e., free from hydrocarbons); otherwise these compounds will be pyrolysed with the waters. Therefore, developing a hydrocarbon separation technique (on-line or post-distillation) will be an important priority moving forward with this technique.

In summary, for the characterization of materials with very low hydraulic conductivities and low water contents, traditional approaches for porewater extraction and characterization are not consistently successful. The VDE and µVDE techniques presented here are shown to be robust methods for the extraction and analysis of porewaters from recalcitrant materials.

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APPENDIX A: PHOTOGRAPHS OF EXPERIMENTAL PROCEDURE

CONTENTS

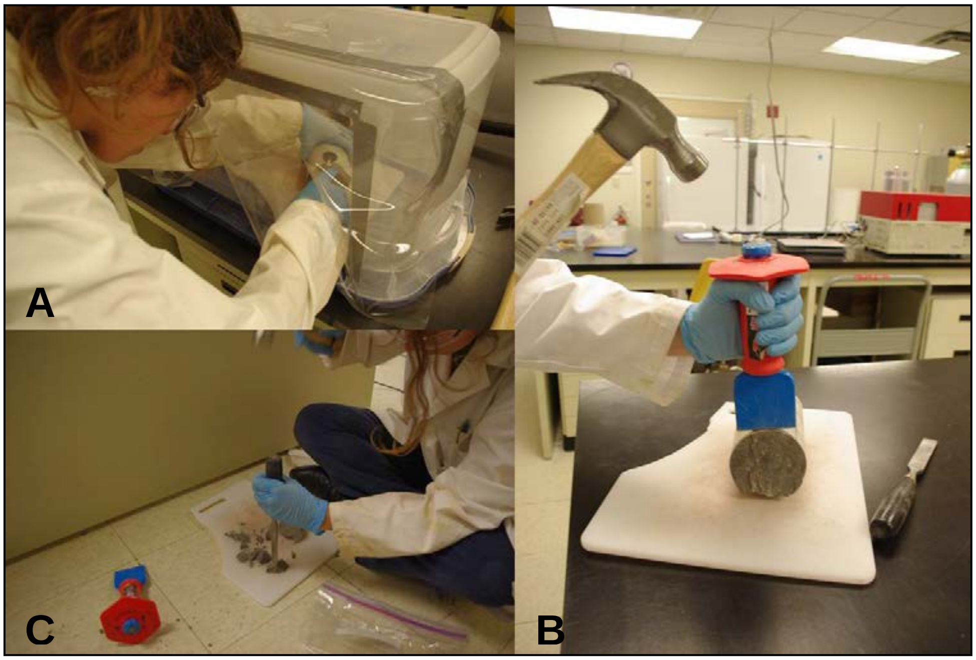

Figure A.1. Core Sample Preparation: A Small Channel is Dry Bored with a Rotary Tool (A) to Facilitate Removal of Outer Edges (B). Following Removal, the Freshly Exposed Pieces are Quickly Sectioned into ~3-10 g Pieces (C), Weighed and Sealed into Stainless Steel Sample Holders

Figure A.2. Individual Stainless Steel Sample Holder with High Temperature Septa (green) and Stainless Steel Ball; Sample Holders are ~3.5 x 6.5 cm

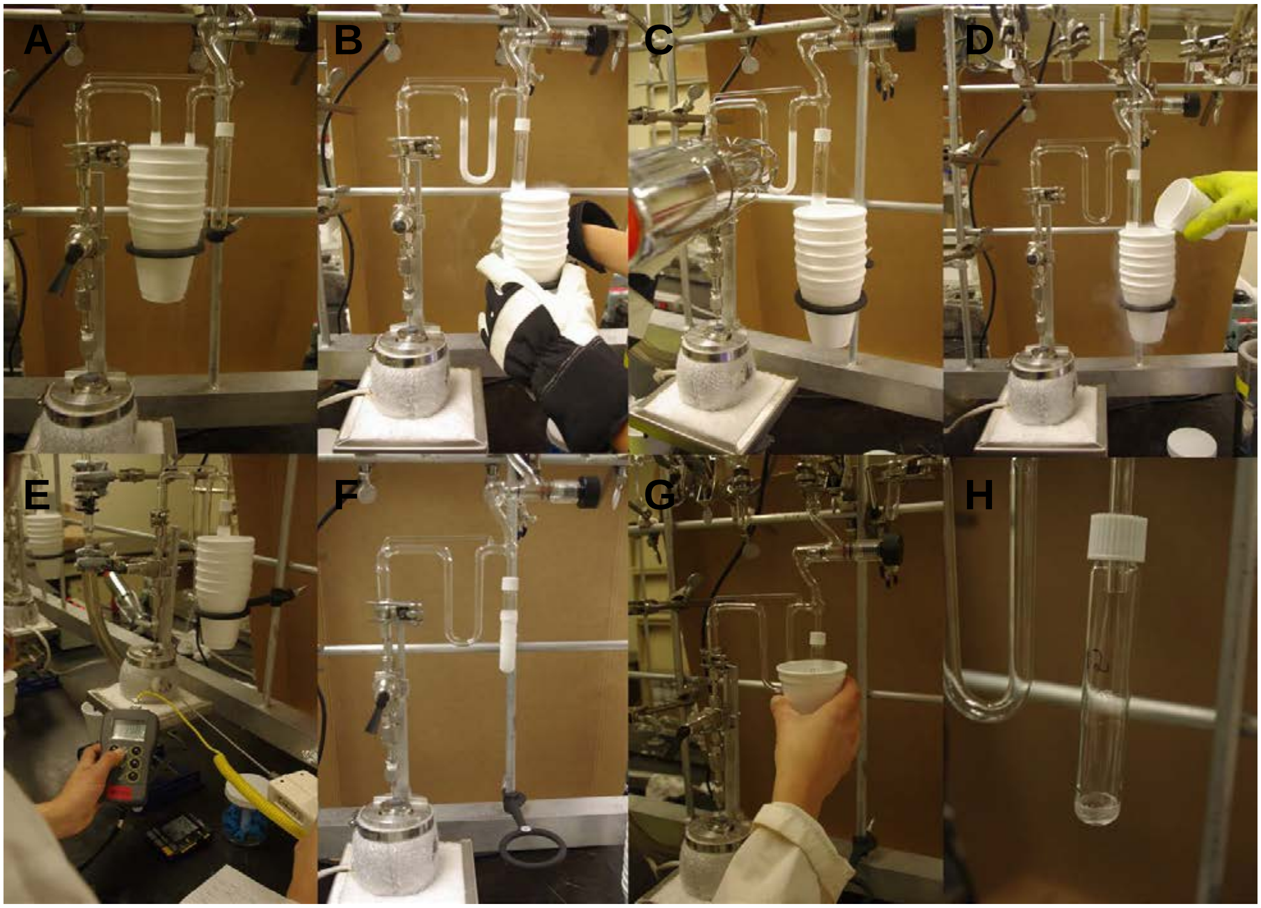

Figure A.3. Vacuum-distillation Experimental Procedure (Phase 1): Milled Sample is Attached to the Vacuum Line Via 1/16" Needle and the Transfer Line and Sample Holder are Evacuated to ~80mT, Trapping Any Moisture Lost During the Evacuation on the Liquid Nitrogen U-trap (A). Following Evacuation, the Liquid Nitrogen Bath is Removed From the U-trap and Placed on the Exetainer to Trap the Transferred Vapour (B), and the U-trap is Returned to Room Temperature With a Heat Gun (C). During the Experiment, the Liquid Nitrogen Levels are Periodically Replenished (D) and the Temperature is Monitored (E). Once the Experiment is Completed, the Valve Connected to the Sample Holder is Closed, and the Liquid Nitrogen Bath is Removed From the Exetainer (F). The Exetainer Containing the Recovered Water is Brought to Near 0˚C With an Ice Water Bath (G) Before the Vacuum is Broken and the Exetainer is Removed From the Line (H)

Figure A.4. Condensation in the Vacuum Transfer Line (although rare) is Symptomatic of Loss of Vacuum, Resulting in Discarding of the Sample. This Problem is Mitigated by Performing a Dynamic Vacuum Extraction Using the U-trap

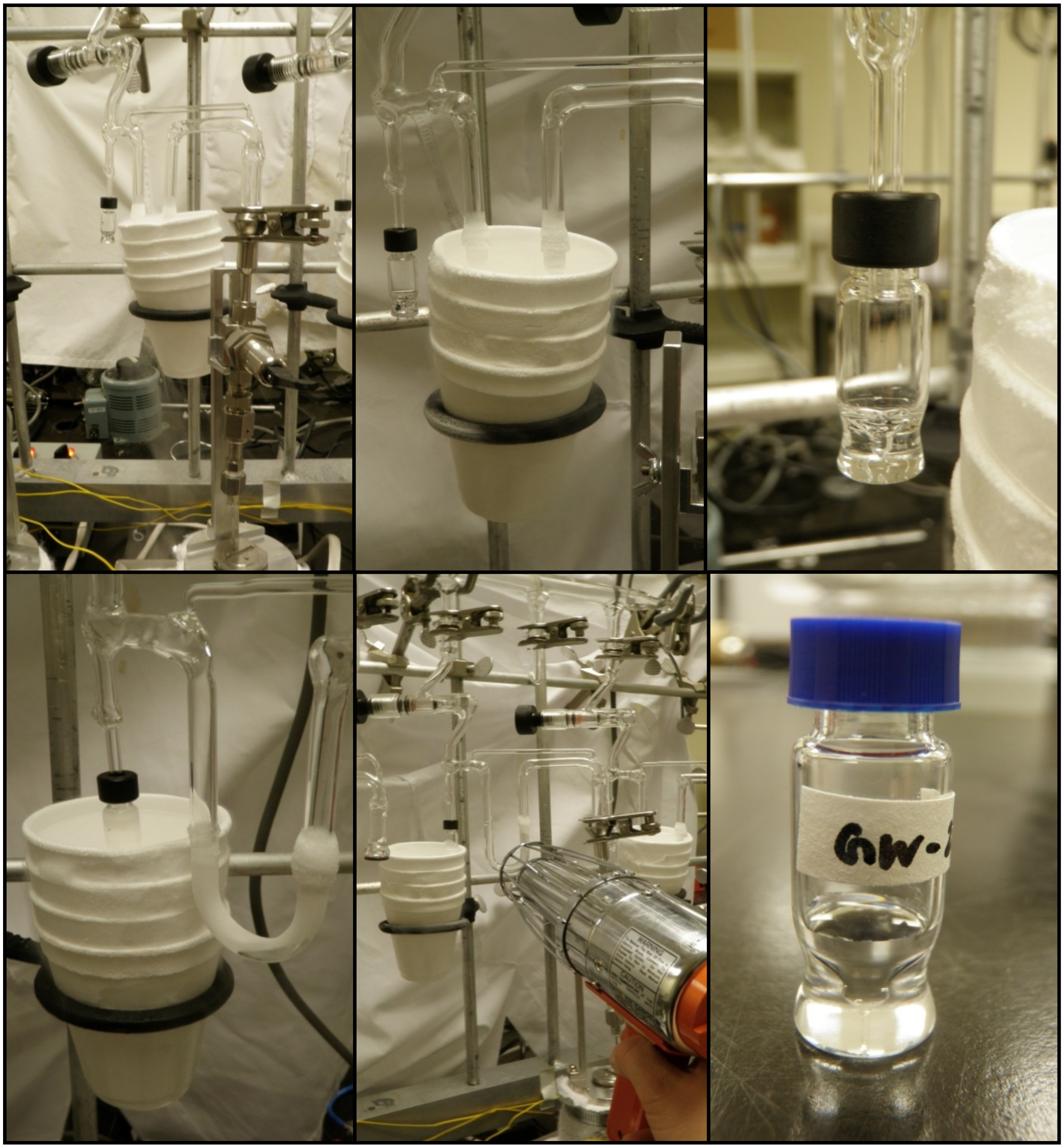

Figure A.5. Closed-system Vacuum-distillation Experiments (Phase 2). Extraction Line (top-left) Showing Primary Transfer of Water Vapour to U-trap (top-middle) and High Recovery Micro-vial (top-right) Under Dynamic Vacuum. Secondary Transfer of Water Vapour to High Recovery Micro-vial Under Static Vacuum (bottom-left). All Water Vapour Trapped in the Transfer Line Via U-trap is Driven Over With a Heat Gun and Trapped Cryogenically in a High Recovery Micro-vial (bottom-middle). Once the Transfer is Complete, Vial Containing the Sample is Removed From the Transfer Line, Capped (bottom-right), and Analyzed by IRIS

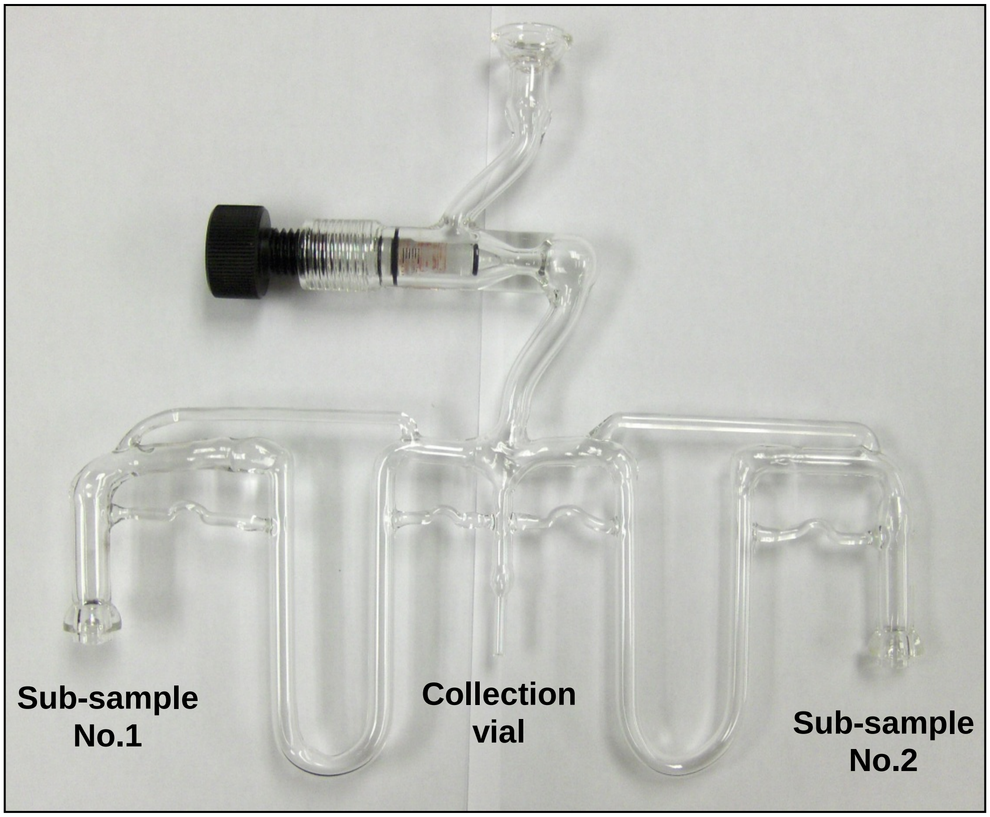

Figure A.6. Dual Water Vapour Extraction Line for Low-porosity Rock Cores

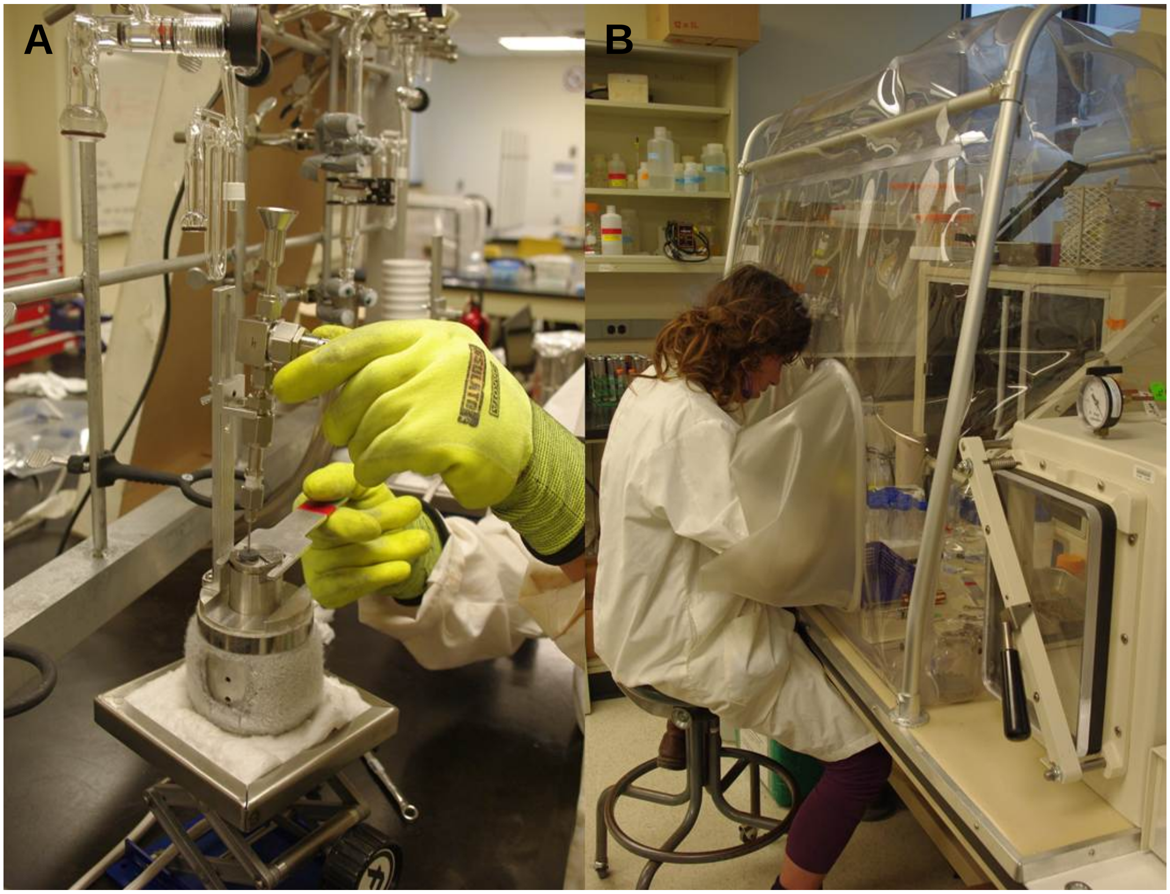

Figure A.7. Aqueous Leaching Method: Following the Vacuum-distillation Experiment, the Needle/valve Unit and Sample Holder Containing the Dehydrated Rock is Detached From the Vacuum Line and Removed From the Heater With the Valve Closed (A). Once Cooled, the Sample Holder and Valve/needle Unit are Transferred to an Anaerobic Chamber for Aqueous Leaching (B)

APPENDIX B: SUPPLEMENTAL DATA

CONTENTS

B.1µVDE EXPERIMENTS (Phase 1)

Table B.1.1. µVDE on Cabot Head Formation 1: DGR6-471.63

Sample ID	Mass wet rock (g)	Mass H_2O recovered (g)	WC_{vol} (%)	Target temp (ºC)	Hold Time	$\delta^{18}O$ (‰)	σ_{18O}	δD (‰)	σ_D
DGR6-471.63-21	8.4718	0.2498	8.20	120	0	-0.92	0.50	-47.99	1.86
DGR6-471.63-22	8.8240	0.2527	7.96	120	0	-1.04	0.13	-48.42	0.68
DGR6-471.63-23	9.2324	0.2642	7.95	120	0	-1.39	0.10	-49.64	0.34
DGR6-471.63-24	8.0503	0.2355	8.14	120	0	-1.43	0.35	-49.66	1.14
DGR6-471.63-25	8.7182	0.2407	7.67	120	15	-1.14	0.07	-47.62	0.06
DGR6-471.63-26	9.3701	0.2831	8.41	120	15	-0.34	0.55	-45.55	3.87
DGR6-471.63-27	8.2257	0.1917	6.44	120	15	-2.35	0.21	-49.12	0.86
DGR6-471.63-28	8.3447	0.1805	5.97	120	15	-1.22	0.13	-48.66	2.98
DGR6-471.63-29	8.8315	0.2562	8.07	120	30	-1.17	0.21	-50.30	1.03
DGR6-471.63-30	8.3853	0.2465	8.18	120	30	-0.76	0.38	-48.61	2.38
DGR6-471.63-31	9.0598	0.2579	7.91	120	30	-0.84	0.48	-50.00	2.46
DGR6-471.63-32	8.1182	0.2206	7.54	120	30	-0.78	0.54	-47.34	4.59
DGR6-471.63-33	8.0789	0.2309	7.94	120	60	-1.04	0.03	-47.73	0.78
DGR6-471.63-34	8.0896	0.2291	7.87	120	60	0.44	0.59	-45.39	3.39
DGR6-471.63-35	9.1792	0.2285	6.89	120	60	-0.36	0.25	-43.18	2.03
DGR6-471.63-36	8.2445	0.2406	8.12	120	60	1.55	0.36	-40.64	2.49
DGR6-471.63-13	10.5398	0.3314	8.77	150	0	-1.55	0.39	-48.10	2.28
DGR6-471.63-14	10.3993	0.3180	8.52	150	0	-2.33	0.24	-46.38	1.22
DGR6-471.63-16	10.6606	0.3077	8.02	150	0	-1.31	0.30	-42.09	2.21
DGR6-471.63-2	9.5243	0.2946	8.62	150	15	-1.99	0.17	-47.39	0.27
DGR6-471.63-3	9.9245	0.3023	8.48	150	15	0.56	0.15	-45.19	1.23
DGR6-471.63-4	12.0123	0.3355	7.76	150	15	-0.61	0.11	-43.87	0.52
DGR6-471.63-5	11.8418	0.3535	8.31	150	15	-1.60	0.26	-44.27	2.48
DGR6-471.63-6	11.3103	0.3608	8.90	150	15	0.06	0.12	-41.84	1.17
DGR6-471.63-7	11.7113	0.3534	8.40	150	15	-2.38	0.44	-46.35	2.71
DGR6-471.63-8	10.3275	0.3223	8.70	150	15	-2.26	0.50	-46.02	2.66
DGR6-471.63-9	10.1034	0.3116	8.59	150	30	-2.41	0.05	-44.26	0.30
DGR6-471.63-10	10.5496	0.3149	8.31	150	30	-0.45	0.11	-46.86	0.51
DGR6-471.63-11	10.5162	0.3117	8.25	150	30	-0.55	0.15	-42.18	0.51
DGR6-471.63-12	10.7907	0.3397	8.78	150	30	-1.20	0.28	-46.03	1.87
DGR6-471.63-18	10.3593	0.3101	8.33	150	60	0.94	0.48	-45.13	3.28
DGR6-471.63-19	10.1274	0.2912	7.99	150	60	0.49	0.10	-46.00	1.13
DGR6-471.63-20	11.2261	0.3354	8.32	150	60	1.05	0.14	-44.40	0.61
DGR6-471.63-1	10.1326	*Failed – poor vac*	---	---	---	---	---	---	---
DGR6-471.63-15	11.0954	*Failed – poor vac*	---	---	---	---	---	---	---
DGR6-471.63-17	10.1861	*Failed – poor vac*	---	---	---	---	---	---	---

Table B.1.2. μVDE on Cabot Head Formation 2: DGR6-477.81

Sample ID	Mass wet rock (g)	Mass H_2O recovered (g)	WC_{vol} (%)	Target temp (ºC)	Hold Time	$\delta^{18}O$ (‰)	σ_{18O}	δD (‰)	σ_D
DGR6-477.81-1	8.4455	0.2058	6.74	60	15	-2.55	0.93	-64.39	6.56
DGR6-477.81-2	7.7108	0.1635	5.85	60	15	-3.25	0.69	-64.56	3.84
DGR6-477.81-3	8.1929	0.2347	7.96	60	30	-2.41	0.13	-59.76	0.61
DGR6-477.81-4	8.5265	0.2235	7.27	60	30	-7.42	0.18	-73.06	0.76
DGR6-477.81-5	8.1672	0.2362	8.04	80	15	-3.52	0.94	-62.16	6.08
DGR6-477.81-6	8.2234	0.0842	2.79	80	15	NaN	NaN	NaN	NaN
DGR6-477.81-7	8.6257	0.2823	9.14	80	30	-2.29	0.52	-58.79	3.39
DGR6-477.81-8	8.5432	0.2295	7.45	80	30	-3.84	0.56	-63.57	4.82
DGR6-477.81-9	8.1800	0.2745	9.38	100	15	-1.93	0.45	-56.62	2.69
DGR6-477.81-10	8.8452	0.2808	8.85	100	15	-2.29	0.32	-64.05	3.00
DGR6-477.81-11	8.3969	0.2907	9.68	100	30	-0.60	0.39	-55.25	2.49
DGR6-477.81-12	8.1143	0.2876	9.92	100	30	-0.92	0.23	-55.39	1.58
DGR6-477.81-13	9.0266	0.3035	9.39	110	15	-0.64	0.71	-56.74	4.51
DGR6-477.81-14	8.7694	0.3543	11.37	110	15	-0.45	0.27	-54.13	1.94
DGR6-477.81-15	8.5043	0.2982	9.81	110	30	-1.44	0.14	-56.69	1.40
DGR6-477.81-16	9.0857	0.2760	8.46	110	30	-1.49	0.04	-56.80	0.77

Table B.1.3. μVDE on Queenston Formation: DGR5-557.65

Sample ID	Mass wet rock (g)	Mass H_2O recovered (g)	WC_{vol} (%)	Target temp (ºC)	Hold Time	$\delta^{18}O$ (‰)	σ_{18O}	δD (‰)	σ_D
DGR5-557.65-1	7.7536	0.2187	7.84	90	15	0.83	0.32	-38.09	3.29
DGR5-557.65-2	8.7240	0.2353	7.48	90	15	-0.01	0.48	-42.56	2.82
DGR5-557.65-3	8.8362	0.1289	4.00	90	30	-2.24	0.21	-42.81	1.41
DGR5-557.65-4	8.7551	0.1372	4.30	90	30	-2.16	0.23	-39.71	1.59
DGR5-557.65-5	8.1556	0.2154	7.32	100	15	-0.05	0.08	-41.19	0.84
DGR5-557.65-9	9.3629	0.2199	6.49	100	15	0.23	0.41	-43.21	1.37
DGR5-557.65-7	8.7946	0.2268	7.15	100	30	-0.88	0.00	-38.14	0.00
DGR5-557.65-11	8.2107	0.2403	8.14	100	30	0.83	0.00	-42.83	0.00
DGR5-557.65-6	7.7986	0.2244	8.00	105	15	0.83	0.03	-35.94	0.29
DGR5-557.65-10	8.1636	0.2066	7.01	105	15	0.79	0.09	-41.78	0.22
DGR5-557.65-8	8.2883	0.2360	7.91	105	30	NaN	NaN	NaN	NaN
DGR5-557.65-12	8.3979	0.1980	6.52	105	30	1.63	0.51	-39.63	2.59
DGR5-557.65-13	8.6439	0.2348	7.54	110	15	0.96	0.33	-40.87	1.53
DGR5-557.65-14	9.2671	0.1592	4.72	110	15	-7.95	0.00	-109.43	0.00
DGR5-557.65-15	8.1484	0.2203	7.50	110	30	1.96	0.07	-36.58	3.93
DGR5-557.65-16	10.3350	0.1952	5.20	110	30	-9.01	0.10	-74.65	0.34

Table B.1.4. μVDE on Georgian Bay Formation: DGR6-662.17

Sample ID	Mass wet rock (g)	Mass H_2O recovered (g)	WC_{vol} (%)	Target temp (ºC)	Hold Time	$\delta^{18}O$ (‰)	σ_{18O}	δD (‰)	σ_D
DGR6-662.17-1	7.8707	0.1515	5.30	90	15	-4.78	0.23	-57.05	1.83
DGR6-662.17-9	9.2180	0.1838	5.49	90	15	-4.38	0.34	-59.37	2.02
DGR6-662.17-2	9.0874	0.2153	6.55	90	30	-4.45	0.15	-59.83	0.67
DGR6-662.17-10	7.8206	0.1188	4.16	90	30	-4.33	0.10	-54.59	0.85
DGR6-662.17-3	7.9494	0.2033	7.09	100	15	-3.62	0.31	-59.29	0.83
DGR6-662.17-11	7.8488	0.0822	2.86	100	15	-5.40	0.49	-54.23	2.48
DGR6-662.17-4	8.7279	0.1933	6.12	100	30	-3.00	0.33	-56.85	1.95
DGR6-662.17-12	9.1669	0.1694	5.08	100	30	-4.14	0.35	-56.62	2.08
DGR6-662.17-5	8.2883	0.1748	5.82	105	15	-3.87	0.97	-57.81	4.56
DGR6-662.17-13	9.1556	0.2132	6.44	105	15	-4.50	0.50	-56.21	2.62
DGR6-662.17-6	8.2355	0.1794	6.01	105	30	-3.57	0.00	-58.26	0.00
DGR6-662.17-14	8.6501	0.1613	5.13	105	30	-4.04	0.53	-60.03	2.30
DGR6-662.17-7	8.1444	0.1948	6.62	110	15	-5.67	0.64	-63.38	2.94
DGR6-662.17-15	8.7286	0.1862	5.89	110	15	-3.65	0.72	-56.37	4.50
DGR6-662.17-8	8.3612	0.2115	7.01	110	30	-4.71	0.54	-58.81	3.87
DGR6-662.17-16	8.1356	0.1578	5.34	110	30	-3.26	0.52	-55.49	3.14

Table B.1.5. μVDE on re-injections on DGR5/6 Core

Sample ID	Mass H_2O injected (g)	Mass H_2O recovered (g)	% Recovery	Target temp (ºC)	Hold Time	$\delta^{18}O$ (‰)	σ_{18O}	δD (‰)	σ_D
DGR6-477.81-2R	0.2054	0.3003	146.2	60	15	-8.15	0.47	-73.35	2.39
DGR6-477.81-4R	0.2831	0.2066	73.0	60	30	-3.79	0.21	-67.54	1.71
DGR6-477.81-6R	0.1783	0.2135	119.7	80	15	-7.01	0.26	-69.30	0.36
DGR6-477.81-8R	0.2018	0.2231	110.6	80	30	-7.76	0.21	-72.11	1.08
DGR6-477.81-10R	0.1765	0.1815	102.8	100	15	-8.49	0.66	-75.66	4.03
DGR6-477.81-12R	0.1902	0.1990	104.6	100	30	-9.65	0.74	-77.97	3.60
DGR6-477.81-14R	0.1923	0.2116	110.0	110	15	-8.41	0.14	-74.53	2.78
DGR6-477.81-16R	0.1926	0.2067	107.3	110	30	-8.89	0.00	-74.95	0.00
DGR5-557.65-2R	0.1873	0.2091	111.6	90	15	NaN	NaN	NaN	NaN
DGR5-557.65-4R	0.1948	0.2398	123.1	90	30	NaN	NaN	NaN	NaN
DGR5-557.65-9R	0.1962	0.2039	103.9	100	15	-8.47	0.00	-72.30	0.00
DGR5-557.65-11R	0.1929	0.1924	99.7	100	30	-9.36	0.57	-76.48	3.01
DGR5-557.65-10R	0.1899	0.2079	109.5	105	15	-9.03	0.47	-75.52	2.18
DGR5-557.65-12R	0.1929	0.1889	97.9	105	30	-8.39	0.00	-71.83	0.00
DGR5-557.65-13R	0.1906	0.1889	99.1	110	15	-9.52	0.00	-75.03	0.00
DGR5-557.65-15R	0.1956	0.2643	135.1	110	30	0.61	0.00	-43.93	0.00
DGR6-662.17-1R	0.1895	0.1907	100.6	90	15	-10.98	0.37	-81.31	1.92
DGR6-662.17-9R	0.1903	0.1913	100.5	90	15	-10.35	0.11	-77.69	1.68
DGR6-662.17-2R	0.1969	0.1976	100.4	90	30	-9.98	0.49	-78.11	2.99
DGR6-662.17-10R	0.1865	0.1910	102.4	90	30	-10.09	0.32	-76.65	1.83
DGR6-662.17-3R	0.1909	0.1907	99.9	100	15	-10.27	0.61	-78.38	3.55
DGR6-662.17-11R	0.1985	0.2156	108.6	100	15	-10.13	0.81	-74.15	4.99
DGR6-662.17-4R	0.1955	0.1941	99.3	100	30	-11.99	0.41	-84.97	2.84
DGR6-662.17-12R	0.1795	0.1751	97.5	100	30	-9.56	0.16	-76.75	1.14
DGR6-662.17-5R	0.1996	0.2011	100.8	105	15	-10.80	0.77	-80.98	2.96
DGR6-662.17-13R	0.1935	0.1961	101.3	105	15	-9.56	0.43	-74.32	3.11
DGR6-662.17-6R	0.1986	0.1988	100.1	105	30	-11.19	0.76	-82.50	3.95
DGR6-662.17-14R	0.2060	0.2010	97.6	105	30	-9.44	0.46	-76.80	2.88
DGR6-662.17-7R	0.1976	0.2040	103.2	110	15	-10.74	0.75	-79.90	3.29
DGR6-662.17-15R	0.2012	0.2729	135.6	110	15	-7.79	0.45	-62.46	3.40
DGR6-662.17-8R	0.1942	0.1957	100.8	110	30	-9.93	1.68	-76.20	9.62
DGR6-662.17-16R	0.2025	0.2012	99.4	110	30	-9.98	0.58	-80.92	4.12

B.2μVDE EXPERIMENTS (Phase 2)

Table B.2.1. New Closed-system μVDE Tests with Lab Water (DDIW) Only (Phase 2)

Sample ID	Comments	Mass H_2O injected (g)	Mass H_2O recovered (g)	% Recovery	Target temp (ºC)	Hold Time	$\delta^{18}O$ (‰)	σ_{18O} (‰)	δD (‰)	σ_D (‰)
NS-1		0.1655	0.1658	100.18	120	60	-9.49	0.25	-77.86	1.23
NS-2	Some diff. transferring water	0.1977	0.1983	100.30	120	60	-10.31	0.24	-79.07	0.30
NS-3	Some diff. transferring water	0.1963	0.1967	100.20	120	60	-10.25	0.18	-78.99	0.92
NS-4		0.2117	0.2087	98.58	120	30	-9.45	0.19	-77.58	0.89
NS-5	Septum replaced	0.2542	0.2536	99.76	120	30	-9.95	0.49	-79.07	1.45
NS-6	Sample holder opened	0.1845	0.1849	100.22	120	30	-8.55	0.40	-74.72	1.24
NS-7		0.2283	0.2286	100.13	150	30	-9.95	0.44	-78.15	1.56
NS-8		0.2185	0.2174	99.50	150	30	-9.99	0.07	-78.73	0.23
NS-9		0.2000	0.1987	99.35	150	30	-9.35	0.52	-76.56	1.21
NS-10		0.2004	0.1936	96.61	150	60	-9.88	0.30	-78.63	1.56
NS-11		0.1912	0.1912	100.00	150	60	-10.03	0.08	-81.00	1.86
NS-12		0.2050	0.2029	98.98	150	60	-9.99	0.02	-78.82	0.13
NS-13		0.2087	0.1833	87.83	120	0	-10.08	0.12	-80.61	0.34
NS-14		0.2287	0.2265	99.04	120	0	-10.28	0.23	-79.44	1.36
NS-15		0.1839	0.2082	113.21	120	0	-10.04	0.33	-79.76	0.03
NS-16	Septum replaced	0.2246	0.2211	98.44	150	0	-10.45	0.15	-80.37	1.35
NS-17		0.1885	0.1874	99.42	150	0	-10.21	0.15	-80.21	0.73
NS-18		0.2120	0.2120	100.00	150	0	-9.88	0.15	-79.47	1.29
NS-19	Failed – vacuum lost	0.1881	0.1719	91.39	150	120	---	---	---	---
NS-20	Failed – vacuum lost	0.2060	0.1547	75.10	150	120	---	---	---	---
NS-21		0.2216	0.2190	98.83	150	120	-9.41	0.26	-79.09	1.71
NS-22		0.1974	0.1972	99.90	120	120	-9.36	0.24	-77.73	0.71
NS-23		0.1902	0.1892	99.47	120	120	-9.54	0.28	-77.56	0.08
NS-24		0.1966	0.1928	98.07	120	120	-9.92	0.17	-77.05	0.78
NS-25		0.1913	0.1461	76.37	40	0	-11.27	0.10	-93.80	1.08
NS-26		0.1931	0.1923	99.59	40	0	-9.34	0.07	-78.89	1.23
NS-27		0.1932	0.1304	67.49	40	0	-11.47	0.11	-93.48	1.08
NS-28	Sample holder open	0.1931	0.0882	45.68	40	0	-12.82	0.14	-104.25	1.11
NS-29		0.1834	0.1818	99.13	200	60	-9.68	0.51	-78.99	1.80
NS-30	Septum replaced	0.1799	0.0807	44.86	200	60	-9.46	0.07	-78.44	0.85
NS-31		0.2045	0.2046	100.05	200	60	-9.37	0.16	-79.37	1.44
NS-32		0.2101	0.2066	98.33	200	60	-9.08	0.12	-76.58	0.60

Table B.2.2. New Closed-system µVDE Tests with Lab Water (DDIW) on ~5g $CaCO_3$

Sample ID	Comments	Mass H_2O injected (g)	Mass H_2O recovered (g)	% Recovery	Target temp (ºC)	Hold Time	$\delta^{18}O$ (‰)	σ_{18O} (‰)	δD (‰)	σ_{D} (‰)
CC-NS-1		0.1970	0.1961	99.54	120	30	-10.17	0.00	-81.33	0.00
CC-NS-2		0.2195	0.2188	99.68	120	30	-9.13	0.28	-79.63	0.35
CC-NS-3		0.2296	0.2286	99.56	120	30	-9.48	0.03	-79.02	0.02
CC-NS-4	Septum replaced	0.1946	0.2128	109.35	120	60	---	---	---	---
CC-NS-5	Flagged in SCI software	0.2062	0.2197	106.55	120	60	---	---	---	---
CC-NS-6		0.1931	0.1920	99.43	120	60	-9.86	0.05	-80.94	0.48
CC-NS-7		0.1852	0.1864	100.65	120	120	-9.77	0.01	-79.12	1.16
CC-NS-8		0.1913	0.1924	100.58	120	120	-9.78	0.11	-79.63	0.43
CC-NS-9		0.1934	0.1939	100.26	120	120	-9.77	0.00	-81.72	0.00
CC-NS-10	Sample holder opened	0.1851	0.1144	61.80	150	30	---	---	---	---
CC-NS-11	Pieces of septum in vial	0.1976	0.2461	124.54	150	30	---	---	---	---
CC-NS-12		0.1846	0.1847	100.05	150	30	-9.98	0.15	-80.82	0.63
CC-NS-13		0.1974	0.1974	100.00	150	60	-10.11	0.05	-80.02	0.29
CC-NS-14		0.1902	0.1906	100.21	150	60	-10.31	0.22	-79.83	0.09
CC-NS-15		0.1795	0.1800	100.28	150	60	-10.26	0.17	-79.87	0.89
CC-NS-16		0.2021	0.2032	100.54	150	120	-9.84	0.12	-80.68	0.70
CC-NS-17		0.2184	0.2189	100.23	150	120	-9.20	0.07	-78.32	0.24
CC-NS-18		0.2131	0.2137	100.28	150	120	-10.02	0.11	-79.06	0.63

Table B.2.3. New Closed-system μVDE Tests with Lab Water (DDIW) on ~5g SiO_2

Sample ID	Comments	Mass H_2O injected (g)	Mass H_2O recovered (g)	% Recovery	Target temp (ºC)	Hold Time	$\delta^{18}O$ (‰)	σ_{18O} (‰)	δD (‰)	σ_D (‰)
SI-NS-1		0.1855	0.1857	100.11	120	30	-9.63	0.08	-78.35	0.11
SI-NS-2		0.1912	0.1914	100.10	120	30	-10.16	0.16	-79.81	0.37
SI-NS-3	Flagged in SCI software	0.1854	0.1855	100.05	120	30	---	---	---	---
SI-NS-4		0.1914	0.1882	98.33	120	60	-10.24	0.15	-79.96	0.50
SI-NS-5		0.1871	0.1874	100.16	120	60	-10.30	0.11	-79.77	1.14
SI-NS-6		0.1835	0.1840	100.27	120	60	-10.51	0.08	-80.66	0.72
SI-NS-7		0.1976	0.1981	100.25	120	120	-9.45	0.15	-77.58	0.64
SI-NS-8		0.1886	0.1891	100.27	120	120	-10.09	0.13	-78.88	0.85
SI-NS-9		0.2084	0.2086	100.10	120	120	-9.40	0.14	-76.71	0.56
SI-NS-10		0.1753	0.1763	100.57	150	30	-10.05	0.30	-80.13	1.06
SI-NS-11		0.1827	0.1832	100.27	150	30	-10.09	0.22	-80.28	1.05
SI-NS-12		0.1918	0.1923	100.26	150	30	-9.09	0.14	-78.03	0.27
SI-NS-13		0.182	0.1826	100.33	150	60	-9.58	0.18	-78.72	0.54
SI-NS-14		0.1865	0.1869	100.21	150	60	-10.25	0.23	-79.77	0.55
SI-NS-15		0.1848	0.1851	100.16	150	60	-9.59	0.08	-79.24	0.31
SI-NS-16		0.1969	0.1974	100.25	150	120	-10.06	0.32	-79.30	1.09
SI-NS-17		0.2068	0.2075	100.34	150	120	-10.31	0.16	-80.13	0.17
SI-NS-18		0.2242	0.2246	100.18	150	120	-10.25	0.20	-79.64	0.54

B.3PRELIMINARY DGR-8 DATA

Table B.3.1. Preliminary DGR-8 Porewater Results: δ^{18}O and δD by µVDE, and Ion Geochemistry by Crush & Leach

Depth (mLBGS)	δ^{18}O (‰)	σ_{18O} (‰)	δD (‰)	σ_D (‰)	Cl mmol/kgw	σ_{Cl}	SO4 mmol/kgw	σ_{SO4}	Ca mmol/kgw	σ_{Ca}	K mmol/kgw	σ_K	Mg mmol/kgw	σ_{Mg}	Na mmol/kgw	σ_{Na}
285.07	-7.37	0.17	-63.88	1.93	1962	913	6334	2356	4799	1842	232	154	749	466	1683	942
333.93	-8.44	---	-72.7	---	1944	624	997	475	830	406	63	22	239	80	1362	495
382.83	-6.58	0.54	-62.26	1.19	6639	214	24	5	163	122	334	63	755	155	4786	122
421.51	-1.44	0.49	-47.66	1.30	6260	50	4	0	1175	85	1063	223	327	31	2202	18
431.5	-1.69	0.50	-51.46	1.38	5904	143	28	47	783	84	988	95	316	73	1733	136
463.33	-1.42	0.21	-48.02	1.42	5893	79	6	1	635	38	933	265	314	54	2055	61
495.42	-2.64	0.32	-56.88	2.77	5558	156	163	61	1018	49	1645	137	347	35	2101	108
521.94	-2.64	0.22	-49.91	2.40	5528	114	62	20	769	20	1149	191	289	35	2018	45
530.81	-4.28	0.04	-56.79	1.73	5680	377	62	68	998	345	870	281	412	190	1991	470
571.68	-5.24	0.19	-64.80	1.36	3888	41	3	0	495	40	572	111	120	14	1281	55
612.82	-2.09	0.48	-50.45	2.05	5554	59	264	152	988	88	863	120	232	52	1915	62
626.22	-1.75	0.23	-54.34	0.76	5362	38	7	1	679	75	777	57	197	12	1711	105
634.64	-2.76	0.20	-61.15	1.04	5198	86	4	1	765	32	926	90	197	13	2369	62
655.63	-2.23	0.22	-50.06	2.35	4910	104	16	2	579	19	1175	103	189	16	2185	33
662.01	-4.03	0.20	-58.93	3.50	3464	60	169	9	245	7	1555	119	119	6	1936	17
670.8	-7.55	0.56	-61.97	3.90	4093	399	210	58	506	27	1792	695	219	12	1856	212
683.08	-5.81	0.30	-61.50	2.10	3476	512	177	162	508	137	1135	131	201	67	1518	275
689.68	-3.08	0.16	-53.82	2.61	5292	130	40	6	600	53	1023	72	239	14	2138	150
695.36	-3.95	0.24	-50.65	3.75	5639	615	175	73	650	125	2422	869	308	38	2632	399
707.56	-5.80	0.63	-65.60	0.85	5233	277	181	45	618	116	1420	24	239	32	2310	144
723.29	-4.67	0.82	-48.13	4.38	4631	128	56	9	549	26	1105	230	173	14	2148	101