Technical Report

Title: *Vacuum Distillation Experiments on DGR Core*

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Date: May 21, 2010

DGR Site Characterization Document
Intera Engineering Project 08-200

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1 Introduction

Intera Engineering Ltd. has been contracted by the Nuclear Waste Management Organization (NWMO) on behalf of Ontario Power Generation to implement the Geoscientific Site Characterization Plan (GSCP) for the Bruce nuclear site located on Lake Huron, Ontario. The purpose of this site characterization work is to assess the suitability of the Bruce site to construct a Deep Geologic Repository (DGR) to store low-level and intermediate-level radioactive waste. The GSCP was originally described for Phase 1 by Intera Engineering Ltd. (2006), which relates to the initial drilling and testing of boreholes DGR-1 and DGR-2. The GSCP was revised for Phase 2 work by Intera Engineering Ltd. (2008a), including drilling and testing of two additional boreholes DGR-3 and DGR-4.

As part of the GSCP, Intera Engineering Ltd. contracted with the University of Ottawa, to complete testing of rock core samples obtained from DGR boreholes to characterize the porewater chemistry. Preliminary experiments undertaken to evaluate various methods concluded that vacuum distillation at 150°C coupled by aqueous leaching using deionized water offered the most reliable approach for determination of the stable isotope content (^{18}O and D) and major ion geochemistry of pore fluids (TR-07-02, Intera Engineering Ltd., 2008b; TR-07-21 – Intera Engineering Ltd., 2010a).

This report contains the results of a new series of vacuum distillation experiments (VDE) that were designed and carried out by the University of Ottawa to more rigorously document effects of extraction temperature and extraction times on the porewater stable isotopes and major ion concentrations. The new series of experiments were undertaken using nine rock core samples from a range of rock types from DGR-4 in order to observe any analytical effects corresponding to lithological variability. Furthermore, an additional experiment was undertaken to demonstrate complete dehydration of porewater salts during vacuum distillation. Concerns have been expressed that the 150°C vacuum extraction protocol may not completely dehydrate the porewater salts, and in particular the calcium chloride porewater that is characteristic in these rocks.

Work described in this Technical Report was completed in accordance with Test Plan TP-08-10 – Laboratory Testing of DGR-3 & DGR-4 Cores for Pore Water Extraction and Analysis (Intera Engineering Ltd., 2008c), and following the requirements of the DGR Project Quality Plan (Intera Engineering Ltd., 2009).

1.1 Approach

The experimental method was designed to test the effects of extraction time and temperature on vacuum distillation for the different rock types. The protocol of 6-hours extraction time at 150°C was used as the standard protocol against which both temperature variation and time variation were tested. Cores were selected from the major rock types present in the DGR section, including dolostone, shale and limestone. In addition, a limestone bed and three adjacent samples of shale from above and below were sampled to observe whether tracers from close proximity would be affected by lithology. For the pure salt dehydration experiment, $CaCl_2 \cdot 2H_2O$ was selected for testing as this is the major divalent cation – chloride salt present in the porewaters (Intera Engineering, 2008c).

2 Experimental Procedure

2.1 Sample Selection

Samples were received by University of Ottawa from the Bruce nuclear site during the drilling of DGR-4, as 20 cm core samples preserved by the standard method of double sealing in polyethylene and aluminum foil sleeves that are evacuated following a N_2-flush. The following samples and corresponding lithologies (Table 1) were received in good condition. Cores were received and stored at 4°C prior to analysis.

Table 1 Sample List and Rock Type

Sample ID	*Rock Type*	*Sample ID*	*Rock Type*
DGR4-357.85	Dolostone	DGR4-550.95	Shale
DGR4-351.75	Dolostone	DGR4-669.18	Limestone
DGR4-550.32	Shale	DGR4-746.53	Limestone
DGR4-550.54	Limestone	DGR4-711.25	Limestone
DGR4-550.75	Shale		

2.2 Experimental Protocol

The experimental method was designed to test the effects of extraction time and temperature on vacuum distillation for the different rock types. The protocol of 6-hours extraction time at 150°C was used as the standard protocol against which both temperature variation and time variation were tested. Extraction temperatures of 50, 100, 150 and 200°C were tested using an extraction time of 6 hours, followed by testing extraction times of 2, 4, 6 and 8 hours at 150°C, giving a total of 8 experiments for each core. Each core sample was crushed and sieved to collect 2.88~4.69 mm diameter size fraction. This size fraction was then mixed and split into 16 aliquots, with approximately 40 g in each. This provided aliquots for the eight different experiments with each run in duplicate.

Crushed and sieved material was stored in air tight Isojars with labels for 4 day duration of the series of extractions. Each ~ 40 g sample aliquot was placed in a 50 mL pre-weighed Erlenmeyer flask, and mounted onto the heater side of the individual vapour-transfer line with a reciprocal pre-weighed exetainer with septum cap attached by needle to the water vapour-recovery side of the line. A total of eight individual extraction lines were connected to a vacuum manifold.

Two temperature experiments were performed each day, with two samples duplicates in each. Prior to heating, all flasks with samples were frozen with liquid nitrogen then individually evacuated to 1.3 Pa (10 mTorr). The exetainer and porewater vapour transfer line were also evacuated during this step. Once this vacuum was reached, the transfer line was isolated from the vacuum pump, the liquid nitrogen bath was removed from the crushed-rock flasks and a liquid nitrogen bath was placed over the bottom 3 cm of the exetainers. Two insulated resistance ovens fitted to enclose four sample flasks were then put into place. The rock sample temperatures were slowly raised to the experimental temperature over the period of one hour and maintained by periodic checks over the extraction period. During this time, water vapour released from the rock diffused through the evacuated transfer line and was trapped in the exetainer.

At the completion of the extraction period, the crushed rock flasks were closed from the transfer line, the heater was removed and the rock samples allowed to cool. The exetainers were removed from the line and allowed to warm to room temperature. When both the rock flasks and exetainers were at room temperature, they were weighed to determine both water loss and water gain as well as dry-rock mass. These measurements were used to calculate gravimetric water loss which is normalized to the percent of volumetric water content using an average mineral density of 2.7 g/cm^3 (Koroleva et al., 2009) and using a density of 1 g/ cm^3 for water according to the following equation.

$$\%\ \text{volumetric water content, } wc_{\text{vol}} = \frac{m_{\text{wet rock}} - m_{\text{dry rock}}}{m_{\text{dry rock}} / 2.7} \cdot 100$$

2.3 Geochemical and Isotope Analysis

Once cooled and weighed, rock sample flasks were emptied into a pre-weighed falcon tube by rinsing from the flask with approximately 20 mL deionized water for solute leaching. The flask was rinsed again 3 times into the falcon tube with about 10 mL deionized water to ensure recovery of all salts originally present in the crushed rock sample flask. The falcon tube was then re-weighed to determine the total mass of deionized leach water. The crushed rock samples were rinsed with deionized water and then left to leach for an 8 week period with periodic shaking. The leach water was then removed with a syringe, filtered and analyzed for major anions ions (Cl^- and SO_4^{2-}) by routine liquid chromatography (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).

The porewaters recovered by vacuum distillation were analyzed for stable isotopes by gas-source continuous-flow stable isotope mass spectrometry on CO_2 and H_2 gases equilibrated with the sample water. A ~10 mg Cu strip was added to each exetainer to remove any S-containing compounds that may have condensed from the heated rock. Charcoal pieces were added to each porewater exetainer to remove any condensed hydrocarbons. The exetainers containing the porewater were then flushed and filled with mixture of 5% 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, the same exetainers with porewater aliquots were analyzed for δD. H_2 gas as a 5% mixture in He was flushed through the exetainer with the porewater and a platinum bead catalyst and left to equilibrate with the porewater prior to mass spectrometer analysis (Coplen et al., 1991). Three laboratory standard waters are run sequentially with samples for both $\delta^{18}O$ and δD for calibration of the measured ratios to the international reference water VSMOW (Vienna Standard Mean Ocean Water). Results are expressed as the parts per thousand (permil) differences between the isotope ratio, R ($^{18}O/^{16}O$ or $D/^1H$) in the sample and the reference standard:

$$\delta^2H \text{ or } \delta^{18}O = [R_{SAMPLE}/R_{VSMOW}) - 1] \times 1000$$

2.3.1 Salt Dehydration Experiment

The potential for retention of water during the 150°C vacuum distillation experiments was evaluated with a salt dehydration experiment. The experiment was designed to test gravimetrically whether all the hydration waters of calcium chloride dihydrate [$CaCl_2{\cdot}2H_2O$] were released during vacuum distillation. If a significant amount of water was retained by these salts at the experimental temperature of 150°C, then fractionation between this reservoir and the released porewater could affect the measured isotopic value of the porewaters.

The vacuum distillation procedure for all extractions was carried out under desiccating conditions. The desiccating conditions were created by freezing the water extracted from core samples with liquid nitrogen, which reduces the water vapour pressure in the vacuum. For the experiment, a new container of reagent grade $CaCl_2{\cdot}2H_2O$ (99% pure, Fisher Scientific Co., Pittsburgh, PA) was used. Three amounts of salt were weighed into dried and pre-weighed vacuum distillation flasks, and then left under vacuum for 6-hours at 150°C. The final weights were then taken and the difference used to determine water loss and to calculate the initial hydration number of the salt.

3 Results

Results of all experiments are tabulated and plotted in the figures of Appendix A. For each rock core, figures are prepared for gravimetric water loss (as volumetric water content in %), $\delta^{18}O$, δD, Na and Cl. For the isotopic values of water and Na and Cl concentrations, the range (average value ± standard deviation) for the four runs under optimized conditions of 150°C and 6 hours extraction are also shown by the solid lines.

In each of two samples (357.85 and 711.25) one outlier value for $\delta^{18}O$ in the standard temperature/time extractions was not included in the calculation of mean and standard deviation (σ).

3.1 Water Loss

Plots of gravimetric water loss results at 150°C for all rock types suggest that 75% to over 90% the water is extracted within the first two hours. Differences between some sample aliquots for the carbonate rocks, such as for duplicates (i.e. two samples extracted under same time/temperature conditions) or samples for which increased extraction time released less water, are considered to reflect heterogeneities in these materials, and not artefacts of the extraction. Sample heterogeneity is not observed in the shale samples, for which more consistent and replicable water contents are measured for all extraction times. This perhaps reflects their higher water content and a more consistent pore geometry.

Progressive increases in gravimetric water content with temperature are observed. Values for extractions at 150°C and 200°C are similar and within the range of experimental uncertainty for most samples. Clearly, for all rock types, extraction at temperatures below 150°C, even with 6 hours of extraction time, is insufficient.

3.2 Stable Isotopes

Data for $\delta^{18}O$ and δD are plotted in the figures for all samples found in Appendix A. The error bars given with the $\delta^{18}O$ and δD data points are the analytical uncertainties associated with the isotope analysis of water by continuous flow isotope-ratio mass spectrometry (±0.2‰ for $\delta^{18}O$ and ±2‰ for δD). For the standard conditions of 150°C and 6-hours, of the 20 paired extractions, 16 vary for ^{18}O within 2σ (σ = 0.2‰) with the balance differing by less than 2‰. For D, duplicates differ by less than 2σ (σ = 2‰) for all but four samples for non-standard conditions, differences between replicates are variable and for over half of the extractions exceed 2σ. This is attributed to the non-standard conditions of these extractions. Routine analysis of quadruplicate splits for each core sample allowed outlier values to be identified and discounted.

For most samples, no significant difference in the mean isotope values occurs between 6 hour and 8 hour extractions although for some samples (DGR4-351.75, DGR4-357.85, DGR4-550.54, DGR4-669.18, DGR4-711.25) greater variation at the 8 hour extraction occurs. Therefore, no improvement in reproducibility is observed with this longer extraction time. A six hour extraction period appears to be close to optimum for these rock types.

It is apparent that incomplete extraction at 50°C and 100°C produces a bias towards ^{18}O isotope depletion (e.g. DGR4-550.95). However, comparison of the 150°C and 200°C extractions shows that measurements for 200°C extractions are on average approximately 0.3‰ more enriched than the extractions at 150°C. By contrast, the D data do not show this systematic trend towards enrichment in the 200°C extractions. For these runs, the δD measurements at 150°C and 200°C are for most samples the same as those measured at 150°C and have excellent reproducibility between duplicates. If the slight $\delta^{18}O$ enrichment was attributed to a minor additional porewater recovery between 150°C and 200°C, this should be accompanied by a similar enrichment in δD. The cause of this bias towards ^{18}O enrichment at 200°C, however, is unlikely related to incomplete extraction at 150°C as $\delta^{18}O$ values were found to be stable for extraction periods of up to 8 hours at this temperature.

A potential $\delta^{18}O$ enrichment at 200°C due to residual salt hydration can be ruled out on the basis of the additional experiment to examine salt dehydration in $CaCl_2$ (Table 2). Table 2 shows the water lost during the course of the 2 hour heating as well as the anticipated loss. The anticipated loss was calculated as the difference in the gram formula weight for the hydrated calcium chloride ($CaCl_2{\cdot}2H_2O$ =147.08 g/mole) and the dehydrated gram formula weight ($CaCl_2$= 111.08 g/mol). Based on the difference in gram formula weights, the anticipated water loss should be approximately 25% of the initial weight of $CaCl_2{\cdot}2H_2O$. The actual water loss measured during the 2 hour heating time at 150 °C was within 5% of the anticipated water loss. This shows complete dehydration of calcium chloride salt following vacuum distillation of pure $CaCl_2 \cdot 2H_2O$ at 150°C. Therefore, salt dehydration is not the cause of the $\delta^{18}O$ increase at 200°C.

Table 2 Salt Dehydration Experiments, Conducted at 150°C

Analyte	***Initial Weight (g)***	***Weight after 2 hr heating (g)***	***Actual H_2O loss (g)***	***Anticipated H_2O loss (g)***	***Calculated hydration number***	***Percent Difference of Actual and Anticipated Water Loss***
Deionized H_2O	1.0060	-0.0002	1.0062			
$CaCl_2 \cdot 2H_2O$	1.3133	0.9879	0.3254	0.321	2.03	1.4%
$CaCl_2 \cdot 2H_2O$	2.3402	1.7606	0.5796	0.573	2.03	1.1%
$CaCl_2 \cdot 2H_2O$	4.6330	3.5466	1.0864	1.134	1.89	-4.9%

Release of smectite hydration waters could also contribute enriched ^{18}O at the high temperature, although smectites were found to be trace components of the clay minerals and in only a few samples. Further, this would also affect the δD measurements, although with a depletion bias due to the opposite sign of the fractionation factor.

A plausible source of the $\delta^{18}O$ enrichment may be oxygen exchange with the carbonate rocks during the 200°C extractions. Such exchange is common for groundwaters in carbonate reservoirs at geothermal temperatures (Craig, 1963; 1966) and imparts an enrichment on the water due to the high heavy oxygen content of carbonate rock ($\delta^{18}O \sim 30‰$ VSMOW) and the reduced fractionation ($\varepsilon^{18}O_{CaCO_3} < 30‰$).

The gravimetric water loss graphs show that despite some heterogeneity between subsamples, stable weights are attained at 150°C within the six hour extraction period; although at 100°C lower weights suggest incomplete extraction. This likely demonstrates release of open porewaters near 100°C. Higher temperatures are required to extract the hydration waters associated with $CaCl_2$ although it was shown in the salt dehydration experiment that $CaCl_2$ is fully dehydrated at 150°C. The highly consistent results, with low error between extractions at different salt masses, demonstrate unambiguously that this hydroscopic salt is anhydrous at our standard experimental temperature.

Thus, at 150°C, it can be concluded that both free porewater and salt hydration waters in the pores are extracted. An extended extraction period does not capture more water at this temperature. Vacuum distillation at 200°C is the standard protocol for removal of smectite hydration waters (Sheppard and Gilg, 1996; O'Neil, 1985). These are not part of the mobile porewater reservoir and so extraction at this high temperature is inappropriate. Accordingly, it seems that extraction at 150°C is sufficiently high to assure sampling the salt hydration waters, yet minimizes dehydration of hydrous clay minerals that may be present.

3.3 Chloride

The third component of the vacuum distillation experiments to be tested was the solute extraction for reconstruction of porewater solute concentration. The mass of rinse water is determined gravimetrically such that subsequent solute concentrations can be converted to total mass leached from the rock mass. Solute mass is then normalized to a porewater concentration using the gravimetric water loss for that individual rock aliquot. Given the high heterogeneity in water content, even for replicate samples of the same core, normalizing to a subsample-specific water content is essential.

Results for Cl extracted following these vacuum distillation experiments show that low temperature extractions are enriched in Cl but decrease with increasing temperatures to converge on a constant value at 150°C to 200°C (Appendix A). This is consistent with the gravimetric porewater content results showing low water yields at low temperatures, and indicates that leaching is efficient in extracting all the Cl, but when normalized to low yields, produces enriched porewater values.

The average standard deviation for Cl concentration in four replicates (at 150°C and 6 hours) of the fourteen sample runs, as a percentage of the average concentration for Cl concentration in the four replicates is 4.5% (varying from 1.9 to 7.9%). As this is less than the 5% error limit normally associated with an acceptable geochemical analysis it can be concluded that solute leaching, following vacuum distillation at 150°C, produces reproducible porewater solute concentration data.

3.4 Comparison of Immediately Adjacent Carbonate and Shale Porewaters

An objective of this work is to demonstrate whether the depletion trend for $\delta^{18}O$ and Cl observed in the Ordovician carbonates relative to the upper Ordovician shales represent in-situ porewater depletion trends or are an experimental artefact related to extraction of porewaters and solutes from these limestones which have water contents that are much lower than the shales. To address this objective, carbonate and three shale samples collected for the vacuum distillation experiments were selected within a 1 m interval of the Georgian Bay shales that included a carbonate hard bed. These closely-spaced samples were presumed to have very similar porewater isotopes and chemistry. Three samples from the Georgian Bay shale were collected at depths of 550.32, 550.75 and 550.95 mBGS. One sample of a Georgian Bay carbonate was collected at the depth of 550.54 mBGS. The results for the extractions undertaken at 150°C and 6 hours are presented in Figure 1 (see Appendix for all original data). The values plotted are the mean of the four extractions at each depth (150°C and 6 hours) and the abscissa error bars represent the standard deviation (σ) for the four measurements. Vertical bars represent the interval sampled by each core.

The gravimetric water loss profile shows that this carbonate unit has 3.1% volumetric water content while the shales average 7.5% volumetric water content. A minor enrichment of some 0.5 ‰ exists for the $\delta^{18}O$ of the carbonate porewater relative to that of the shale porewaters. A corresponding enrichment of about 5‰ is observed for the measured δD values. If the reduced water content of the carbonate unit had imparted an analytical artefact on porewater extraction, the measured isotope values would be lighter. This suggests that a systematic bias towards depleted isotope values in lower water content rocks does not exist with this 150°C vacuum distillation method.

The Cl results in Figure 1 (Cl is normalized to porewater content) show there is an enrichment in Cl of up to 1000 mmol/kgw or about 15% in the porewater of the limestone bed relative to those in the adjacent shale beds. Correcting the shale porewaters for the reduced anion accessible porosity of 0.85 (as modeled by PHREEQC assuming halite saturation; Intera Engineering Ltd., 2010b.), the shale and limestone Cl concentrations become aligned. However, a similar increase in Na is evident for the limestone porewaters compared to the shale porewaters, suggesting that rather than anion exclusion, an additional reservoir of water in the shales may be contributing to this relative dilution. Therefore, there appears to be no systematic depletion of Cl and Na in carbonate porewaters as an artefact of the vacuum distillation method. The stable isotope data suggest that, if present, the additional shale water component is not clay structural waters, as this component is considered to be enriched in ^{18}O and depleted in D relative to free porewater, and not released below about 200°C (Lawrence and Taylor, 1971; O'Neil and Kharaka, 1974). More likely this is adsorbed water, which exchanges rapidly with and reflects the isotopic composition of the bulk porewater (Savin and Epstein, 1970).

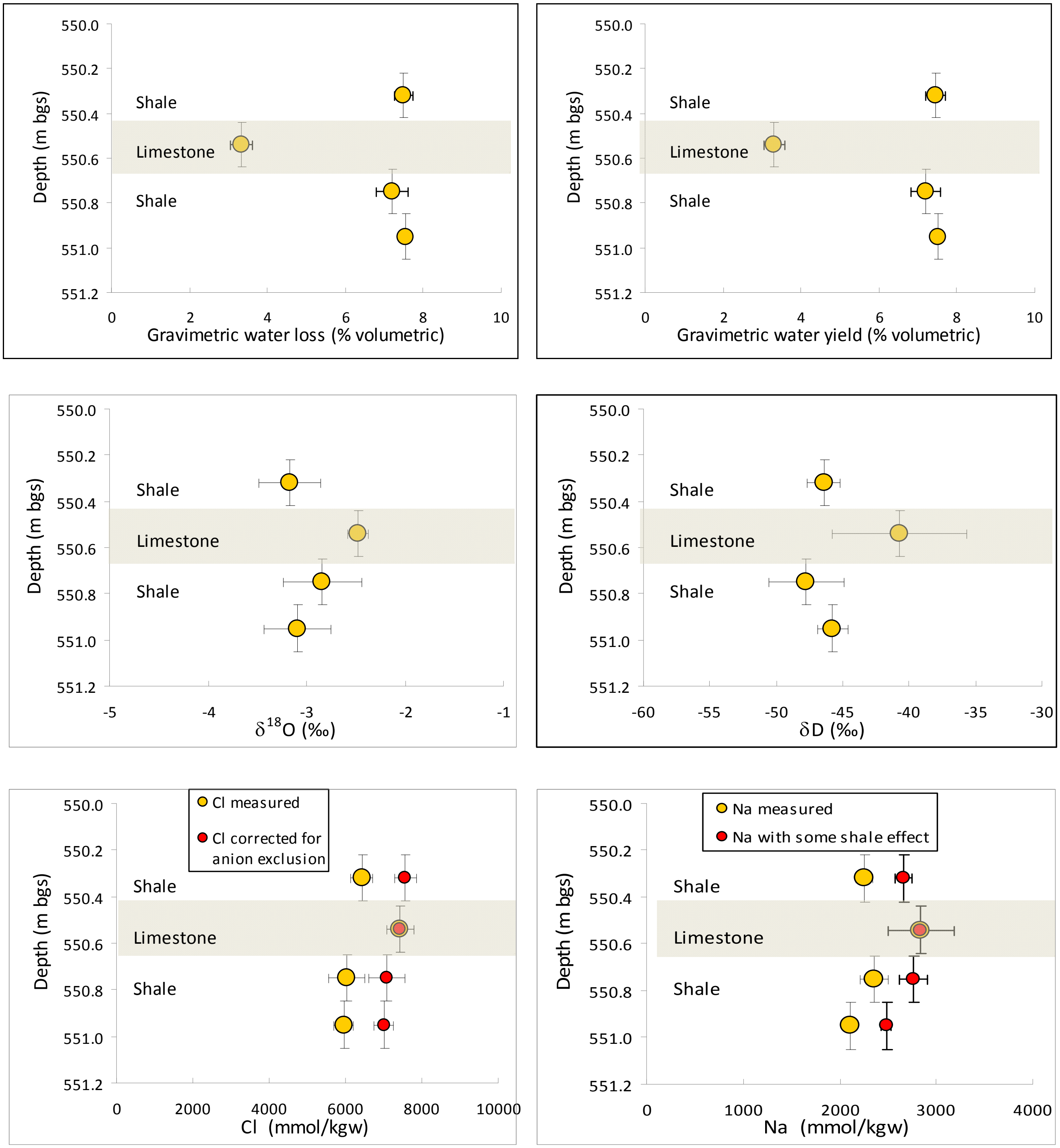

Figure 1 Comparison of gravimetric water loss, water yield, $\delta^{18}O$, δD, Cl and Na in adjacent core samples of carbonate and shale. Horizontal error bars represent standard deviation of the four replicates analyzed at 150°C and 6-hour extraction time

It is unlikely that any significant change in the chemistry or stable isotopes of the connected porewaters would occur over the less than 1 m section comprising the shale and carbonate bed. However, the carbonate porewater is enriched by about 0.5‰ in $\delta^{18}O$ and by about 5‰ in δD. Whether this is a minor systematic difference between carbonate and shale porewaters or a characteristic of this interval is the object of on-going experimental work.

4 Conclusions

The characterization of high salinity porewaters in the low porosity and low permeability rocks of the Lower Ordovician strata at the Bruce site for isotope and geochemical analysis is an analytical challenge. These and earlier tests undertaken on a variety of rock types from the site suggest that vacuum distillation at 150°C with a 6 hour extraction period provides reproducible and representative measurements of gravimetric water loss, $\delta^{18}O$, δD, and solutes. The experimental uncertainty for ^{18}O and D, based on the replicates in these tests, is in most cases close or within to the analytical uncertainty of continuous-flow mass spectrometry (±0.2‰ and ±2‰). This is consistent with the findings of Altinier et al. (2007). The potential for outliers and erroneous data is mitigated by the routine analysis of samples in quadruplicate.

Vacuum distillation at 150°C, followed by leaching and normalization to subsample-specific water content, provides reproducible and interpretable chloride concentration data. The average of the standard deviations calculated for the four replicates of fourteen samples (at 150°C and 6 hours) is 4.5% (varying from 1.9 to 7.9%). The advantage of normalizing to water contents from the same sample aliquot used for the leaching is essential given that water content can vary substantially even within the same core sample.

Extraction at temperatures of 100°C and 50°C resulted in incomplete extraction of the porewaters and imparts a fractionation on porewater isotopes. It also provides solute concentrations above expected values due to the normalization of leachate results to water content values that are too low.

Experiments to dehydrate pure hydrous calcium chloride salt ($CaCl_2{\cdot}2H_2O$) showed that no hydration waters remain following vacuum distillation at 150°C for 6 hours. Accordingly, measured ^{18}O and D values of water extracted at this temperature will be representative of in-situ Porewaters, unaffected by fractionation with salt hydration waters. Indeed, vacuum distillation at 150°C for 6 hours was shown to extract salt hydration waters in addition to free porewaters. Extended extraction times did not result in systematic increases in porewater recovery or in $\delta^{18}O$ enrichments, suggesting that complete extraction of free porewater and salt hydration water takes place in 6 hours. Extraction at 200°C seems to impart a systematic increase in $\delta^{18}O$ although no δD enrichment is observed. This slight ^{18}O enrichment at 200°C may reflect ^{18}O-exchange with the host carbonate minerals, as observed in geothermal waters from carbonate reservoirs. Accordingly it is concluded that extraction at temperatures above 150°C is not recommended.

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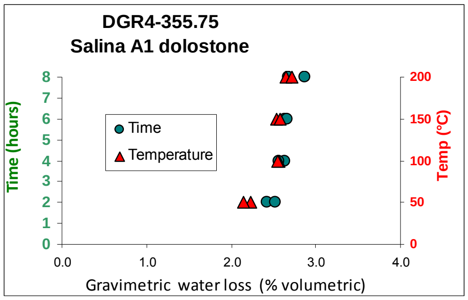
APPENDIX A

Experimental Results


DGR4-355.75
Salina A1 dolostone
Time (hours)
Temp (°C)
Time
Temperature
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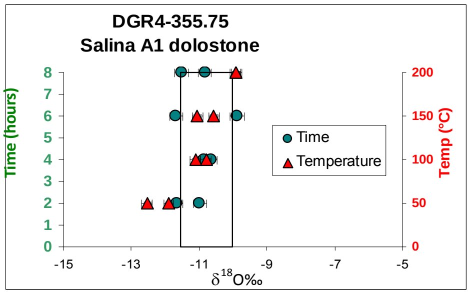
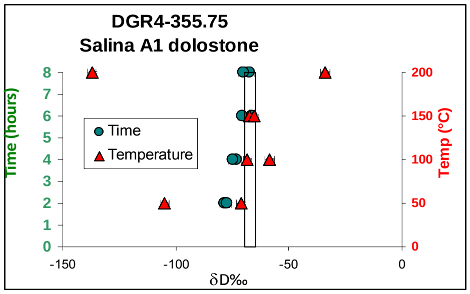
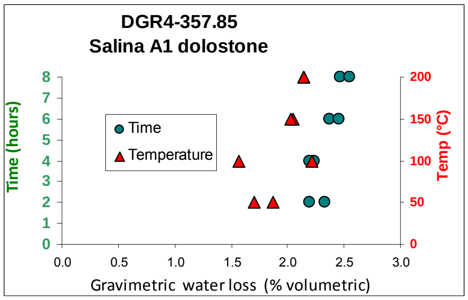
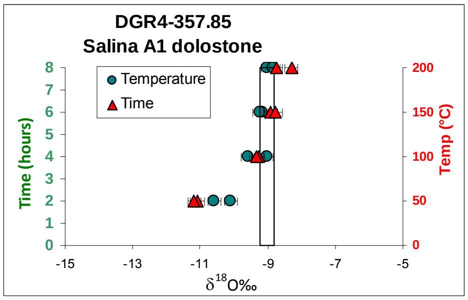
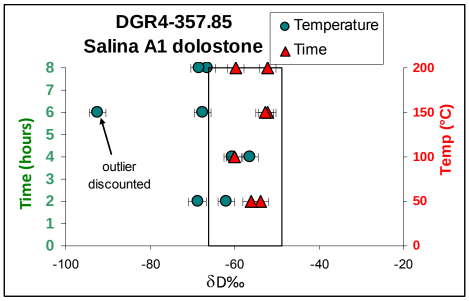
0 50 100 150 200
0.0 1.0 2.0 3.0 4.0
Gravimetric water loss (% volumetric)

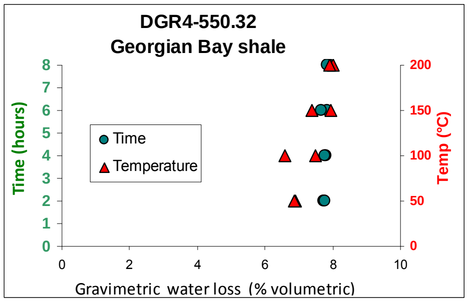

DGR4-355.75
Salina A1 dolostone
Time (hours)
Temp (°C)
Time
Temperature
0 1 2 3 4 5 6 7 8
0 50 100 150 200
-15 -13 -11 -9 -7 -5
δ18O‰

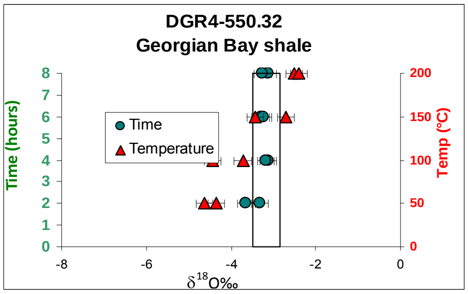

DGR4-355.75
Salina A1 dolostone
Time (hours)
Temp (°C)
Time
Temperature
0 1 2 3 4 5 6 7 8
0 50 100 150 200
-150 -100 -50 0
δD‰

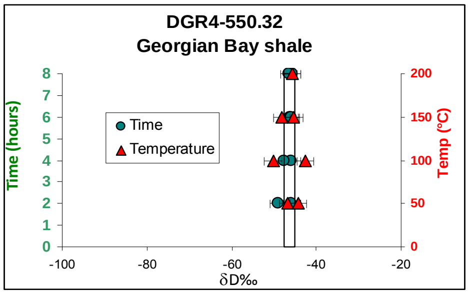

DGR4-357.85
Salina A1 dolostone
Time (hours)
Temp (°C)
Time
Temperature
0 1 2 3 4 5 6 7 8
0 50 100 150 200
0.0 0.5 1.0 1.5 2.0 2.5 3.0
Gravimetric water loss (% volumetric)

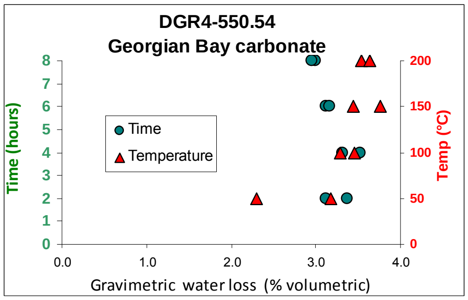

DGR4-357.85
Salina A1 dolostone
Time (hours)
Temp (°C)
Temperature
Time
0 1 2 3 4 5 6 7 8
0 50 100 150 200
-15 -13 -11 -9 -7 -5
δ18O‰

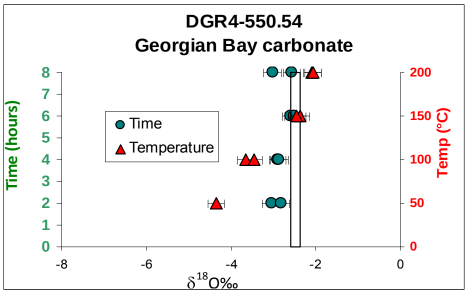

DGR4-357.85
Salina A1 dolostone
Temperature
Time
Time (hours)
Temp (°C)
outlier discounted
0 1 2 3 4 5 6 7 8
0 50 100 150 200
-100 -80 -60 -40 -20
δD‰

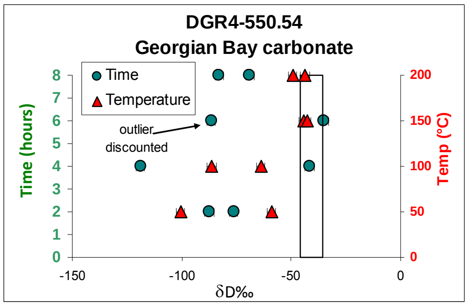

DGR4-550.32
Georgian Bay shale
Time (hours)
Temp (°C)
Time
Temperature
0 1 2 3 4 5 6 7 8
0 50 100 150 200
0 2 4 6 8 10
Gravimetric water loss (% volumetric)

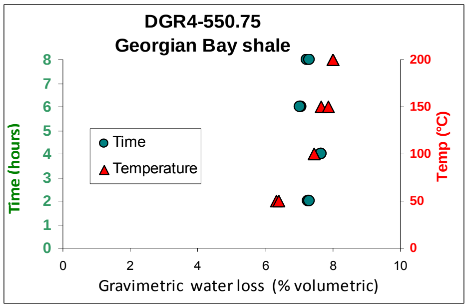

DGR4-550.32
Georgian Bay shale
Time (hours)
Temp (°C)
Time
Temperature
0 1 2 3 4 5 6 7 8
0 50 100 150 200
-8 -6 -4 -2 0
δ18O‰

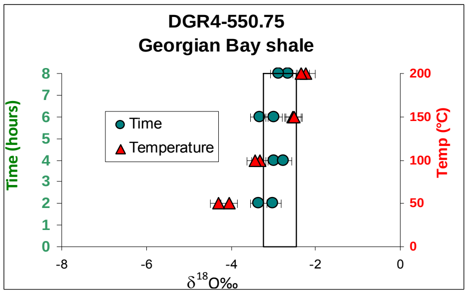

DGR4-550.32
Georgian Bay shale
Time (hours)
Temp (°C)
Time
Temperature
0 1 2 3 4 5 6 7 8
0 50 100 150 200
-100 -80 -60 -40 -20
δD‰

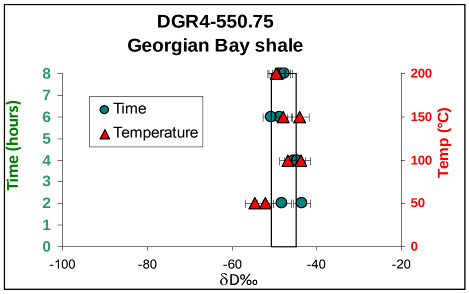

DGR4-550.54
Georgian Bay carbonate
Time (hours)
Temp (°C)
Time
Temperature
0 1 2 3 4 5 6 7 8
0 50 100 150 200
0.0 1.0 2.0 3.0 4.0
Gravimetric water loss (% volumetric)

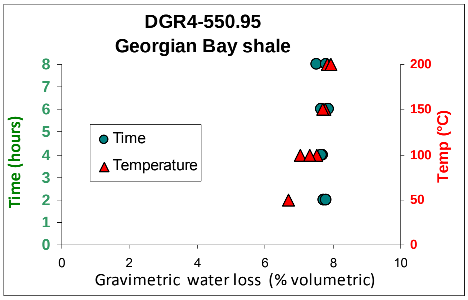

DGR4-550.54
Georgian Bay carbonate
Time (hours)
Temp (°C)
Time
Temperature
0 1 2 3 4 5 6 7 8
0 50 100 150 200
-8 -6 -4 -2 0
δ18O‰

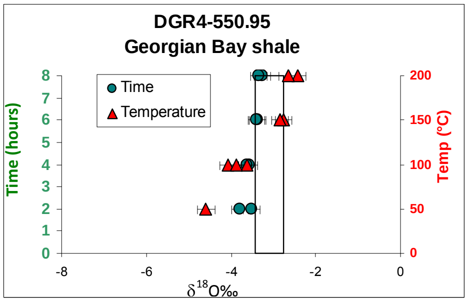

DGR4-550.54
Georgian Bay carbonate
Time
Temperature
outlier discounted
Time (hours)
Temp (°C)
0 1 2 3 4 5 6 7 8
0 50 100 150 200
-150 -100 -50 0
δD‰

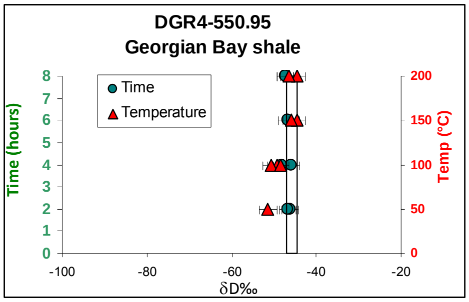

DGR4-550.75
Georgian Bay shale
Time (hours)
Temp (°C)
Time
Temperature
0 1 2 3 4 5 6 7 8
0 50 100 150 200
0 2 4 6 8 10
Gravimetric water loss (% volumetric)

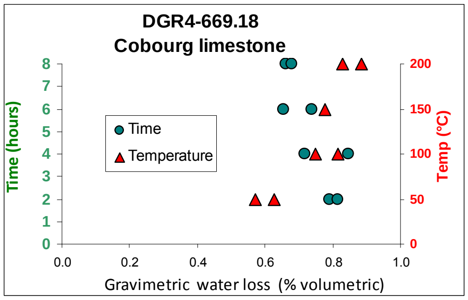

DGR4-550.75
Georgian Bay shale
Time (hours)
Temp (°C)
Time
Temperature
0 1 2 3 4 5 6 7 8
0 50 100 150 200
-8 -6 -4 -2 0
δ18O‰

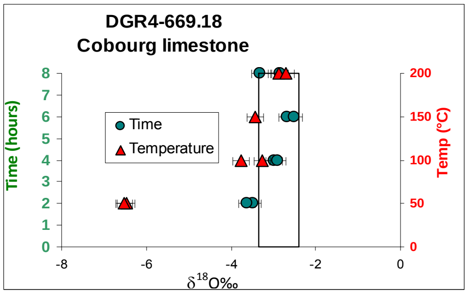

DGR4-550.75
Georgian Bay shale
Time (hours)
Temp (°C)
Time
Temperature
0 1 2 3 4 5 6 7 8
0 50 100 150 200
-100 -80 -60 -40 -20
δD‰

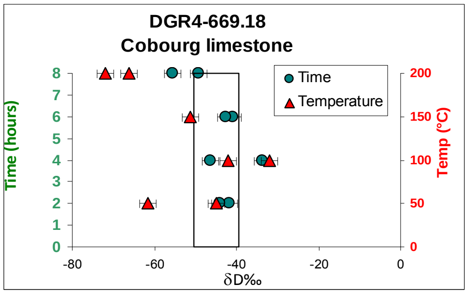


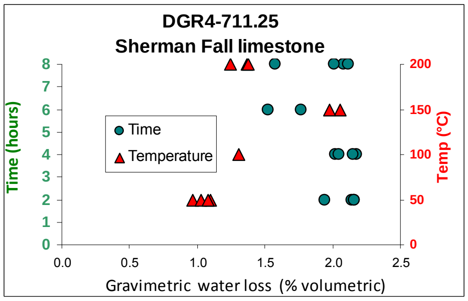


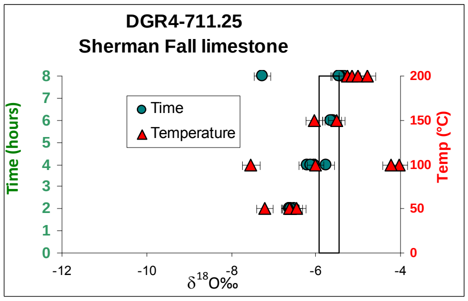


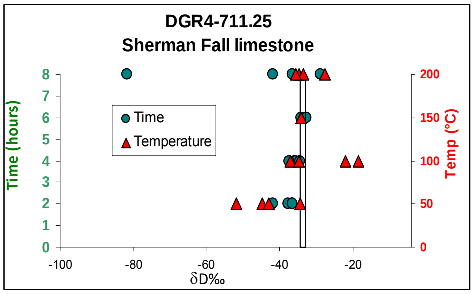


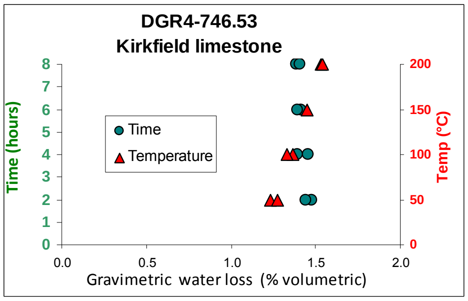


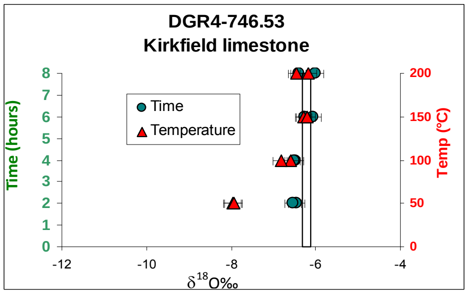


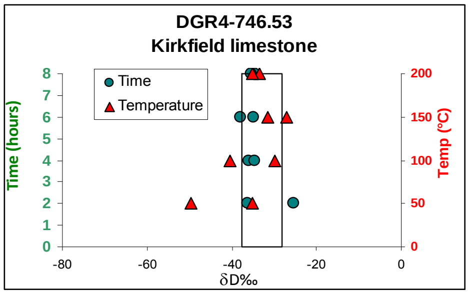












Note: Outlined box shows the range (average value ± standard error) for the four extractions at 150°C and 6 hours.

Table A1. Water content, δ^{18}O, δD and Cl results.

Sample ID	ID	Extraction		Wet rock weight	Dry rock weight	Water loss	Water gain	Grav. water loss	Volum. water content	δ^{18}O	δD	Cl
		T (°C)	Time	(g)	(g)	(g)	(g)	(g/g)	%	‰	‰	mmol/ kgw
DGR4-357.85-1	A	150	6	54.1634	53.6920	0.4714	0.4583	0.0088	2.37	-9.15	-67.62	3937
DGR4-357.85-2	B	150	6	59.1175	58.5851	0.5324	0.5162	0.0091	2.45	-9.24	-92.51	3735
DGR4-357.85-5	E	150	8	57.0053	56.4893	0.5160	0.4965	0.0091	2.47	-9.01	-66.37	3800
DGR4-357.85-6	F	150	8	56.3075	55.7812	0.5263	0.4137	0.0094	2.55	-8.85	-68.4	3821
DGR4-357.85-1	I	150	2	45.5641	45.1968	0.3673	0.3550	0.0081	2.19	-10.58	-68.81	4084
DGR4-357.85-2	J	150	2	44.3817	44.0013	0.3804	0.3656	0.0086	2.33	-10.09	-62.03	4007
DGR4-357.85-5	M	150	4	42.8531	42.5007	0.3524	0.3522	0.0083	2.24	-9.03	-56.46	4003
DGR4-357.85-6	N	150	4	43.4704	43.1198	0.3506	0.3384	0.0081	2.20	-9.59	-60.46	3821
DGR4-357.85-1	Q	50	6	35.6447	35.4207	0.2240	0.2140	0.0063	1.71	-11.09	-53.82	5062
DGR4-357.85-2	R	50	6	37.0298	36.7753	0.2545	0.2452	0.0069	1.87	-11.18	-56.14	4643
DGR4-357.85-5	U	100	6	37.3821	37.1664	0.2157	0.0078	0.0058	1.57	-9.28	failed	failed
DGR4-357.85-6	V	100	6	32.8933	32.6258	0.2675	0.2538	0.0082	2.21	-9.34	-59.96	3913
DGR4-357.85-1	Y	150	6	29.4176	29.1957	0.2219	0.2118	0.0076	2.05	-8.92	-52.28	3971
DGR4-357.85-2	Z	150	6	30.7468	30.5181	0.2287	0.2159	0.0075	2.02	-8.78	-52.83	3858
DGR4-357.85-5	AC	200	6	43.7489	43.4037	0.3452	0.3187	0.0080	2.15	-8.3	-59.63	3889
DGR4-357.85-6	AD	200	6	43.0387	42.7002	0.3385	0.3160	0.0079	2.14	-8.75	-52.16	3823
DGR4-351.75-3	C	150	6	53.3442	52.8282	0.5160	0.4944	0.0098	2.64	-9.87	-66.22	3485
DGR4-351.75-4	D	150	6	54.1719	53.6437	0.5282	0.5021	0.0098	2.66	-11.68	-70.37	3442
DGR4-351.75-7	G	150	8	52.3705	51.8559	0.5146	0.4927	0.0099	2.68	-10.83	-67.43	3556
DGR4-351.75-8	H	150	8	53.6642	53.1002	0.5640	0.5329	0.0106	2.87	-11.51	-70.23	3569
DGR4-351.75-3	K	150	4	48.5255	48.0567	0.4688	0.4526	0.0098	2.63	-10.84	-73.03	3559
DGR4-351.75-4	L	150	4	47.4660	47.0183	0.4477	0.4256	0.0095	2.57	-10.66	-74.78	3524
DGR4-351.75-7	O	150	2	42.7701	42.3885	0.3816	0.3544	0.0090	2.43	-11.67	-78.47	3949
DGR4-351.75-8	P	150	2	46.8592	46.4255	0.4337	0.4152	0.0093	2.52	-10.98	-77.11	3633
DGR4-351.75-3	S	50	6	36.6097	36.3095	0.3002	0.2936	0.0083	2.23	-11.9	-71.27	4324
DGR4-351.75-4	T	50	6	39.0291	38.7214	0.3077	0.2998	0.0079	2.15	-12.54	-104.87	4155
DGR4-351.75-7	W	100	6	31.5294	31.2332	0.2962	0.2810	0.0095	2.56	-11.11	-58.51	3830
DGR4-351.75-8	X	100	6	39.0925	38.7272	0.3653	0.3396	0.0094	2.55	-10.8	-68.24	3714
DGR4-351.75-3	AA	150	6	36.8672	36.5237	0.3435	0.3233	0.0094	2.54	-10.56	-67.24	3652
DGR4-351.75-4	AB	150	6	32.0583	31.7550	0.3033	0.2776	0.0096	2.58	-11.05	-65.12	3651
DGR4-351.75-7	AE	200	6	43.9828	43.5551	0.4277	0.3989	0.0098	2.65	-9.93	-33.9	3645
DGR4-351.75-8	AF	200	6	42.7729	42.3456	0.4273	0.3889	0.0101	2.72	-9.9	-137.12	3489
DGR4-550.54-3	AI	150	6	54.3517	53.7310	0.6207	0.6239	0.0116	3.12	-2.31	-34.9	7632
DGR4-550.54-4	AJ	150	6	50.8757	50.2853	0.5904	0.5910	0.0117	3.17	-2.52	-86.49	7807
DGR4-550.54-7	AM	150	8	51.7388	51.1698	0.5690	0.5649	0.0111	3.00	-3.02	-68.84	7530
DGR4-550.54-8	AN	150	8	49.9252	49.3849	0.5403	0.5344	0.0109	2.95	-2.56	-82.88	7426
DGR4-550.54-3	AQ	150	2	48.4311	47.8778	0.5533	0.5585	0.0116	3.12	-3.05	-76.22	7447
DGR4-550.54-4	AR	150	2	49.4949	48.8851	0.6098	0.6132	0.0125	3.37	-2.82	-87.36	6939
DGR4-550.54-7	AU	150	4	51.9784	51.3487	0.6297	0.6305	0.0123	3.31	-2.89	-118.82	7007
DGR4-550.54-8	AV	150	4	52.0865	51.4158	0.6707	0.6718	0.0130	3.52	-2.81	-41.51	7414
DGR4-550.54-3	AY	50	6	48.0792	47.6732	0.4060	0.2567	0.0085	2.30	-9.54	-100.54	10351
DGR4-550.54-4	AZ	50	6	46.0375	45.5021	0.5354	0.5292	0.0118	3.18	-4.34	-58.98	8015
DGR4-550.54-7	AAC	100	6	47.9238	47.3479	0.5759	0.5746	0.0122	3.28	-3.65	-63.92	7523
DGR4-550.54-8	AAD	100	6	46.7180	46.1272	0.5908	0.5862	0.0128	3.46	-3.45	-86.28	7411
DGR4-550.54-3	AAG	150	6	64.0483	63.2432	0.8051	0.7977	0.0127	3.44	-2.2	-44.36	6964
DGR4-550.54-4	AAH	150	6	58.8488	58.0397	0.8091	0.8001	0.0139	3.76	-2.22	-42.86	7352
DGR4-550.54-7	AAK	200	6	59.3284	58.5592	0.7692	0.7569	0.0131	3.55	-1.94	-49.31	6512

Sample ID	ID	Extraction		Wet rock weight	Dry rock weight	Water loss	Water gain	Grav. water loss	Volum. water content	δ^{18}O	δD	Cl
		T (°C)	Time	(g)	(g)	(g)	(g)	(g/g)	%	‰	‰	mmol/kgw
DGR4-550.54-8	AAL	200	6	59.9904	59.1935	0.7969	0.7867	0.0135	3.63	-1.92	-43.78	7437
DGR4-550.75-1	AG	150	6	45.3986	44.2424	1.1562	1.1539	0.0261	7.06	-2.8	-48.74	5357
DGR4-550.75-2	AH	150	6	48.0318	46.8114	1.2204	1.2233	0.0261	7.04	-2.73	-50.63	6390
DGR4-550.75-5	AK	150	8	44.2544	43.0974	1.1570	1.1509	0.0268	7.25	-2.58	-48.3	6369
DGR4-550.75-6	AL	150	8	44.0683	42.9085	1.1598	1.1553	0.0270	7.30	-2.74	-47.62	6425
DGR4-550.75-1	AO	150	2	37.5839	36.5971	0.9868	0.9913	0.0270	7.28	-3.19	-48.02	6378
DGR4-550.75-2	AP	150	2	38.1073	37.1036	1.0037	1.0069	0.0271	7.30	-3.12	-43.4	6323
DGR4-550.75-5	AS	150	4	38.0705	37.0190	1.0515	1.0543	0.0284	7.67	-2.9	-45.5	6590
DGR4-550.75-6	AT	150	4	37.1830	36.1577	1.0253	1.0271	0.0284	7.66	-2.92	-44.6	6291
DGR4-550.75-1	AW	50	6	36.4484	35.6145	0.8339	0.8234	0.0234	6.32	-4.11	-52.07	7318
DGR4-550.75-2	AX	50	6	35.4093	34.5904	0.8189	0.8123	0.0237	6.39	-4.25	-54.69	7317
DGR4-550.75-5	AAA	100	6	34.2997	33.3793	0.9204	0.9183	0.0276	7.44	-3.32	-46.66	6241
DGR4-550.75-6	AAB	100	6	36.8876	35.8957	0.9919	0.9909	0.0276	7.46	-3.38	-43.6	6168
DGR4-550.75-1	AAE	150	6	27.6962	26.9335	0.7627	0.7601	0.0283	7.65	-2.55	-43.88	6329
DGR4-550.75-2	AAF	150	6	36.9904	35.9412	1.0492	1.0439	0.0292	7.88	-2.55	-47.77	6037
DGR4-550.75-5	AAI	200	6	42.9465	41.7105	1.2360	1.2261	0.0296	8.00	-2.21	-49.34	6308
DGR4-550.75-6	AAJ	200	6	41.8545	40.6512	1.2033	1.1938	0.0296	7.99	-2.25	-49.47	6248
DGR4-550.32-1	AAM	150	6	38.8467	37.7521	1.0946	1.0879	0.0290	7.83	-3.02	-46.28	6183
DGR4-550.32-2	AAN	150	6	39.3737	38.2869	1.0868	1.0819	0.0284	7.66	-3.1	-46.04	6348
DGR4-550.32-5	AAQ	150	8	36.5016	35.4619	1.0397	1.0306	0.0293	7.92	-3.08	-45.64	6367
DGR4-550.32-6	AAR	150	8	42.4152	41.2180	1.1972	1.1878	0.0290	7.84	-3.14	-46.41	6278
DGR4-550.32-1	AAU	150	2	39.6051	38.4999	1.1052	1.1042	0.0287	7.75	-3.55	-45.83	6429
DGR4-550.32-2	AAV	150	2	38.2363	37.1673	1.0690	1.0697	0.0288	7.77	-3.54	-49.05	6432
DGR4-550.32-5	AAY	150	4	35.2837	34.2903	0.9934	0.9956	0.0290	7.82	-3.11	-45.83	6177
DGR4-550.32-6	AAZ	150	4	39.9508	38.8320	1.1188	1.1218	0.0288	7.78	-3.12	-47.71	6312
DGR4-550.32-1	AAAC	100	6	40.8533	39.8818	0.9715	0.9741	0.0244	6.58	-4.40	-50.2	7458
DGR4-550.32-2	AAAD	50	6	37.1459	36.2207	0.9252	0.9251	0.0255	6.90	-4.67	-46.63	7327
DGR4-550.32-4	AAAF	50	6	37.7217	36.7858	0.9359	0.9346	0.0254	6.87	-4.42	-44.3	6382
DGR4-550.32-5	AAAG	100	6	35.6051	34.6438	0.9613	0.9595	0.0277	7.49	-3.71	-42.52	6130
DGR4-550.32-1	AAAK	150	6	47.4846	46.2174	1.2672	1.2538	0.0274	7.40	-3.57	-48.17	6854
DGR4-550.32-2	AAAL	150	6	50.8439	49.3892	1.4547	1.4515	0.0295	7.95	-2.65	-45.25	6366
DGR4-550.32-5	AAAO	200	6	49.6098	48.1791	1.4307	1.4395	0.0297	8.02	-2.50	Failed	6225
DGR4-550.32-6	AAAP	200	6	47.0741	45.7346	1.3395	1.3463	0.0293	7.91	-2.34	-45.6	6278
DGR4-550.95-3	AAO	150	6	40.4298	39.2844	1.1454	1.1443	0.0292	7.87	-3.30	-46.87	5970
DGR4-550.95-4	AAP	150	6	36.8822	35.8632	1.0190	1.0122	0.0284	7.67	-3.38	failed	5619
DGR4-550.95-7	AAS	150	8	36.3839	35.3975	0.9864	0.9795	0.0279	7.52	-3.19	-47.28	6033
DGR4-550.95-8	AAT	150	8	39.9804	38.8577	1.1227	1.1120	0.0289	7.80	-3.29	-47.34	6113
DGR4-550.95-3	AAW	150	2	38.2340	37.1683	1.0657	1.0688	0.0287	7.74	-3.79	-46.27	6136
DGR4-550.95-4	AAX	150	2	39.7472	38.6315	1.1157	1.1148	0.0289	7.80	-3.51	-46.72	5724
DGR4-550.95-7	AAAA	150	4	40.0194	38.9093	1.1101	1.1123	0.0285	7.70	-3.56	-45.89	6592
DGR4-550.95-8	AAAB	150	4	35.9502	34.9584	0.9918	1.0037	0.0284	7.66	-3.53	-48.11	6075
DGR4-550.95-3	AAAE	50	6	37.3710	36.4671	0.9039	0.9068	0.0248	6.69	-4.58	-51.4	7122
DGR4-550.95-6	AAAH	100	6	34.7363	33.7962	0.9401	0.9366	0.0278	7.51	-3.61	-49.38	6262
DGR4-550.95-7	AAAI	100	6	32.8186	31.9834	0.8352	0.8196	0.0261	7.05	-4.00	-50.66	6380
DGR4-550.95-8	AAAJ	100	6	36.3219	35.3632	0.9587	0.9571	0.0271	7.32	-3.86	-48.39	6371
DGR4-550.95-3	AAAM	150	6	36.0531	35.0446	1.0085	1.0084	0.0288	7.77	-2.76	-44.54	6225
DGR4-550.95-4	AAAN	150	6	35.9238	34.9289	0.9949	0.9910	0.0285	7.69	-2.78	-45.85	6031
DGR4-550.95-7	AAAQ	200	6	39.7152	38.5936	1.1216	1.1281	0.0291	7.85	-2.46	-44.56	6209
DGR4-550.95-8	AAAR	200	6	39.0203	37.9057	1.1146	1.1229	0.0294	7.94	-2.62	-46.45	6216

Sample ID	ID	Extraction		Wet rock weight	Dry rock weight	Water loss	Water gain	Grav. water loss	Volum. water content	$\delta^{18}O$	δD	Cl
		T (°C)	Time	(g)	(g)	(g)	(g)	(g/g)	%	‰	‰	mmol/kgw
DGR4-669.18-1	A1	150	6	30.7074	30.6330	0.0744	0.0696	0.0024	0.66	-2.68	-40.97	6330
DGR4-669.18-2	A2	150	6	35.8657	35.7677	0.0980	0.0915	0.0027	0.74	-2.52	-42.72	6200
DGR4-669.18-5	A5	150	8	37.3027	37.2116	0.0911	0.0901	0.0024	0.66	-3.31	-55.66	6255
DGR4-669.18-6	A6	150	8	33.7424	33.6579	0.0845	0.0862	0.0025	0.68	-2.85	-49.3	6254
DGR4-669.18-1	A9	150	2	28.1687	28.0865	0.0822	0.0788	0.0029	0.79	-3.49	-41.75	6297
DGR4-669.18-2	AB1	150	2	32.0234	31.9271	0.0963	0.0875	0.0030	0.81	-3.62	-43.9	6254
DGR4-669.18-5	AB4	150	4	28.1302	28.0422	0.0880	0.0868	0.0031	0.85	-2.98	-46.29	6161
DGR4-669.18-6	AB5	150	4	30.2862	30.2058	0.0804	0.0736	0.0027	0.72	-2.9	-33.75	6478
DGR4-669.18-1	AB8	50	6	36.8637	36.7785	0.0852	0.0801	0.0023	0.63	-6.48	-44.84	7497
DGR4-669.18-2	AB9	50	6	35.0645	34.9904	0.0741	0.0432	0.0021	0.57	-6.52	-61.52	9076
DGR4-669.18-5	AC3	100	6	36.7955	36.6848	0.1107	0.1075	0.0030	0.81	-3.76	-31.82	6475
DGR4-669.18-6	AC4	100	6	32.8283	32.7374	0.0909	0.0856	0.0028	0.75	-3.27	-41.98	6244
DGR4-669.18-1	AC7		6	33.7772	33.6829	0.0943	0.0198	0.0028	0.76	failed	failed	6780
DGR4-669.18-2	AC8	150	6	29.8093	29.7239	0.0854	0.0809	0.0029	0.78	-3.42	-51.26	6093
DGR4-669.18-5	AD2	200	6	41.4651	41.3298	0.1353	0.1335	0.0033	0.88	-2.87	-66.3	6263
DGR4-669.18-6	AD3	200	6	39.5002	39.3792	0.1210	0.1202	0.0031	0.83	-2.7	-71.84	7367
DGR4-746.53-3	A3	150	6	49.6455	49.3872	0.2583	0.2548	0.0052	1.41	-6.07	-38.04	4737
DGR4-746.53-4	A4	150	6	46.7606	46.5208	0.2398	0.2370	0.0052	1.39	-6.25	-34.92	4838
DGR4-746.53-7	A7	150	8	49.2598	49.0087	0.2511	0.2509	0.0051	1.38	-6.01	-34.65	5072
DGR4-746.53-8	A8	150	8	47.4439	47.1983	0.2456	0.2472	0.0052	1.40	-6.39	-35.38	5042
DGR4-746.53-3	AB2	150	2	43.4853	43.2482	0.2371	0.2345	0.0055	1.48	-6.45	-25.45	4775
DGR4-746.53-4	AB3	150	2	42.6222	42.3952	0.2270	0.2202	0.0054	1.45	-6.54	-36.16	4642
DGR4-746.53-7	AB6	150	4	45.4985	45.2654	0.2331	0.2282	0.0051	1.39	-6.48	-35.91	4955
DGR4-746.53-8	AB7	150	4	44.9249	44.6841	0.2408	0.2400	0.0054	1.46	-6.52	-34.49	4919
DGR4-746.53-3	AC1	50	6	47.8723	47.6548	0.2175	0.2145	0.0046	1.23	-7.97	-35.26	5809
DGR4-746.53-4	AC2	50	6	48.2232	47.9968	0.2264	0.2208	0.0047	1.27	-7.94	-49.48	5424
DGR4-746.53-7	AC5	100	6	48.5801	48.3351	0.2450	0.2435	0.0051	1.37	-6.58	-29.8	4484
DGR4-746.53-8	AC6	100	6	49.2154	48.9746	0.2408	0.2369	0.0049	1.33	-6.81	-40.29	5121
DGR4-746.53-3	AC9	150	6	51.2536	50.9731	0.2805	0.2802	0.0055	1.49	-6.29	-31.42	4630
DGR4-746.53-4	AD1	150	6	53.6917	53.4048	0.2869	0.2834	0.0054	1.45	-6.21	-27.02	4545
DGR4-746.53-7	AD4	200	6	58.0845	57.7564	0.3281	0.3230	0.0057	1.53	-6.17	-33.54	4815
DGR4-746.53-8	AD5	200	6	52.1915	51.8961	0.2954	0.2929	0.0057	1.54	-6.44	-35.05	4622
DGR4-711.25-1	AD6	150	2	41.7107	41.4127	0.2980	0.2879	0.0072	1.94	-6.52	-36.44	5108
DGR4-711.25-2	AD7	150	2	37.7691	37.4720	0.2971	0.2897	0.0079	2.14	-6.61	-37.82	5004
DGR4-711.25-3	AD8	150	2	40.9652	40.6400	0.3252	0.3188	0.0080	2.16	-6.62	-41.79	4920
DGR4-711.25-4	AD9	150	2	36.1477	35.8613	0.2864	0.2810	0.0080	2.16	-6.59	-36.36	5035
DGR4-711.25-5	AE1	150	4	37.3075	37.0091	0.2984	0.2848	0.0081	2.18	-6.19	-35.8	4979
DGR4-711.25-6	AE2	150	4	40.5835	40.2823	0.3012	0.2837	0.0075	2.02	-6.03	-35.75	5015
DGR4-711.25-7	AE3	150	4	36.9784	36.6998	0.2786	0.2647	0.0076	2.05	-5.75	-34.3	5104
DGR4-711.25-8	AE4	150	4	40.7182	40.3958	0.3224	0.3097	0.0080	2.15	-6.12	-37.4	4932
DGR4-711.25-1	AE5	150	6	41.1748	40.9072	0.2676	0.2666	0.0065	1.77	-5.58	-34.16	4544
DGR4-711.25-2	AE6	150	6	39.9030	39.6794	0.2236	0.2189	0.0056	1.52	-5.64	-32.57	4637
DGR4-711.25-5	AE9	150	8	39.9816	39.6751	0.3065	0.2873	0.0077	2.09	-5.33	-81.67	4764
DGR4-711.25-6	AF1	150	8	38.1543	37.8716	0.2827	0.2726	0.0075	2.02	-5.43	-36.62	4672
DGR4-711.25-7	AF2	150	8	38.7390	38.5147	0.2243	0.2108	0.0058	1.57	-5.45	-28.86	5256
DGR4-711.25-8	AF3	150	8	37.6431	37.3500	0.2931	0.2601	0.0078	2.12	-7.27	-41.82	5237
DGR4-711.25-3	AE7	150	6	37.8694	37.5837	0.2857	0.2859	0.0076	2.05	-5.5	-34.04	5286
DGR4-711.25-4	AE8	150	6	36.0123	35.7508	0.2615	0.2600	0.0073	1.97	-6.03	-34.15	4755
DGR4-711.25-1	AF4	200	6	40.5005	40.3142	0.1863	0.1879	0.0046	1.25	-5.25	-34.82	5061

Sample ID	ID	Extraction		Wet rock weight	Dry rock weight	Water loss	Water gain	Grav. water loss	Volum. water content	$\delta^{18}O$	δD	Cl
		T (°C)	Time	(g)	(g)	(g)	(g)	(g/g)	%	‰	‰	mmol/ kgw
DGR4-711.25-2	AF5	200	6	35.0969	34.9196	0.1773	0.1743	0.0051	1.37	-5.14	-33.48	4981
DGR4-711.25-3	AF6	200	6	54.8734	54.5977	0.2757	0.2730	0.0050	1.36	-4.99	-35.62	5104
DGR4-711.25-4	AF7	200	6	35.6440	35.4636	0.1804	0.1719	0.0051	1.37	-4.78	-27.77	4946
DGR4-711.25-5	AF8	100	6	35.9973	35.8544	0.1429	0.1355	0.0040	1.08	-4.04	-18.39	6745
DGR4-711.25-6	AF9	100	6	32.5682	32.4117	0.1565	0.1477	0.0048	1.30	-4.22	-22.05	6236
DGR4-711.25-7	AG1	100	6	52.3838	52.1869	0.1969	0.1763	0.0038	1.02	-7.53	-37.1	6531
DGR4-711.25-8	AG2	100	6	55.4524	55.2300	0.2224	0.2155	0.0040	1.09	-6.00	-34.69	6036
DGR4-711.25-9	AG3	50	6	50.9367	50.7554	0.1813	0.1824	0.0036	0.96	-7.21	-44.9	7204
DGR4-711.25-10	AG4	50	6	52.6006	52.3884	0.2122	0.2128	0.0041	1.09	-6.59	-51.9	6142
DGR4-711.25-11	AG5	50	6	51.6650	51.4688	0.1962	0.1985	0.0038	1.03	-6.61	-42.9	6553
DGR4-711.25-12	AG6	50	6	56.2560	56.0311	0.2249	0.2223	0.0040	1.08	-6.44	-34.5	5649

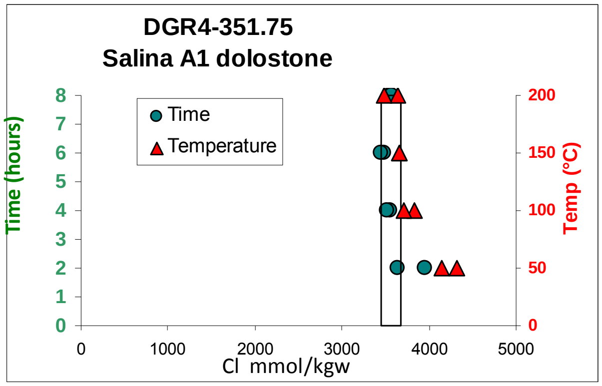
Table A2. Major ion concentrations

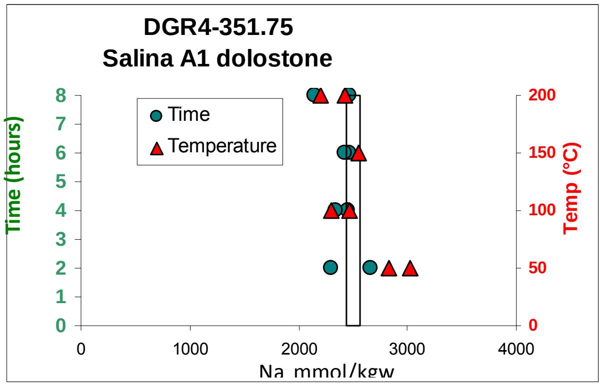
sample	ID	T°C	Time	Vol. % water content	Cl	SO4	B	Na	K	Ca	Mg	Sr
					mmol/ kgw	mmol/ kgw	mmol/ kgw	mmol/ kgw	mmol /kgw	mmol/ kgw	mmol/ kgw	mmol/ kgw
DGR4-357.85-1	A	150	6	2.8	3937	963	14.7	1668	107	1357	686	13.4
DGR4-357.85-2	B	150	6	3.0	3735	781	14.0	1706	108	1180	648	15.6
DGR4-357.85-5	E	150	8	3.8	3800	827	13.7	1642	104	1228	638	12.7
DGR4-357.85-6	F	150	8	21.4	3821	776	13.9	1650	108	1173	653	15.1
DGR4-357.85-1	I	150	2	3.3	4084	1169	15.8	1652	113	1535	693	18.9
DGR4-357.85-2	J	150	2	3.9	4007	968	15.8	1719	119	1419	669	27.6
DGR4-357.85-5	M	150	4	0.1	4003	1067	14.9	1646	113	1448	684	17.2
DGR4-357.85-6	N	150	4	3.5	3821	1254	17.7	1752	122	1629	716	25.0
DGR4-357.85-1	Q	50	6	4.5	5062	1953	17.6	2093	137	2363	907	16.7
DGR4-357.85-2	R	50	6	3.7	4643	1495	17.3	1985	130	1938	794	18.0
DGR4-357.85-5	U	100	6	96.4		2238	23.2	2237	169	2646	986	34.2
DGR4-357.85-6	V	100	6	5.1	3913	1356	18.4	1741	130	1700	746	34.5
DGR4-357.85-1	Y	150	6	4.6	3971	1925	21.3	1765	134	2258	801	35.1
DGR4-357.85-2	Z	150	6	5.6	3858	1560	18.0	1731	123	1872	794	21.5
DGR4-357.85-5	AC	200	6	7.7	3889	1237	17.2	1639	109	1563	726	12.2
DGR4-357.85-6	AD	200	6	6.6	3823	1311	17.0	1645	109	1622	728	11.4
DGR4-351.75-3	C	150	6	4.2	3485	1175	13.4	2460	63	1181	630	8.9
DGR4-351.75-4	D	150	6	4.9	3442	1257	14.6	2431	73	1350	634	14.9
DGR4-351.75-7	G	150	8	4.3	3556	1278	13.7	2462	62	1288	628	10.7
DGR4-351.75-8	H	150	8	5.5	3569	1217	13.1	2150	59	1227	570	10.7
DGR4-351.75-3	K	150	4	3.5	3559	1313	15.3	2453	65	1328	651	12.7
DGR4-351.75-4	L	150	4	4.9	3524	902	15.3	2341	63	1013	600	21.0
DGR4-351.75-7	O	150	2	7.1	3949	1048	15.5	2658	70	1083	664	19.6
DGR4-351.75-8	P	150	2	4.3	3633	1195	14.5	2303	61	1182	632	17.7
DGR4-351.75-3	S	50	6	2.2	4324	1102	17.2	3030	79	1205	709	25.0
DGR4-351.75-4	T	50	6	2.6	4155	1399	13.9	2824	70	1431	717	12.8
DGR4-351.75-7	W	100	6	5.1	3830	1197	15.1	2467	65	1206	668	19.5
DGR4-351.75-8	X	100	6	7.0	3714	1286	13.6	2305	59	1235	642	13.0
DGR4-351.75-3	AA	150	6	5.9	3652	1266	15.3	2555	73	1246	699	13.9

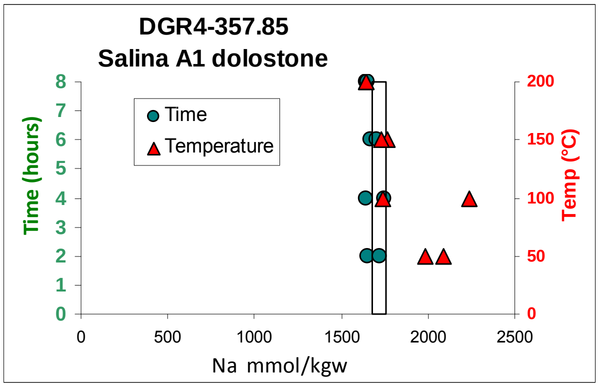
DGR4-351.75-4	AB	150	6	8.5	3651	1496	18.5	2545	71	1444	738	22.1
DGR4-351.75-7	AE	200	6	6.7	3645	1210	15.7	2430	64	1230	643	13.3
DGR4-351.75-8	AF	200	6	9.0	3489	1291	13.8	2207	58	1267	625	8.8
DGR4-550.54-3	AI	150	6	-0.5	7632	339	12.4	3226	413	1713	506	22.2
DGR4-550.54-4	AJ	150	6	-0.1	7807	387	13.7	2984	399	1668	506	22.1
DGR4-550.54-7	AM	150	8	0.7	7530	349	14.0	3260	449	1680	534	23.7
DGR4-550.54-8	AN	150	8	1.1	7426	409	14.7	3207	454	1723	534	25.3
DGR4-550.54-3	AQ	150	2	-0.9	7447	260	12.0	2834	402	1562	524	20.1
DGR4-550.54-4	AR	150	2	-0.6	6939	321	12.9	2557	384	1535	486	21.4
DGR4-550.54-7	AU	150	4	-0.1	7007	248	15.3	3005	458	1549	500	20.3
DGR4-550.54-8	AV	150	4	-0.2	7414	246	13.1	3099	463	1546	514	20.8
DGR4-550.54-3	AY	50	6	36.8	10351	584	19.9	3919	597	2475	706	30.6
DGR4-550.54-4	AZ	50	6	1.2	8015	370	15.1	2862	444	1770	534	21.6
DGR4-550.54-7	AAC	100	6	0.2	7523	553	13.2	3219	477	1926	520	23.2
DGR4-550.54-8	AAD	100	6	0.8	7411	246	13.6	3085	471	1562	529	21.2
DGR4-550.54-3	AAG	150	6	0.9	6964	303	13.9	2740	413	1585	493	21.1
DGR4-550.54-4	AAH	150	6	1.1	7352	278	11.8	2420	378	1525	444	19.1
DGR4-550.54-7	AAK	200	6	1.6	6512	438	14.6	2846	460	1698	464	21.3
DGR4-550.54-8	AAL	200	6	1.3	7437	327	15.0	3359	456	1594	466	20.8
DGR4-550.75-1	AG	150	6	0.2	5357	67	6.8	2141	360	1231	341	14.9
DGR4-550.75-2	AH	150	6	-0.2	6390	72	7.5	2465	403	1389	377	17.0
DGR4-550.75-5	AK	150	8	0.5	6369	78	7.1	2337	385	1361	367	16.3
DGR4-550.75-6	AL	150	8	0.4	6425	75	6.6	2112	351	1308	350	15.0
DGR4-550.75-1	AO	150	2	-0.5	6378	100	9.8	2379	431	1353	393	16.8
DGR4-550.75-2	AP	150	2	-0.3	6323	112	9.5	2467	437	1388	400	16.9
DGR4-550.75-5	AS	150	4	-0.3	6590	97	8.7	2402	419	1377	384	16.5
DGR4-550.75-6	AT	150	4	-0.2	6291	89	8.8	2204	393	1309	367	15.8
DGR4-550.75-1	AW	50	6	1.3	7318	140	10.9	2852	517	1632	476	19.6
DGR4-550.75-2	AX	50	6	0.8	7317	145	10.8	2877	510	1605	469	19.7
DGR4-550.75-5	AAA	100	6	0.2	6241	106	8.3	2324	413	1359	391	16.1
DGR4-550.75-6	AAB	100	6	0.1	6168	109	7.8	2240	397	1331	380	15.6
DGR4-550.75-1	AAE	150	6	0.3	6329	101	12.0	2368	448	1293	386	16.4
DGR4-550.75-2	AAF	150	6	0.5	6037	90	9.6	2430	436	1312	375	16.5
DGR4-550.75-5	AAI	200	6	0.8	6308	87	9.7	2118	381	1286	346	14.9
DGR4-550.75-6	AAJ	200	6	0.8	6248	88	8.6	1982	353	1250	329	14.0
DGR4-550.32-1	AAM	150	6	0.6	6183	71	7.2	2250	369	1396	336	16.5
DGR4-550.32-2	AAN	150	6	0.5	6348	63	7.1	2176	364	1357	344	16.1
DGR4-550.32-5	AAQ	150	8	0.9	6367	62	6.7	2088	352	1341	337	15.5
DGR4-550.32-6	AAR	150	8	0.8	6278	57	6.6	2106	350	1358	344	15.7
DGR4-550.32-1	AAU	150	2	0.1	6429	58	6.5	2263	366	1392	347	16.6
DGR4-550.32-2	AAV	150	2	-0.1	6432	71	6.9	2199	361	1396	347	16.3
DGR4-550.32-5	AAY	150	4	-0.2	6177	70	8.5	2275	386	1415	353	16.7
DGR4-550.32-6	AAZ	150	4	-0.3	6312	77	7.7	2128	365	1356	348	15.9
DGR4-550.32-1	AAAC	100	6	-0.3	7458	86	6.8	2676	441	1669	446	19.6
DGR4-550.32-2	AAAD	50	6	0.0	7327	110	6.1	2606	434	1661	425	19.5
DGR4-550.32-4	AAAF	50	6	0.1	6382	96	8.5	2436	420	1559	421	18.2
DGR4-550.32-5	AAAG	100	6	0.2	6130	82	7.3	2164	371	1419	370	16.3
DGR4-550.32-1	AAAK	150	6	1.1	6854	70	7.2	2382	401	1502	374	17.7
DGR4-550.32-2	AAAL	150	6	0.2	6366	62	6.4	2235	373	1412	350	16.7
DGR4-550.32-5	AAAO	200	6	-0.6	6225	56	8.3	2082	360	1359	325	15.6
DGR4-550.32-6	AAAP	200	6	-0.5	6278	55	7.8	2193	379	1367	334	16.3

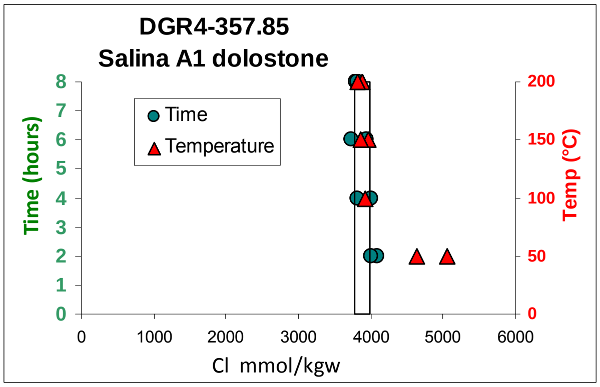
DGR4-550.95-3	AAO	150	6	0.1	5970	60	6.9	2064	354	1244	324	14.7
DGR4-550.95-4	AAP	150	6	0.7	5619	63	6.9	2082	357	1228	318	14.4
DGR4-550.95-7	AAS	150	8	0.7	6033	70	6.9	2241	384	1306	345	15.4
DGR4-550.95-8	AAT	150	8	1.0	6113	59	5.9	2001	344	1248	322	14.1
DGR4-550.95-3	AAW	150	2	-0.3	6136	76	7.6	2063	359	1275	336	14.8
DGR4-550.95-4	AAX	150	2	0.1	5724	74	7.7	2217	385	1313	343	15.2
DGR4-550.95-7	AAAA	150	4	-0.2	6592	85	6.8	2294	393	1371	359	15.9
DGR4-550.95-8	AAAB	150	4	-1.2	6075	93	8.5	2005	383	1241	341	14.3
DGR4-550.95-3	AAAE	50	6	-0.3	7122	102	6.9	2516	429	1516	413	17.7
DGR4-550.95-6	AAAH	100	6	0.4	6262	80	8.3	2259	401	1310	360	15.9
DGR4-550.95-7	AAAI	100	6	1.9	6380	112	8.9	2354	428	1397	390	16.7
DGR4-550.95-8	AAAJ	100	6	0.2	6371	92	8.2	2268	400	1343	367	16.0
DGR4-550.95-3	AAAM	150	6	0.0	6225	87	9.8	2180	400	1282	342	15.4
DGR4-550.95-4	AAAN	150	6	0.4	6031	89	9.3	2110	394	1283	343	14.9
DGR4-550.95-7	AAAQ	200	6	-0.6	6209	65	8.1	2159	379	1285	328	14.9
DGR4-550.95-8	AAAR	200	6	-0.7	6216	66	8.1	2006	356	1246	312	14.0
DGR4-669.18-1	A1	150	6	6.5	6330	7824	30.3	2750	546	7780	954	39.1
DGR4-669.18-2	A2	150	6	6.6	6200	6648	28.4	2656	511	6716	903	35.1
DGR4-669.18-5	A5	150	8	1.1	6255	5818	28.5	2715	500	6087	913	34.2
DGR4-669.18-6	A6	150	8	-2.0	6254	7469	29.7	2685	516	7382	906	37.5
DGR4-669.18-1	A9	150	2	4.1	6297	6695	31.1	2732	538	6772	945	35.2
DGR4-669.18-2	AB1	150	2	9.1	6254	5227	27.9	2501	473	5369	853	29.8
DGR4-669.18-5	AB4	150	4	1.4	6161	6542	29.6	2822	552	6890	940	35.9
DGR4-669.18-6	AB5	150	4	8.5	6478	5760	27.3	2704	503	5835	916	32.5
DGR4-669.18-1	AB8	50	6	6.0	7497	6621	31.1	3306	585	7022	1037	38.9
DGR4-669.18-2	AB9	50	6	41.7	9076	7536	34.9	3682	675	7827	1195	42.7
DGR4-669.18-5	AC3	100	6	2.9	6475	4970	26.0	2841	512	5219	890	30.9
DGR4-669.18-6	AC4	100	6	5.8	6244	5869	28.3	2780	528	6028	883	33.5
DGR4-669.18-1	AC7		6	79.0	6780	5549	30.8	2835	532	5765	911	32.6
DGR4-669.18-2	AC8	150	6	5.3	6093	6435	28.7	2626	517	6597	874	34.2
DGR4-669.18-5	AD2	200	6	1.3	6263	3772	28.3	2692	490	4163	814	26.6
DGR4-669.18-6	AD3	200	6	0.7	7367	5051	30.1	2914	530	5202	954	30.8
DGR4-746.53-3	A3	150	6	1.4	4737	463	13.2	2247	314	890	363	10.3
DGR4-746.53-4	A4	150	6	1.2	4838	490	13.0	2220	311	907	367	10.5
DGR4-746.53-7	A7	150	8	0.1	5072	466	13.0	2477	335	965	401	11.2
DGR4-746.53-8	A8	150	8	-0.7	5042	456	14.5	2469	364	914	359	11.0
DGR4-746.53-3	AB2	150	2	1.1	4775	473	13.5	2233	320	877	357	10.3
DGR4-746.53-4	AB3	150	2	3.0	4642	473	13.5	2071	310	844	336	9.7
DGR4-746.53-7	AB6	150	4	2.1	4955	455	13.5	2439	335	967	392	10.8
DGR4-746.53-8	AB7	150	4	0.3	4919	490	13.5	2349	331	904	374	10.5
DGR4-746.53-3	AC1	50	6	1.4	5809	546	15.7	2778	386	1097	443	12.7
DGR4-746.53-4	AC2	50	6	2.5	5424	511	14.7	2500	357	1001	404	11.5
DGR4-746.53-7	AC5	100	6	0.6	4484	418	14.2	2182	313	899	355	10.0
DGR4-746.53-8	AC6	100	6	1.6	5121	535	13.5	2351	338	946	380	10.7
DGR4-746.53-3	AC9	150	6	0.1	4630	448	13.9	2188	321	871	345	10.4
DGR4-746.53-4	AD1	150	6	1.2	4545	484	13.5	2107	301	871	351	10.3
DGR4-746.53-7	AD4	200	6	1.6	4815	475	13.7	2318	326	928	379	10.7
DGR4-746.53-8	AD5	200	6	0.8	4622	472	14.7	2275	326	903	359	10.4
DGR4-711.25-1	AD6	150	2	3.4	5108	417	14.3	2418	361	1104	298	10.4
DGR4-711.25-2	AD7	150	2	2.5	5004	404	13.1	2347	356	1082	291	10.1
DGR4-711.25-3	AD8	150	2	2.0	4920	419	12.6	2306	349	1127	298	11.7

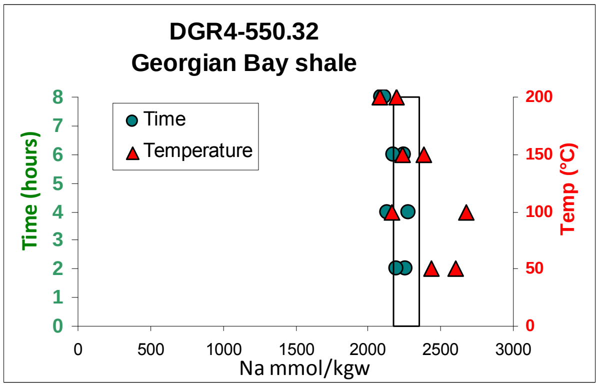
DGR4-711.25-4	AD9	150	2	1.9	5035	475	14.3	2506	397	1144	305	10.8
DGR4-711.25-5	AE1	150	4	4.6	4979	475	13.7	2419	388	1092	300	10.3
DGR4-711.25-6	AE2	150	4	5.8	5015	488	12.4	2200	343	1092	297	11.1
DGR4-711.25-7	AE3	150	4	5.0	5104	452	11.9	2323	358	1063	299	10.7
DGR4-711.25-8	AE4	150	4	3.9	4932	427	11.3	2323	354	1105	301	10.0
DGR4-711.25-1	AE5	150	6	0.4	4544	372	13.1	2190	346	972	279	9.8
DGR4-711.25-2	AE6	150	6	2.1	4637	596	15.1	2217	361	1157	309	12.3
DGR4-711.25-5	AE9	150	8	6.3	4764	384	12.3	2302	360	991	272	10.3
DGR4-711.25-6	AF1	150	8	3.6	4672	395	11.9	2063	321	989	267	8.9
DGR4-711.25-7	AF2	150	8	6.0	5256	491	14.7	2357	392	1115	326	14.0
DGR4-711.25-8	AF3	150	8	11.3	5237	403	13.5	2460	390	1127	318	10.6
DGR4-711.25-3	AE7	150	6	-0.1	5286	445	15.0	2516	400	1127	315	11.0
DGR4-711.25-4	AE8	150	6	0.6	4755	412	12.7	2271	358	1063	300	9.8
DGR4-711.25-1	AF4	200	6	-0.9	5061	708	20.5	2306	398	1293	322	17.6
DGR4-711.25-2	AF5	200	6	1.7	4981	732	21.4	2204	398	1318	318	13.0
DGR4-711.25-3	AF6	200	6	1.0	5104	666	19.8	2412	390	1324	335	14.1
DGR4-711.25-4	AF7	200	6	4.7	4946	633	19.9	2246	403	1229	303	13.6
DGR4-711.25-5	AF8	100	6	5.2	6745	759	20.6	2961	499	1564	453	20.0
DGR4-711.25-6	AF9	100	6	5.6	6236	658	17.8	2713	467	1362	398	14.9
DGR4-711.25-7	AG1	100	6	10.5	6531	827	19.5	2887	493	1587	458	19.9
DGR4-711.25-8	AG2	100	6	3.1	6036	678	17.5	2784	439	1430	437	17.0
DGR4-711.25-9	AG3	50	6	-0.6	7204	829	20.0	3375	536	1738	525	19.6
DGR4-711.25-10	AG4	50	6	-0.3	6142	789	16.8	2825	455	1558	455	16.1
DGR4-711.25-11	AG5	50	6	-1.2	6553	746	19.1	3013	489	1625	481	17.9
DGR4-711.25-12	AG6	50	6	1.2	5649	944	16.6	2672	429	1659	451	15.3

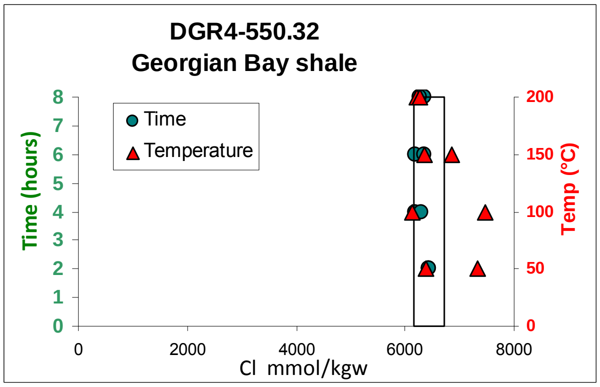

DGR4-351.75
Salina A1 dolostone
Time
Temperature
Time (hours)
0 1 2 3 4 5 6 7 8
Temp (°C)
0 50 100 150 200
0 1000 2000 3000 4000 5000
Cl mmol/kgw

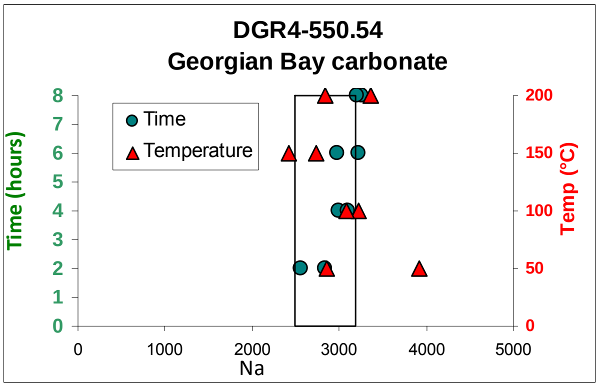

DGR4-351.75
Salina A1 dolostone
Time
Temperature
Time (hours)
0 1 2 3 4 5 6 7 8
Temp (°C)
0 50 100 150 200
0 1000 2000 3000 4000
Na mmol/kgw

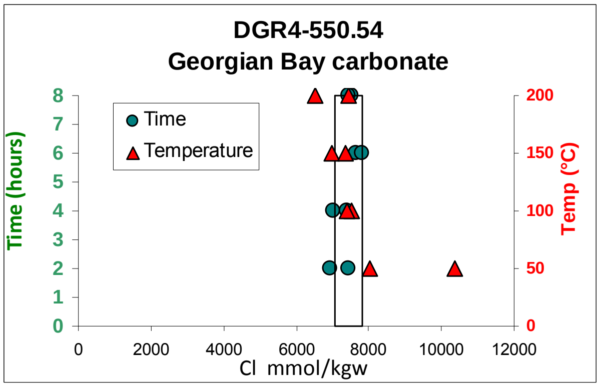

DGR4-357.85
Salina A1 dolostone
Time
Temperature
Time (hours)
0 1 2 3 4 5 6 7 8
Temp (°C)
0 50 100 150 200
0 500 1000 1500 2000 2500
Na mmol/kgw

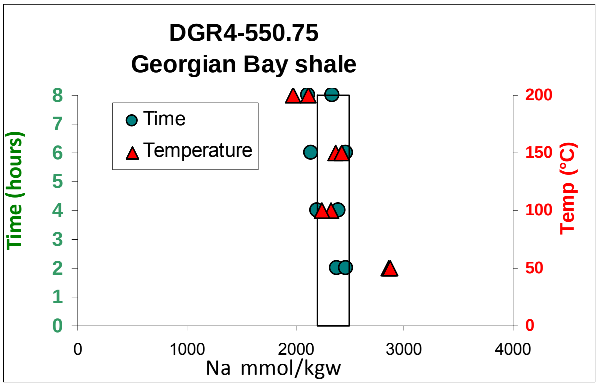

DGR4-357.85
Salina A1 dolostone
Time
Temperature
Time (hours)
0 1 2 3 4 5 6 7 8
Temp (°C)
0 50 100 150 200
0 1000 2000 3000 4000 5000 6000
Cl mmol/kgw

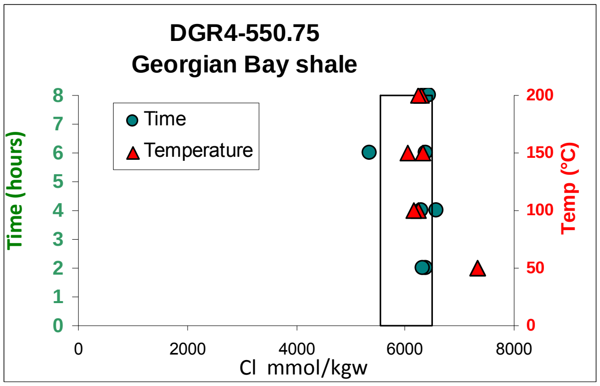

DGR4-550.32
Georgian Bay shale
Time
Temperature
Time (hours)
0 1 2 3 4 5 6 7 8
Temp (°C)
0 50 100 150 200
0 500 1000 1500 2000 2500 3000
Na mmol/kgw

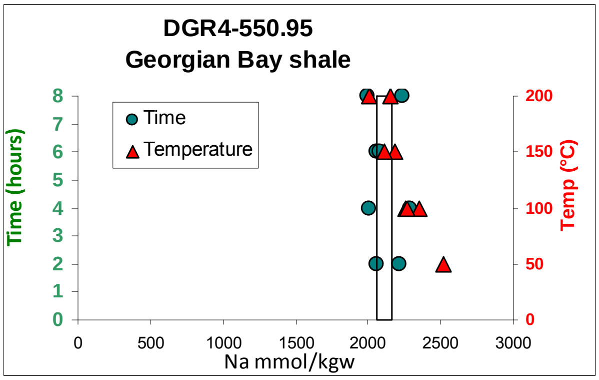

DGR4-550.32
Georgian Bay shale
Time
Temperature
Time (hours)
0 1 2 3 4 5 6 7 8
Temp (°C)
0 50 100 150 200
0 2000 4000 6000 8000
Cl mmol/kgw

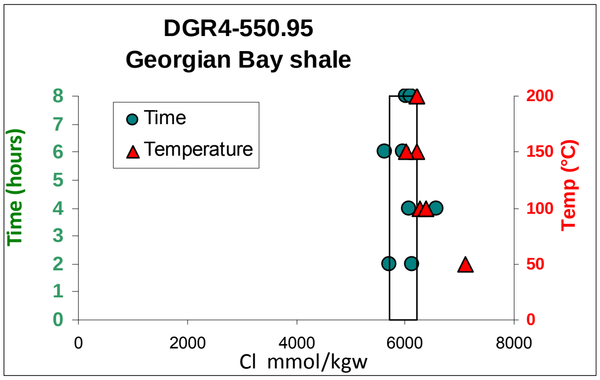

DGR4-550.54
Georgian Bay carbonate
Time
Temperature
Time (hours)
0 1 2 3 4 5 6 7 8
Temp (°C)
0 50 100 150 200
0 1000 2000 3000 4000 5000
Na

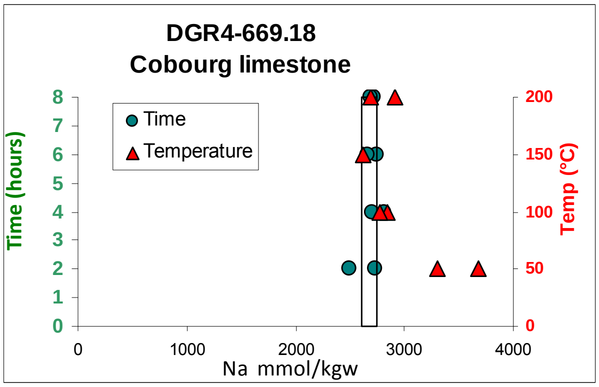

DGR4-550.54
Georgian Bay carbonate
Time
Temperature
Time (hours)
0 1 2 3 4 5 6 7 8
Temp (°C)
0 50 100 150 200
0 2000 4000 6000 8000 10000 12000
Cl mmol/kgw

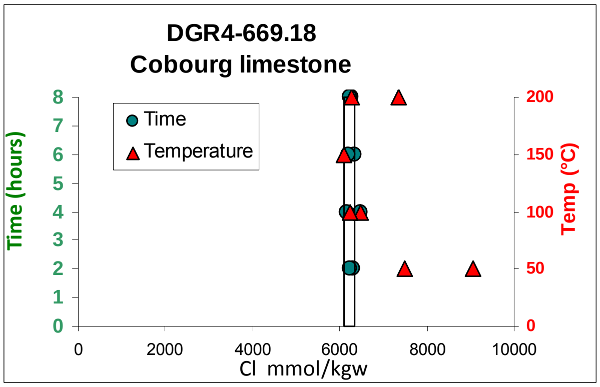

DGR4-550.75
Georgian Bay shale
Time
Temperature
Time (hours)
Temp (°C)
Na mmol/kgw
0
1
2
3
4
5
6
7
8
0
50
100
150
200
0
1000
2000
3000
4000

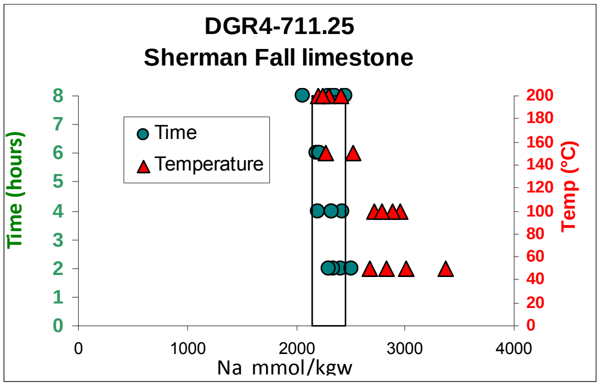

DGR4-550.75
Georgian Bay shale
Time
Temperature
Time (hours)
Temp (°C)
Cl mmol/kgw
0
1
2
3
4
5
6
7
8
0
50
100
150
200
0
2000
4000
6000
8000

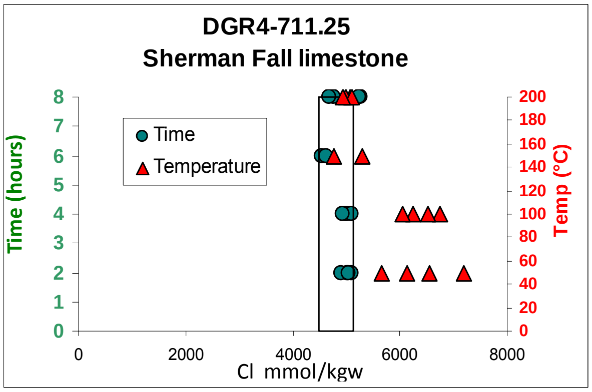

DGR4-550.95
Georgian Bay shale
Time
Temperature
Time (hours)
Temp (°C)
Na mmol/kgw
0
1
2
3
4
5
6
7
8
0
50
100
150
200
0
500
1000
1500
2000
2500
3000

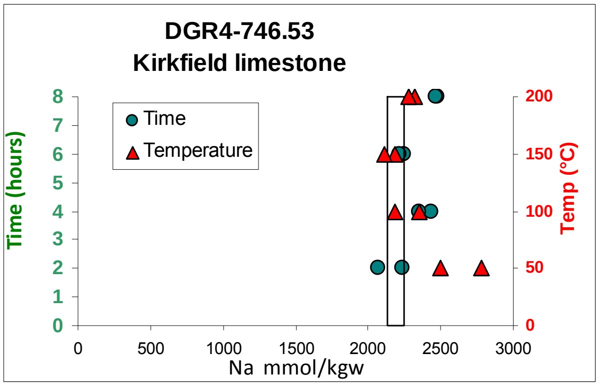

DGR4-550.95
Georgian Bay shale
Time
Temperature
Time (hours)
Temp (°C)
Cl mmol/kgw
0
1
2
3
4
5
6
7
8
0
50
100
150
200
0
2000
4000
6000
8000

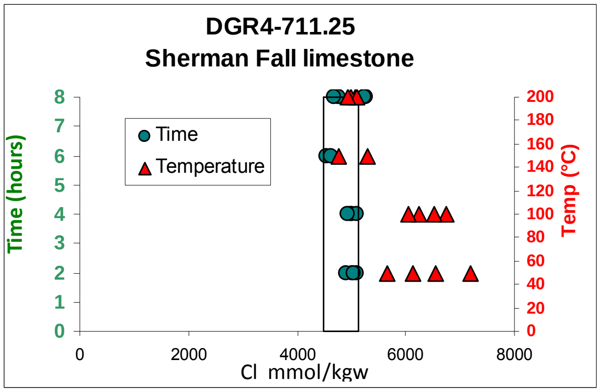

DGR4-669.18
Cobourg limestone
Time
Temperature
Time (hours)
Temp (°C)
Na mmol/kgw
0
1
2
3
4
5
6
7
8
0
50
100
150
200
0
1000
2000
3000
4000


DGR4-669.18
Cobourg limestone
Time
Temperature
Time (hours)
Temp (°C)
Cl mmol/kgw
0
1
2
3
4
5
6
7
8
0
50
100
150
200
0
2000
4000
6000
8000
10000


DGR4-711.25
Sherman Fall limestone
Time
Temperature
Time (hours)
Temp (°C)
Na mmol/kgw
0
1
2
3
4
5
6
7
8
0
20
40
60
80
100
120
140
160
180
200
0
1000
2000
3000
4000


DGR4-711.25
Sherman Fall limestone
Time
Temperature
Time (hours)
Temp (°C)
Cl mmol/kgw
0
1
2
3
4
5
6
7
8
0
20
40
60
80
100
120
140
160
180
200
0
2000
4000
6000
8000


DGR4-746.53
Kirkfield limestone
Time
Temperature
Time (hours)
Temp (°C)
Na mmol/kgw
0
1
2
3
4
5
6
7
8
0
50
100
150
200
0
500
1000
1500
2000
2500
3000


DGR4-711.25
Sherman Fall limestone
Time
Temperature
Time (hours)
Temp (°C)
Cl mmol/kgw
0
1
2
3
4
5
6
7
8
0
20
40
60
80
100
120
140
160
180
200
0
2000
4000
6000
8000