Squeezing of Porewater from Core Samples of DGR Boreholes: Feasibility Study

NWMO TR-2013-19 **November 2013**

Martin Mazurek[1], Takahiro Oyama[2], Florian Eichinger[3] and Antoine De Haller[1]

[1]Rock-Water Interaction (RWI), Institute of Geological Sciences, University of Bern, Switzerland

[2]Nuclear Fuel Cycle Backend Research Center, CRIEPI, Abiko-shi, Chiba-ken, Japan

[3]Hydroisotop GmbH, Schweitenkirchen, Germany

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

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

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[3]Hydroisotop GmbH, Schweitenkirchen, Germany

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Rock-Water Interaction, Institute of Geological Sciences, University of Bern			
Authored by:	Martin Mazurek and Antoine De Haller		
CRIEPI (Japan)			
Authored by:	Takahiro Oyama		
HYDROISOTOP GmbH			
Authored by:	Florian Eichinger		
Nuclear Waste Management Organization			
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ABSTRACT

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Report No.: **NWMO TR-2013-19**
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Company: [1]Rock-Water Interaction (RWI), Institute of Geological Sciences, University of Bern, Switzerland, [2]Nuclear Fuel Cycle Backend Research Center, CRIEPI, Abiko-shi, Chiba-ken, Japan, [3]Hydroisotop GmbH, Schweitenkirchen, Germany
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Abstract

Three archived core samples from boreholes DGR-4, DGR-5 and DGR-6 from the Salina F Unit, Queenston Formation and the Georgian Bay Formation were subjected to squeezing tests at pressures of up to 500 MPa. Two samples did not yield any water, while a total of 0.88 g pore water was obtained from a clay-rich sample from the Blue Mountain Formation (water content = 2.8 wt.%, porosity = 8 %). This water mass was sufficient for a full chemical and water-isotope analysis – the first direct determination of porewater composition in rocks from the DGR boreholes. The results are generally in reasonable agreement with those of independent methods, or the observed differences can be explained. Ancillary investigations included the determination of water content, densities and mineralogy, aqueous extraction of squeezed cores, and SEM investigations to characterise the microtexture of unsqueezed and squeezed rock materials.

It is concluded that squeezing is a promising method of porewater extraction and characterisation and is recommended as a complementary method for future studies. Selection criteria for potentially squeezable samples include high clay-mineral content (correlating to high water content) and low carbonate content (low stiffness, limited cementation). Potential artefacts of the method, such as ion filtration or pressure solution, should be explored and quantified in future efforts.

TABLE OF CONTENTS

LIST OF TABLES

Page

LIST OF FIGURES

Page

1. INTRODUCTION

In order to recover porewater from low-permeability rocks, squeezing of core samples under high pressure has been applied in the past. Originally, the method was targeted at soft sediments with water contents >10 wt.% (e.g., Bath et al. 1989). More recently, the method has also been applied to moderately indurated shales, such as Opalinus Clay from Mont Terri, Switzerland (Pearson et al. 2003). Samples of Opalinus Clay from the Benken borehole (water contents of 4.3–4.6 wt.%) were squeezed at 512 MPa and yielded 0.4–3.3 g water per experiment (Waber et al. 2003). Recently, samples of Mesozoic clay-rich rocks from the Schlattingen borehole (northern Switzerland) with water contents of 3.9–6.1 wt.% were subjected to squeezing at pressures of 200–500 MPa (Figure 1; Wersin et al. 2013). Most of these samples yielded small amounts of water even at the lowest pressure of 200 MPa. Given the advances of analytical methods within the last few years, full chemical and water-isotopic compositions can now be obtained for the smallest of water samples (<0.5 g).

This encouraging experience was the motivation to launch a feasibility study targeted at squeezing porewaters from rocks of the DGR boreholes. It was evident from the outset that, given the deeper geological burial of the Palaeozoic rocks of the Michigan Basin penetrated by the DGR boreholes, water contents would be even lower, and so the squeezing method would come close to (if not beyond) its limits. In order to maximize success, samples rich in clay minerals were selected because of the known positive correlation between clay-mineral and water content.

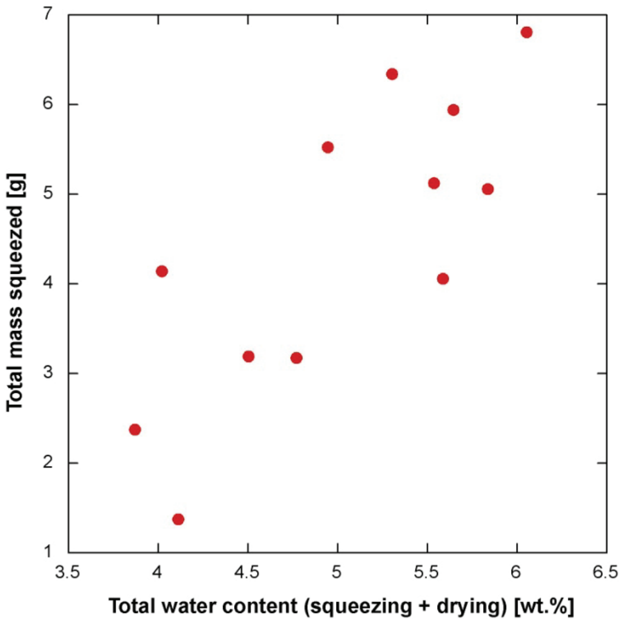


Figure 1: Total Water Mass Squeezed as a Function of Water Content of Clay-rich Samples from the Mesozoic of the Schlattingen Borehole (from Wersin et al. 2013)

2. SAMPLE SELECTION

2.1 SITUATION AT THE ONSET OF THE WORK PROGRAM

At the time of sample selection, no drilling activities were underway; therefore, no dedicated, fresh samples could be taken for this study. Sampling was limited to archived core specimens that were available in Ontario Power Generation's core storage facility at the Bruce site. The number of available samples of the appropriate lithology that were stored cool since core recovery, double-sealed in Al/plastic foil with intact seals (no inflation of the foils), was limited. A list of these samples was made available by NWMO. This list included the core IDs (borehole, depth), core length and geological formation. However, no further data on these samples were available, such as sample-specific lithology or mineralogy.

2.2 SAMPLING CRITERIA

In practice, the following sampling criteria were applied.

1. Preference toward formations with high clay-mineral content according to laboratory data summarized in Intera (2011, Section 3.7):

    - Blue Mountain Formation,
    - Georgian Bay Formation (but mixed with horizons of lower clay-mineral contents in the upper two thirds of the formation), and
    - Queenston Formation.

2. Preference toward formations with relatively high liquid porosity according to laboratory data summarized in Intera (2011, Section 4.3):

    - Average values around 8 vol.% in Blue Mountain–Georgian Bay–Queenston formations;
    - Frequently high, but scattered, values in Salina A2–Salina G Units – at least, in some cases, the high porosities may be due to the presence of gypsum, whose dehydration leads to analytical artefacts when measuring water content by weight loss upon heating.

3. Preference toward formations with high values in geophysical gamma logs (Pehme & Melaney 2010, 2011), indicative of high clay-mineral contents:

    - Consistently high in Georgian Bay Formation (except uppermost 10 m) and the Blue Mountain Formation,
    - High in the uppermost 35 m of the Queenston Formation, and
    - Low to intermediate in centre of Salina F (DGR-4: 190–208 m) and Salina B, C (DGR-4: 248–288 m).

4. Information from selected lithologic descriptions (Intera 2011, Section 4.3).

    - Salina F – *"The upper part of the unit is grey to green fine-grained dolomitic shale with white and orange anhydrite/gypsum veins throughout. A 0.2-m-thick layer of tan massive dolostone found at depths of 181.5 to 200.5 mBGS in DGR-1 to DGR-4 is a formation marker. Below, the unit is often stained reddish-brown with increasing content of anhydrite as veins, layers and large nodules that infill and surround brecciated shale and dolostone fragments. The bottom 6.0 m is composed of tan*

brown brecciated dolostone with abundant veins and layers. Estimated clay content of the whole unit: 33%."
Conclusion: The uppermost part, above the tan massive dolostone could be used; the rest is less clay-rich and/or more heterogeneous.

- Salina C – *"The C Unit typically consists of an upper 6.4 m of red and green shale and a lower 7.9 m of dolomitic shale. Anhydrite veins and nodules are common throughout the C Unit. The lower section of the C Unit includes broken shale and dolostone infilled and healed with white to blue anhydrite as a secondary mineral. The fragmentation or brecciation of the D and C Units is greatest in DGR-6. Estimated clay content of the whole unit: 44%."*
  Conclusion: Could be suitable, particularly the more homogeneous upper part (6 m).

- Salina B – *"In descending order, the B Unit typically consists of 21.2 to 40.8 m of grey-green brecciated argillaceous dolostone and a basal bed of 1.6 to 4.0 m thick grey anhydrite with brown dolostone layers. The upper brecciated unit consists of angular tan to grey dolomitic mudstone and dolostone clasts within a grey dolomitic shale matrix that is infilled with secondary white to bluish-grey anhydrite/gypsum veins, layers and nodules. The lower evaporite bed is grey with brown dolostone layers."*
  Conclusion: Heterogeneous and presumably not overly clay-rich; therefore, not recommended.

- Queenston Formation – *"The upper 35-36 m of the formation is massive red-maroon calcareous shale with grey-green calcareous shale layers and lenses. The middle ~26 m of the formation is green shale interbedded with medium to light grey, medium- to coarse-grained fossiliferous limestone layers. The limestone layers represent about 25 to 50% of the middle part of the Queenston Formation. The bottom 10-11 m of the formation is red-maroon shale interbedded with grey-green shale layers and minor limestone beds."*
  Conclusion: Concentrate on the upper 35 m and lower 10 m.

- Georgian Bay Formation – *"The upper 30 m of the formation is dark grey-green shale with grey, fine- to medium-grained, occasionally fossiliferous limestone, siltstone and sandstone layers or hardbeds. The lower 60 m of the formation is dark grey-green shale with occasional layers and laminations of fossiliferous limestone, siltstone and sandstone, the frequency of which decreases with depth."*
  Conclusion: Concentrate on the lower 60 m, but the unit is more heterogeneous than the Queenston Formation.

- Blue Mountain Formation – *"The upper member is typically a 38.1- to 41.1-m-thick sequence of dark greenish-grey shale interbedded with grey siliceous siltstone and sandstone layers and fossiliferous limestone layers. The lower member is a 4.0- to 4.6-m-thick bed of hard dark grey calcareous shale."*
  Conclusion: Could be suitable, but the unit is more heterogeneous than the Queenston Formation.

2.3 CONCLUSIONS ON SAMPLING PRIORITIES

Combining the various criteria detailed above, the following depth intervals were considered to be best suited for the purpose of assessing the applicability of the squeezing technique.

1. Uppermost 35 and lowermost 10 m of the Queenston Formation
    - DGR-4: 446 - 481 m, 509 - 517 m
    - DGR-5: 487 - 522 m, 551 - 558 m
    - DGR-6: 508 - 543 m, 573 - 581 m

2. Lowermost 60 m of the Georgian Bay Formation and Blue Mountain Formation
    - DGR-4: 548 - 649 m
    - DGR-5: 593 - 700 m
    - DGR-6: 625 - 738 m

3. Salina F Unit, central part
    - DGR-4: 190 - 208 m
    - DGR-5: 211 - 222 m
    - DGR-6: 226 - 236 m

4. Salina C Unit, uppermost 6 m
    - DGR-4: 248 - 254 m
    - DGR-5: 258 - 263 m
    - DGR-6: 275 - 278 m

2.4 SELECTED CORE SAMPLES

The number of available sealed core samples from the intervals derived above turned out to be quite limited. Only two out of the three samples finally selected for squeezing tests fall into the selected intervals, as shown in Table 1.

Table 1: List of Samples Selected for Squeezing Tests

Sample ID	Formation	Remarks	Core direction	Estimated water content [wt.%]	Qualification	Priority
DGR-4 610.48	Blue Mountain Formation	Only suitable sample available from this formation	Vertical	3	"Easiest sample"	1
DGR-6 512.15	Queenston Formation	Only suitable sample available from this formation	Inclined, 60°	2–3	"Intermediate sample"	2
DGR-5 225.68	Salina F Unit	Sample is some m out of the intervals selected in Section 2.3	Inclined, 65°	2	"Difficult sample"	3

Notes: "Priority" is a qualitative measure of the chance of success, based on the information available prior to the squeezing tests.

3. LABORATORY METHODS

3.1 SQUEEZING EXPERIMENTS

Squeezing tests were performed at the Central Research Institute of Electric Power Industry (CRIEPI), Abiko, Japan. One of the reasons for choosing this laboratory was the ability of CRIEPI's rig to work at pressures of up to 500 MPa. Given the expected low water contents of the rock samples from the Michigan Basin, it was anticipated that such high pressures might be needed in order to collect amounts of porewater sufficient for chemical and isotopic analysis. The rig is shown in Figure 2, and Figure 3 is an illustrated schematic of the device. The sample chamber is cylindrical (diameter 5 cm, height 10 cm), and fiber glass filters (Whatman GF/B 1.0 µm, 47 mm diameter) are attached on the upper and lower sample surfaces, where porewater is collected in syringes. Pressure is exerted by a piston located above the sample chamber.

The dead volume of the squeezing apparatus consists of: 1) the pore volume of the fiberglass filters on both sides of the sample (4 filters in total; Figure 3), 2) the volume of the indents in the water-gathering plates on each side of the sample (Figure 3), and 3) the volume of the tubes connected to the syringes. The respective volumes can be estimated as follows.

1. Assuming that the water content of the fiberglass filters does not exceed 5 wt.% (equivalent to a porosity of about 12%) under squeezing conditions, and considering the mass of 0.245 g for each filter, a maximum water mass of 0.05 g (corresponding to a volume of 0.05 mL) is estimated for all 4 filters.
2. The volume of the indents in the water-gathering plates is 0.1 mL each (i.e.*,* 0.2 mL in total). Note that these indents are partially filled with solid material after the squeezing experiment, so this volume may overestimate the dead volume.
3. Given the fact that all water is drawn off into the syringes after the experiment, the tubes do not contribute to the dead volume.

In total, the maximum dead volume is estimated at 0.25 mL but likely is even smaller.

Samples received by CRIEPI were dry cut to polygonal prisms to fit the size needed for the squeezing apparatus (Figure 4a). Building on the experience of the campaign targeted at the core from the Schlattingen borehole, Switzerland (Wersin et al. 2013), samples were prepared with axes parallel to that of the original core, i.e.*,* normal to bedding (or, in the case of the sample from inclined sample from DGR-6, at a high angle to bedding). After trimming, samples were weighed and then inserted into the sample chamber (Figure 4b). This procedure required a maximum of 15–20 minutes. The volume of air in the sample chamber was on the order of tens of mL, maximum, and was fully expelled during approximately the first half hour of the squeezing experiment.

The experimental protocol included squeezing pressures of 200, 300, 400 and 500 MPa (Figure 5). The standing times at each pressure step, again based on experience from the campaign documented in Wersin et al. (2013), are shown in Table 2. Given the successful retrieval of water from sample DGR-4 610.48 I, a second piece of the same core sample (DGR-4 610.48 II) was prepared and squeezed. Waters collected during the squeezing experiments were stored cool, in 4 mL plastic bottles, and were sent to RWI, University of Bern, for chemical and isotopic analysis.

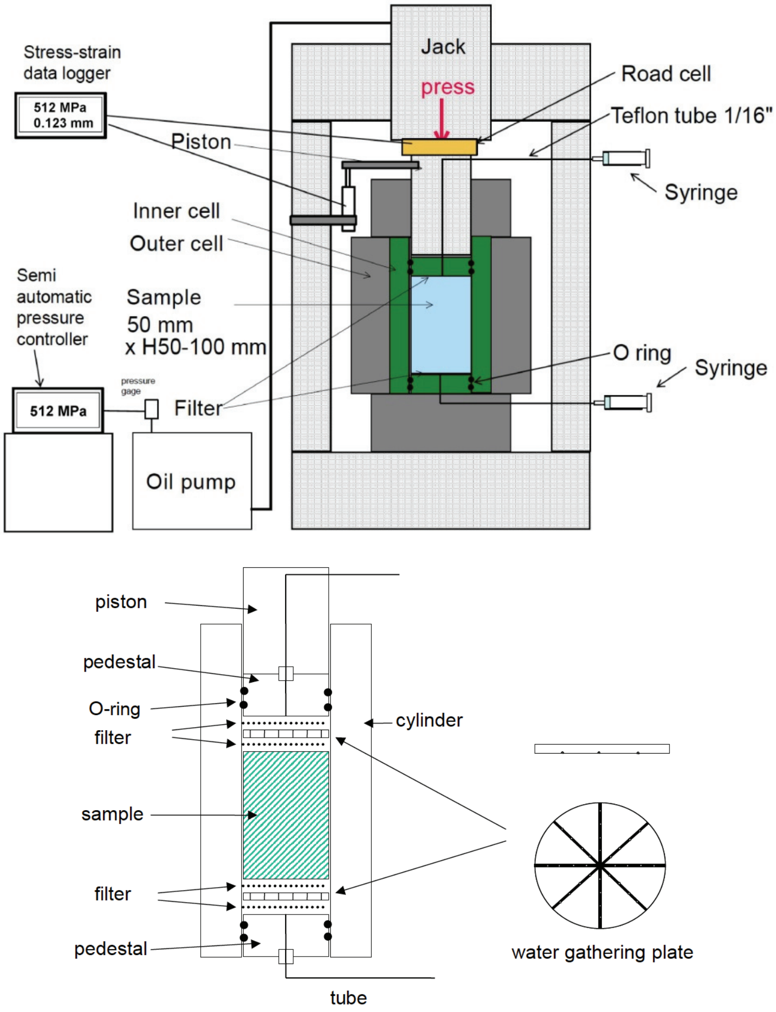
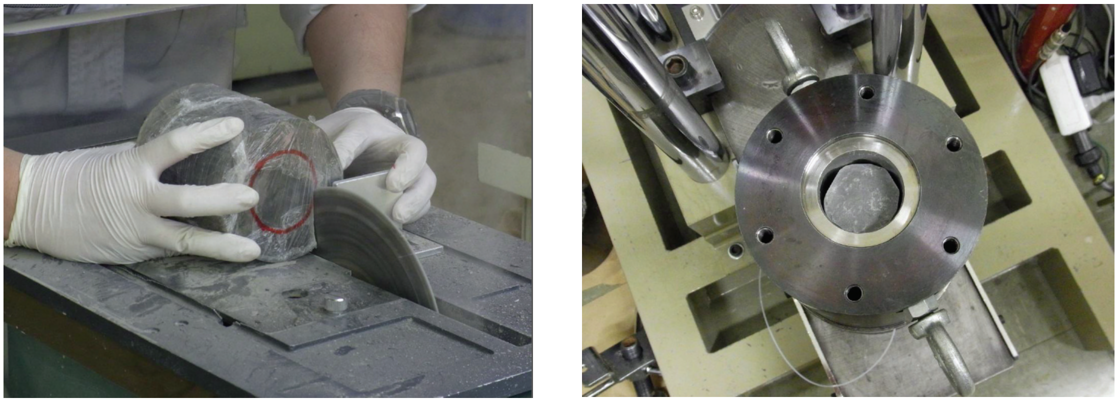


Figure 2: Rock Squeezing Apparatus at CRIEPI

Figure 3: Schematic of CRIEPI's Squeezing Rig



a.)

b.)

Figure 4: a.) Dry Cutting of Sample, and b.) Placement in Sample Chamber of the Squeezing Apparatus

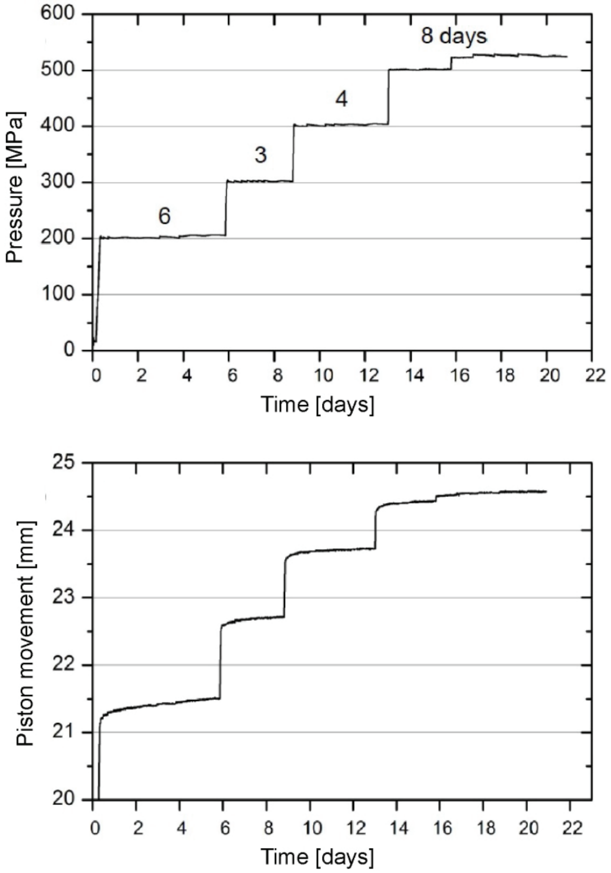


Figure 5: Experiment With Sample DGR-4 610.48 I - Squeezing Pressure (top) and Piston Movement (bottom) as a Function of Time

Table 2: Pressure Steps and Standing Times for Squeezing Experiments

Sample ID	Time @ 200 MPa [d]	Time @ 300 MPa [d]	Time @ 400 MPa [d]	Time @ 500 MPa [d]	Total time [d]
DGR-4 610.48 I	6	3	4	8	21
DGR-4 610.48 II	4	2	2	10	18
DGR-6 512.15	4	3	4	4	15
DGR-5 225.68	3	4	3	11	21

3.2 MINERALOGY

The mineralogical composition of the samples was determined by X-ray diffraction and IR spectrometry. Details of the methodology are given in Koroleva et al. (2009).

3.3 WATER CONTENT

Water contents of the rock materials were measured at both CRIEPI and RWI.

- CRIEPI used several unsqueezed rock pieces (masses of typically 15–30 g each), immediately adjacent to the sample targeted in the squeezing experiments, for the determination of gravimetric water content, which was determined by heating of the sample to 60°C. Drying time was 13 days.

- Water contents of cores previously subjected to squeezing were determined by heating to 105°C at RWI, Bern. The core masses ranged between 400 and 450 g. The samples were dried until constant weight was attained, which took about 2–3 weeks.

Wet and dry water contents WC_{wet} and WC_{dry} were calculated from the sample masses before and after drying from the following equations:

$$WC_{wet} = \frac{m_{wet} - m_{dry}}{m_{wet}} \quad , \qquad \text{and} \tag{1}$$

$$WC_{dry} = \frac{m_{wet} - m_{dry}}{m_{dry}} \quad , \tag{2}$$

with m_{wet} = wet mass of the rock and m_{dry} = dry mass of the rock (see Koroleva et al. 2009 for more detail). Porewater contents PWC_{wet} and PWC_{dry}, i.e., the mass fractions of porewater and dissolved salts, can be calculated from:

$$PWC_{wet} = \frac{(m_{wet} - m_{dry})/(1-s)}{m_{wet}} \quad , \qquad \text{and} \tag{3}$$

$$PWC_{dry} = \frac{(m_{wet} - m_{dry})/(1-s)}{m_{wet} - (m_{wet} - m_{dry})/(1-s)} = \frac{m_{wet} - m_{dry}}{m_{dry} - m_{wet}s} \quad , \tag{4}$$

with s = salinity in units of $kg/kg_{porewater}$ (see Hobbs et al. 2011). Porewater loss porosity Φ_{PWL}, is obtained from gravimetric porewater contents using

$$\phi_{PWL} = \frac{PWC_{wet}\,\rho_g}{PWC_{wet}\,\rho_g + (1 - PWC_{wet})\,\rho_{pw}} \cdot 100\% \tag{5}$$

with ρ_g = grain density and ρ_{pw} = porewater density (see Hobbs et al. 2011).

3.4 GRAIN DENSITY

Grain density was determined by kerosene pycnometry, and further details are provided in Koroleva et al. (2009).

3.5 CHEMICAL ANALYSIS OF SQUEEZED WATER

Ion compositions were measured by ion chromatography using a Metrohm ProfIC AnCat MCS IC system with automated 5 μL and 50 μL injection loops. The detection limit of this technique is 0.016 mg/L for anions and 0.1 mg/L for cations, with an analytical error of ± 5% based on multiple measurements of standard solutions.

3.6 AQUEOUS EXTRACTION

Aqueous leaching was performed on dried rock material. Samples were milled to a grain size of about ≤60 μm using a ring mill. Extraction tests were performed under atmospheric conditions with ultra-pure water using about 30 g of powdered rock material at a solid:liquid (S:L) mass ratio of 1. Each sample was shaken end-over-end for 24 hours in a polypropylene tube. Aliquots from sample DGR-4 610.48 were also extracted for 10 minutes. After filtration (0.45 μm), the solutions were immediately analysed for alkalinity (by titration). Major ions were analysed by ion chromatography. The error of these analyses is ± 5% based on multiple measurements of standard solutions.

3.7 ISOTOPIC ANALYSIS OF SQUEEZED WATER

Isotope measurements of water samples were carried out with a Picarro CRDS (Cavity Ring-Down Spectroscopy) isotope analyser L2130-i. The method enables measurement of the near-infrared laser absorption spectrum of different isotope species in water vapour with high precision. Every standard and sample was measured 6 times through 6 subsequent manual injections into the vaporisation module, with each injection containing 2 μL of water. Because of memory effects, only 4 of 6 measurements were used for calculation of the mean value. Calibration was performed using 4 internal standards (δ^{18}O values ranging between -15.41 and -0.96 $‰_{V\text{-}SMOW}$ and δ^{2}H values between -113.8 and -2.3 $‰_{V\text{-}SMOW}$), which are frequently calibrated against international standards. The analytical uncertainties are $1\sigma = \pm 0.1$ ‰ for δ^{18}O and $1\sigma = \pm 1$ ‰ for δ^{2}H.

4. RESULTS

4.1 MINERALOGY AND TEXTURE

The mineralogical compositions of the samples subjected to squeezing tests are listed in Table 3. The sample from the Blue Mountain Formation is a clayrock, the sample from the Queenston Formation is a sandy calcitic marl, and the sample from the Salina F Unit is a sandy dolomitic marl.

Macro- and microscopic illustrations of all samples are provided in Figure 6 through Figure 11. The sample from the Blue Mountain Formation (DGR-4 610.48) is a reasonably homogeneous clayrock (Figure 6, Figure 7) with minor laminae of clastic quartz and calcite. Sample DGR-6 512.15 from the Queenston Formation has a heterogeneous texture on the scale of millimetres to centimetres, consisting of clay-rich and calcite-rich domains, most likely enhanced by diagenetic processes (Figure 8, Figure 9). Sample DGR-5 225.68 from the Salina F Unit has a breccious texture of dolomite-rich clasts embedded in a more clay-rich matrix (Figure 10, Figure 11).

Table 3: Whole-rock Mineralogy of Squeezed Samples

Sample ID	Unit	Quartz [wt.%]	K-feldspar [wt.%]	Albite [wt.%]	Calcite [wt.%]	Dolomite / Ankerite [wt.%]	Pyrite* [wt.%]	C(org) [wt%]	Sheet silicates [wt.%]
DGR-4 610.48 I	Blue Mountain Formation	20	2.0	1.0	8	1.5	2.1	<0.1	66
DGR-4 610.48 II	Blue Mountain Formation	20	2.0	1.0	7	2	1.9	<0.1	66
DGR-6 512.15	Queenston Formation	11	1.0	0.0	38	9	0.6	<0.1	41
DGR-5 225.68	Salina F Unit	12	4.0	0.0	1	37	0.4	<0.1	45

*Pyrite contents were calculated from the determination of total S, assuming that pyrite is the only S-bearing phase. In sample DGR-5 225.68, traces of gypsum were identified in microfractures, so the 0.4 wt.% pyrite may be an overestimation.

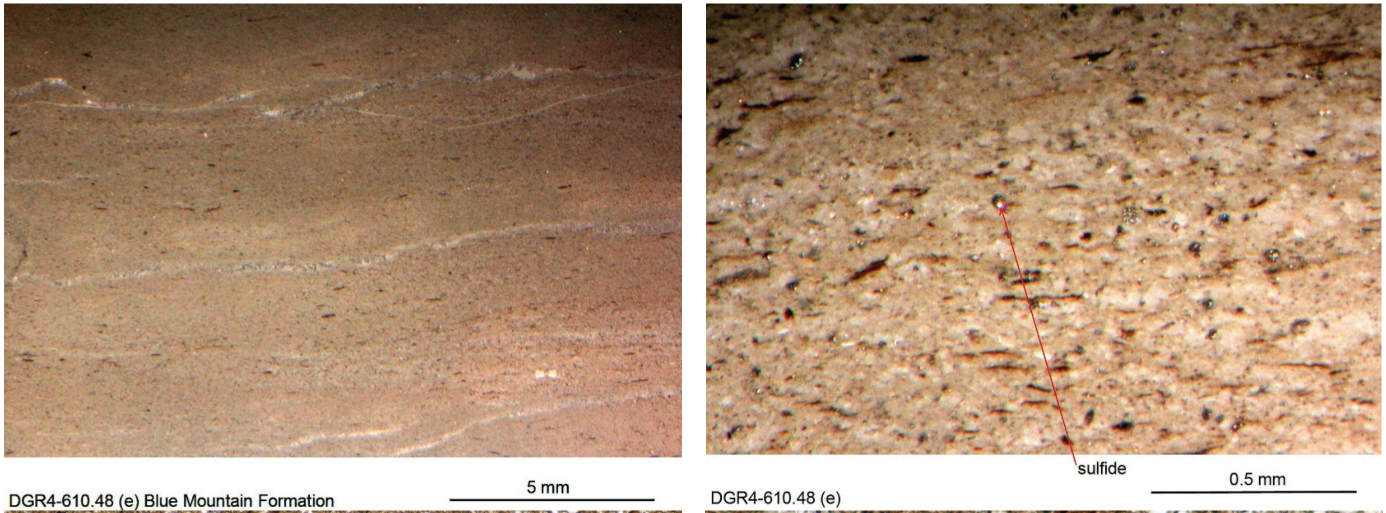


Figure 6: Unsqueezed Sample DGR-4 610.48; Finely Laminated Clayrock

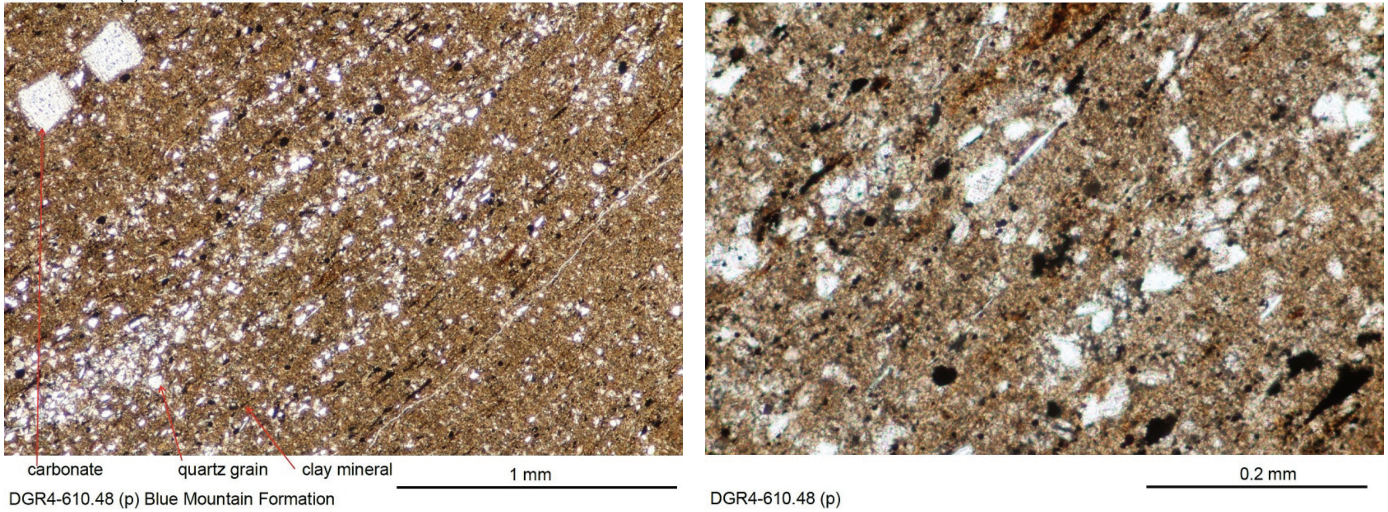


Figure 7: Aspect of Unsqueezed Sample DGR-4 610.48 in Thin Section (parallel polars); Brown, Clay-rich Matrix with Laminae Rich in Quartz and Calcite

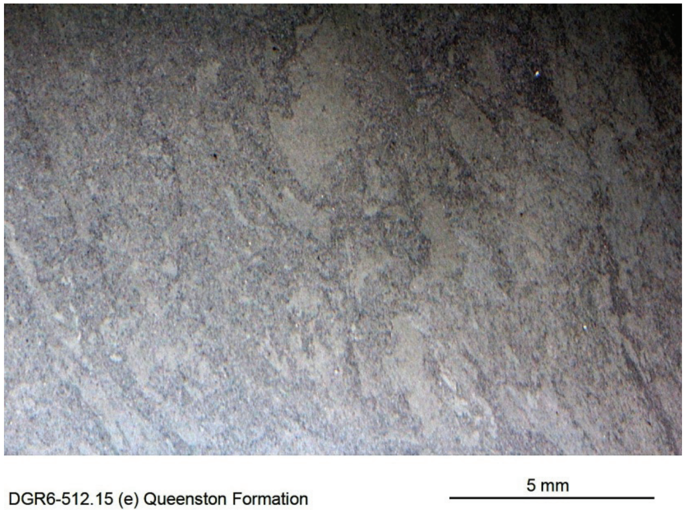


Figure 8: Unsqueezed Sample DGR-6 512.15: Weak Bedding, Major Heterogeneity of Clay and Carbonate Contents on a Scale of 1 cm

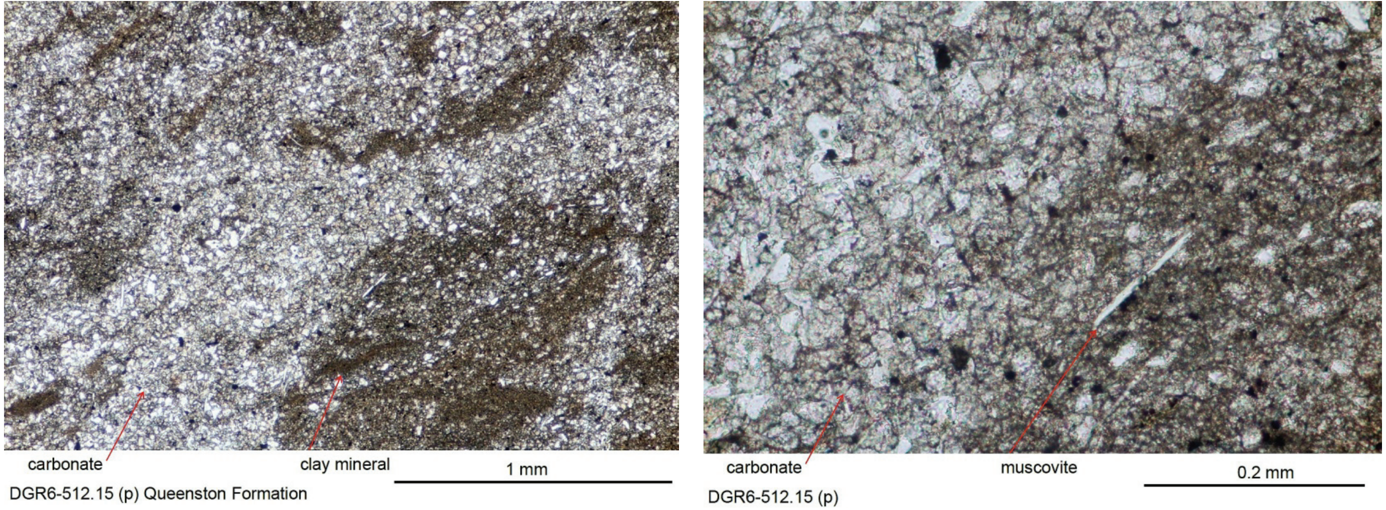
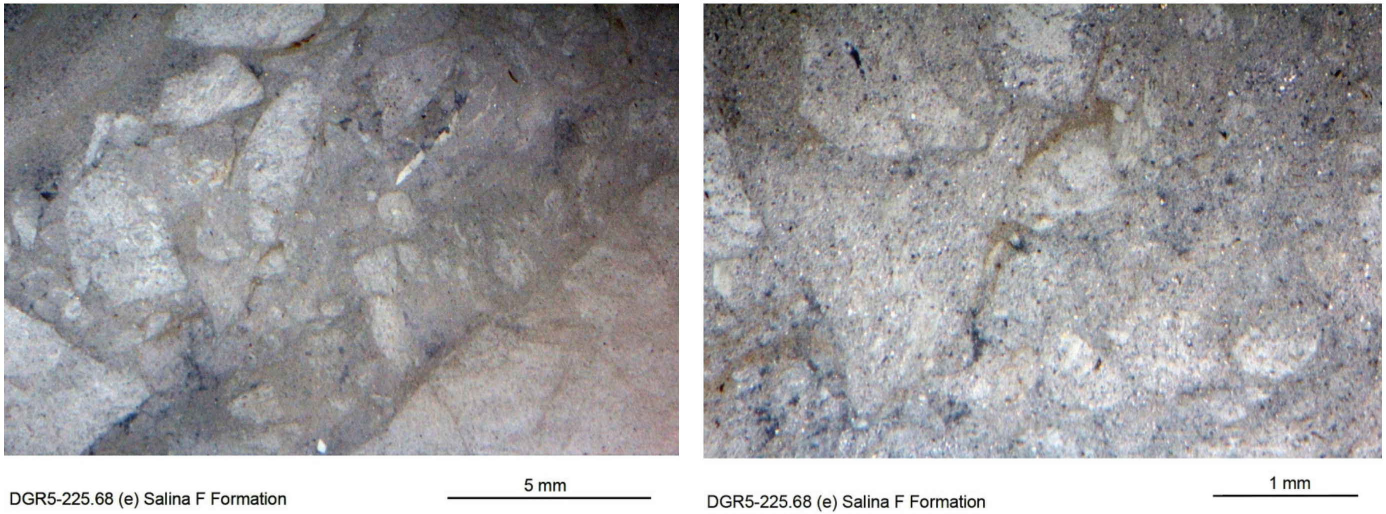


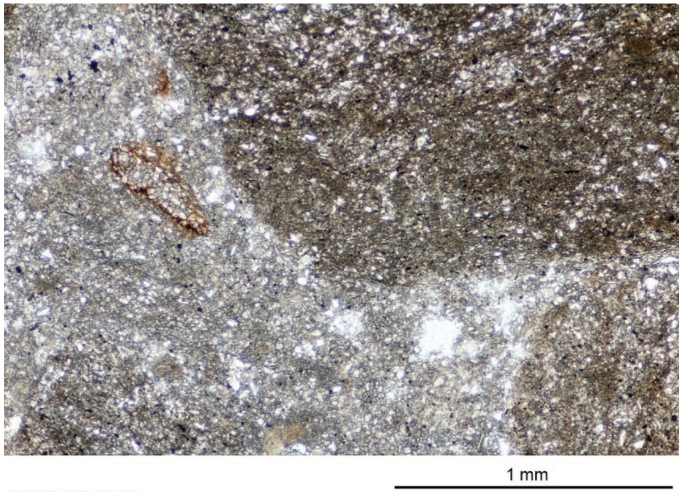
Figure 9: Unsqueezed Sample DGR-6 512.15 in Thin Section (parallel polars): Irregular, Heterogeneous Texture of Clay-rich (dark) and Calcite-quartz-rich Domains (light)



DGR5-225.68 (e) Salina F Formation

DGR5-225.68 (e) Salina F Formation

Figure 10: Unsqueezed Sample DGR-5 225.68: Breccious Texture with Dolomite-rich Clasts in a Clay-rich Matrix



DGR5-225.68 (p)

Figure 11: Unsqueezed Sample DGR-5 225.68 in Thin Section (parallel polars): Heterogeneous Texture of Clay-rich Domains (dark) and Dolomite-rich Domains (light)

4.2 SEM INVESTIGATIONS

Uncoated polished thin-sections of rock segments that were previously subjected to squeezing, as well as adjacent unsqueezed materials, were studied under the SEM with the objective to identify soluble minerals in the rocks, as well as to characterise changes in the rock fabric during squeezing.

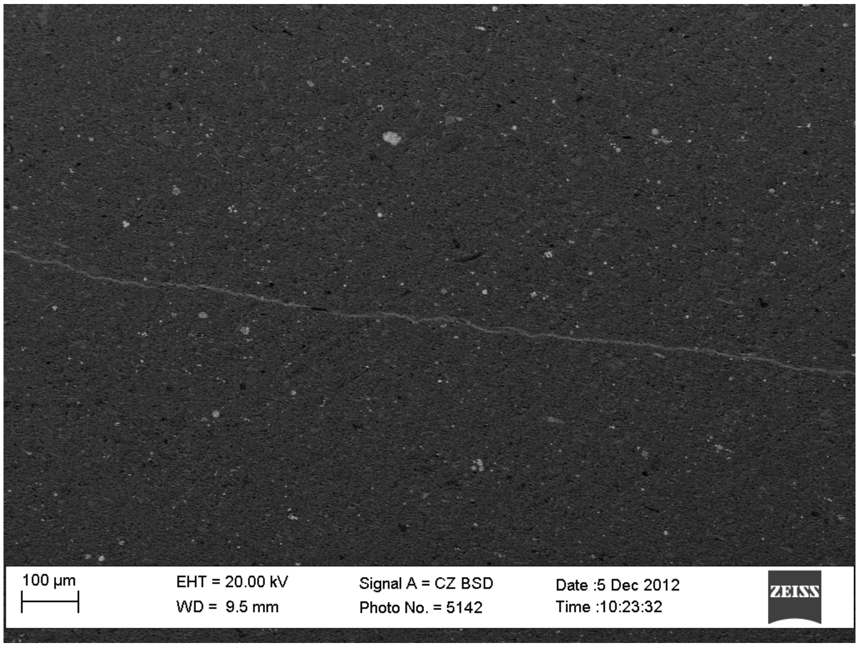
4.2.1 Sample DGR-4 610.48 (Blue Mountain Formation)

Unsqueezed rock

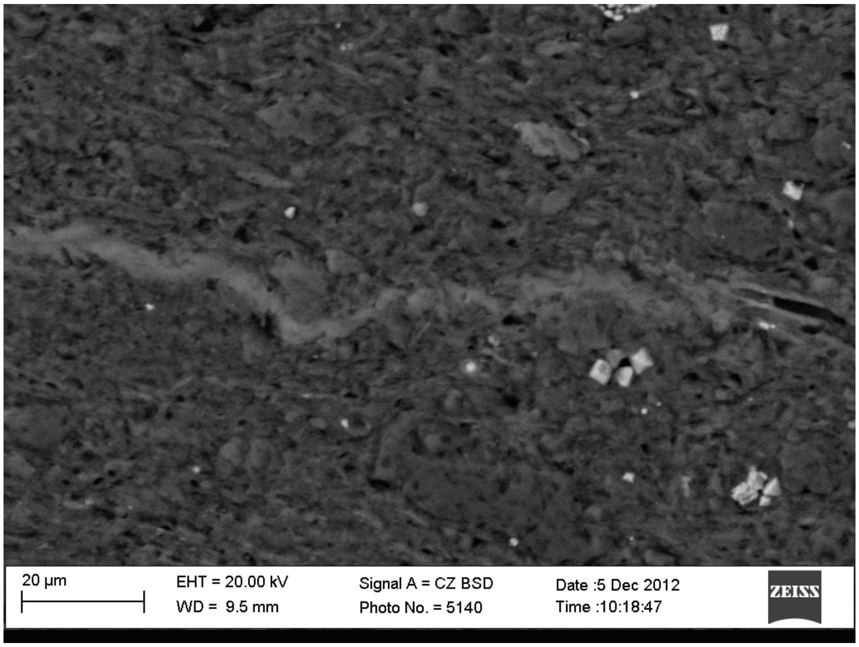
- Homogeneous, fine-grained, clay-rich rock (Figure 12a)
- Trace minerals identified in the matrix: pyrite, apatite, Ti-oxides
- Occasional bedding-parallel fractures are filled with halite. The filling is incomplete (see open space on the right side of Figure 12b). Such bedding-parallel fractures are commonly related to sample shrinkage due to drying. Also, halite is only present in the fracture but not in the rock matrix. Both the fracture and its filling are interpreted as artefacts of sample drying and porewater evaporation and are not considered to be natural features.

Squeezed rock

- Highly deformed rock, contains 2 sets of microfractures that constitute a network (conjugate system; Figure 13a, b). These fractures may be open (likely due to drying after squeezing) or contain some halite due to porewater evaporation (Figure 13b, d).
- Apart from the microfractures, variable proportions of the fabric of the rock matrix are destroyed, resulting in fault gouges (Figure 13b, c).

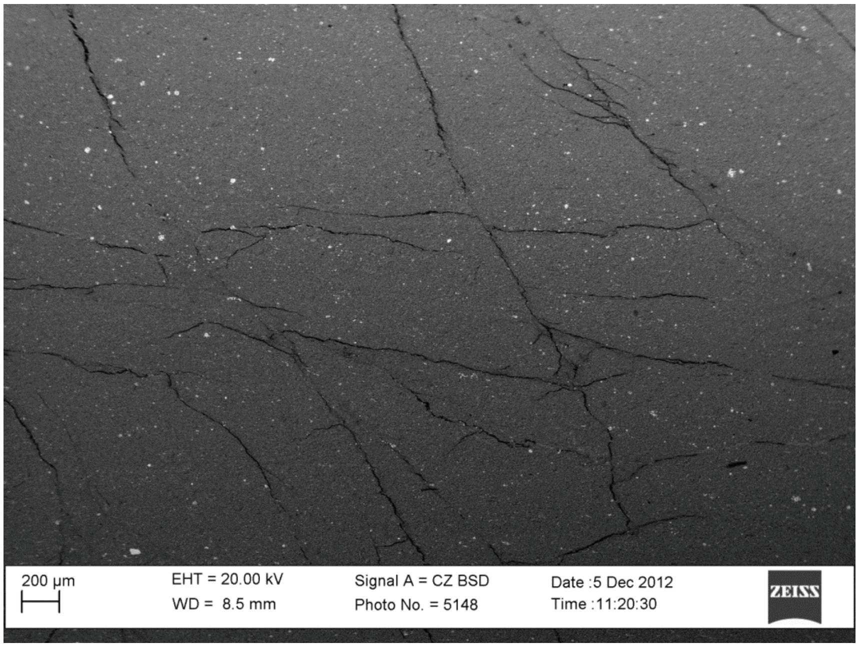


a.) Homogeneous, clay-rich rock matrix cross cut by a halite-filled microfracture (probably formed during sample drying)

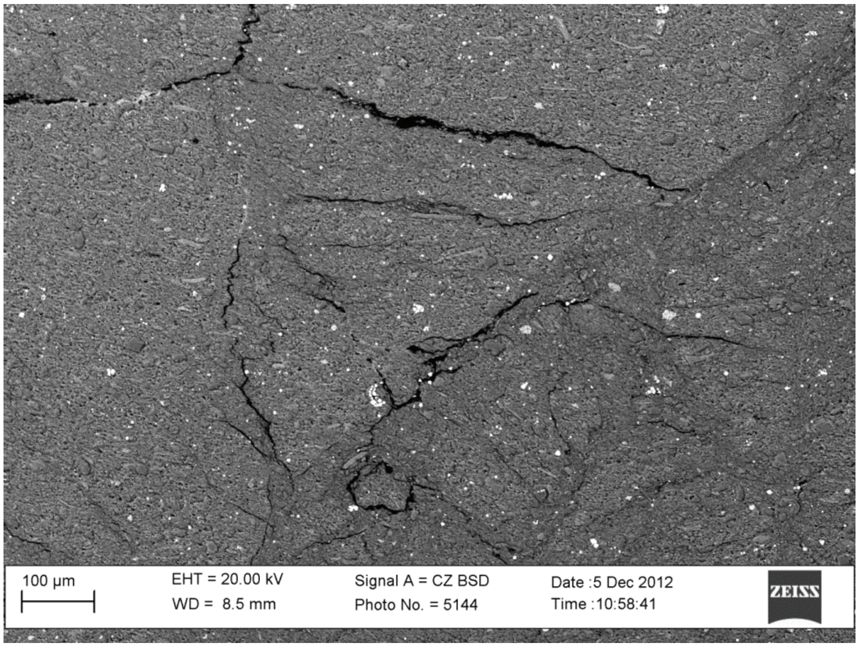


b.) Detail of a.). The halite infill is incomplete, some space remains open on the right side

Figure 12: SEM Images (backscatter mode) of Unsqueezed Sample DGR-4 610.48 (Blue Mountain Formation)

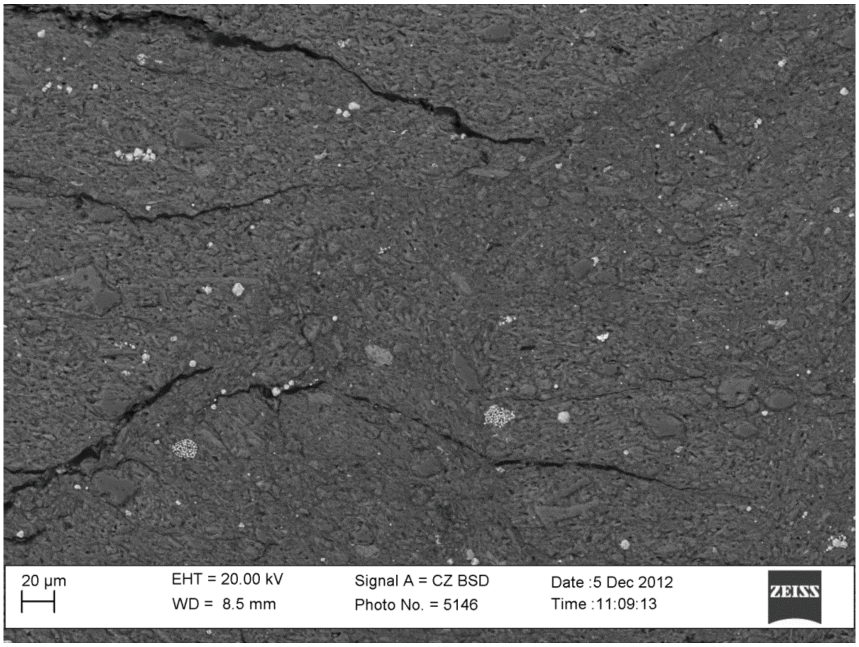


a.) Network of 2 sets of microfractures induced by squeezing

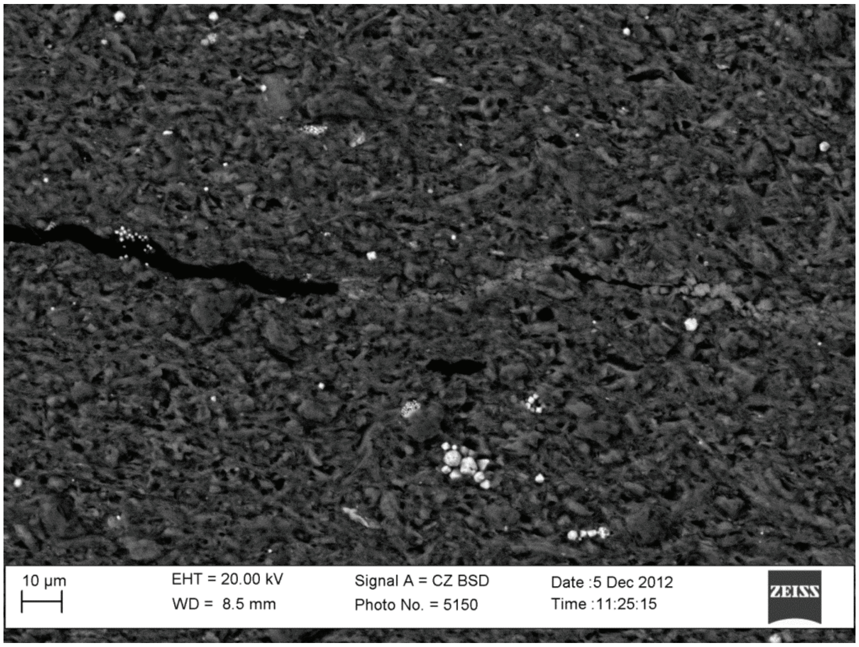


b.) Tectonised fabric with microfractures. Darker grey areas indicate destruction of the matrix fabric due to squeezing (formation of fault gouges). Bright area within microfracture in the upper left corner shows partial infill by halite

Figure 13: SEM Images (backscatter mode) of Sample DGR-4 610.48 (Blue Mountain Formation) after Squeezing



c.) Detail of b.). The lower right half of the image is a fault gouge



d.) Microfracture partially filled with halite

Figure 13 (continued)

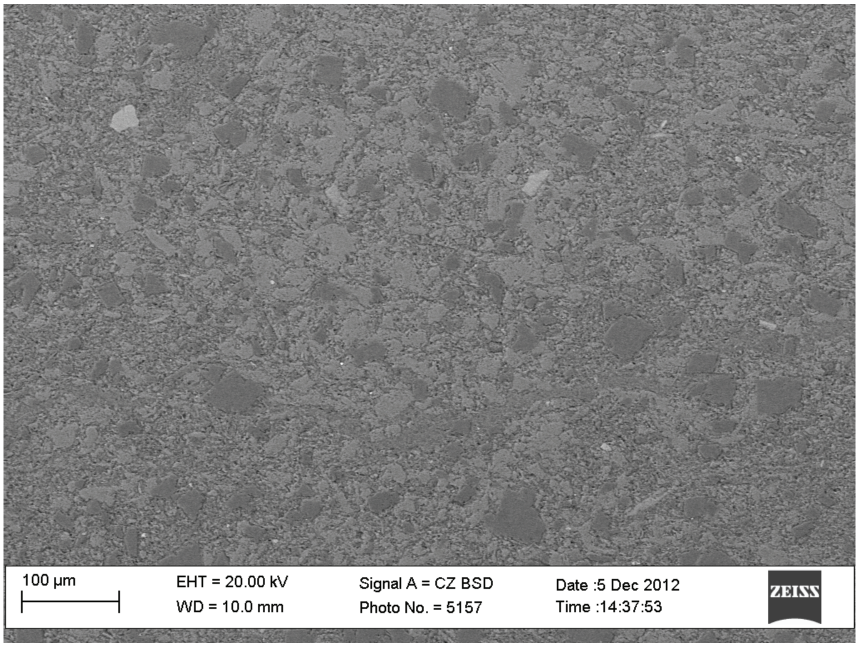
4.2.2 Sample DGR-6 512.15 (Queenston Formation)

Unsqueezed rock

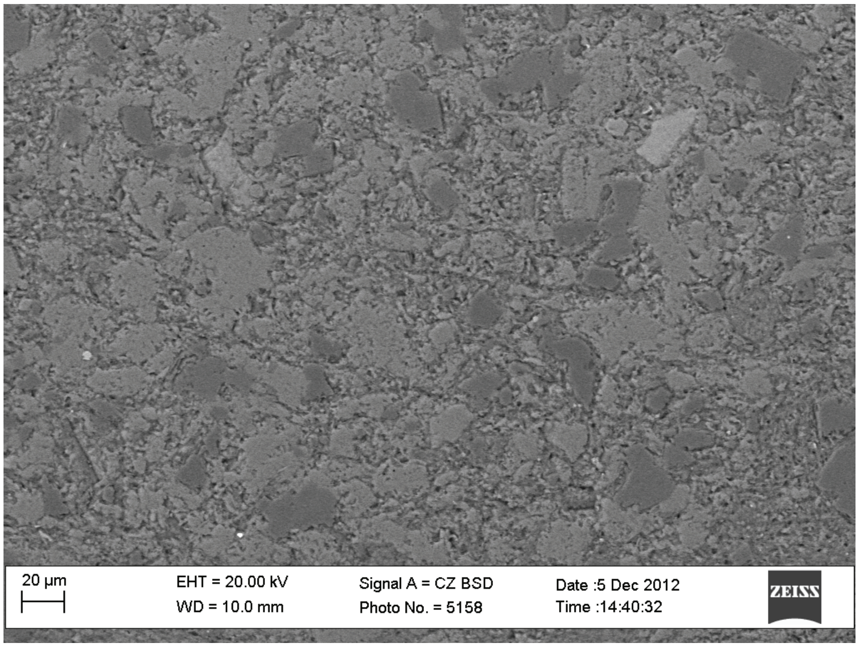
- Massive, fine-grained fabric, rich in carbonates (Figure 14a, b).
- Trace phases identified: apatite, Ti-oxide.
- No microfractures and no soluble minerals identified.

Squeezed rock

- Intensely microfractured (Figure 15a).
- Fabric of the matrix is partially disintegrated (fault gouges; Figure 15b, c). Carbonate and quartz clasts are embedded in a clay-rich ground mass.

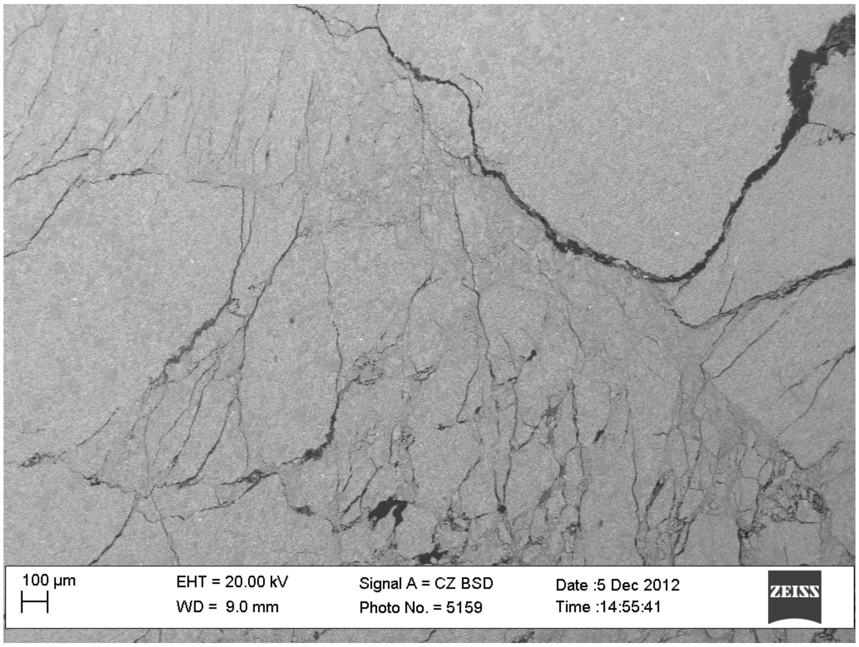


a.) Massive fabric; light grains are apatite

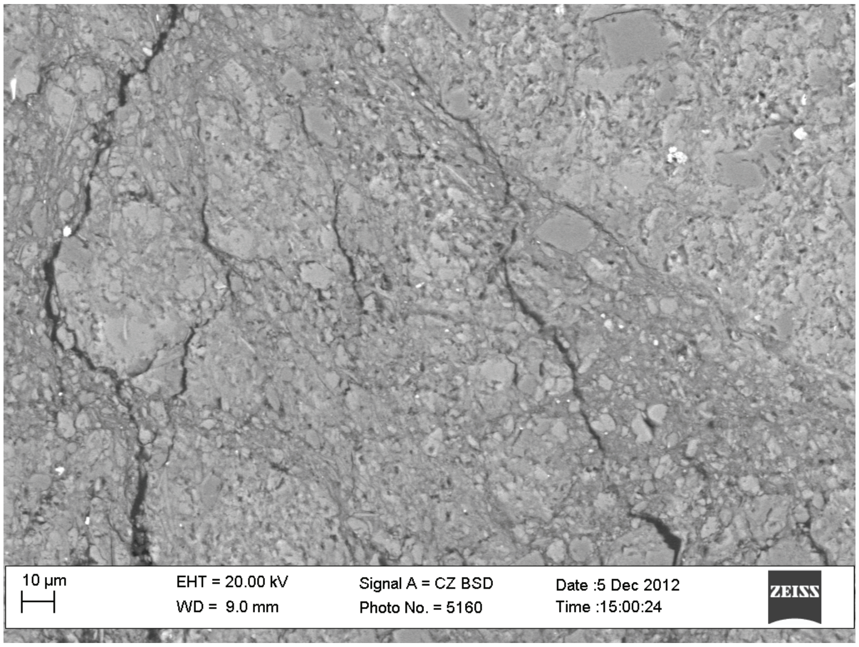


b.) Detail of a.)

Figure 14: SEM Images (backscatter mode) of Unsqueezed Sample DGR-6 512.15 (Queenston Formation)

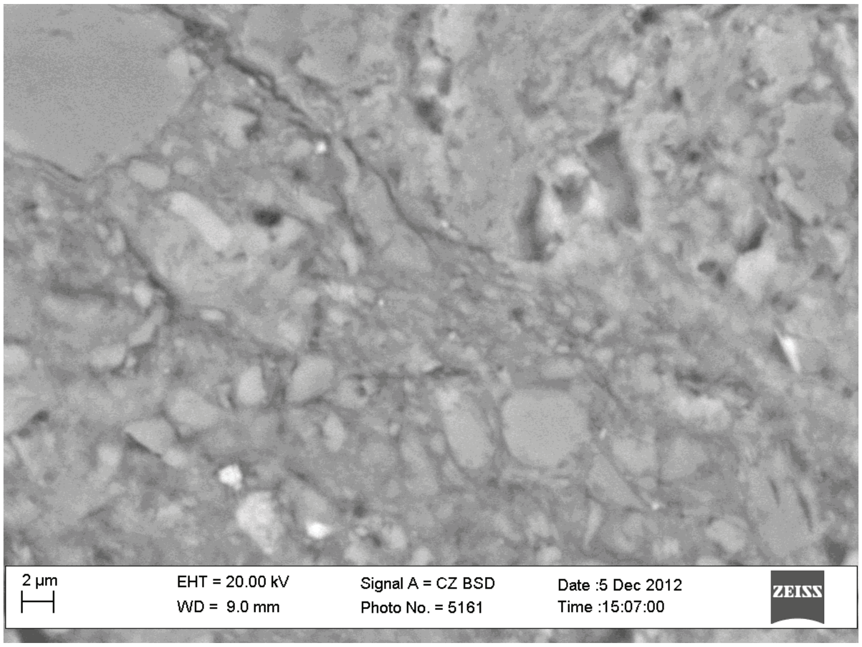


a.) Intense microfracturing



b.) Matrix destroyed due to fault gouge. Intact portion of the matrix in upper right corner

Figure 15: SEM Images (backscatter mode) of Sample DGR-6 512.15 (Queenston Formation) after Squeezing



c.) Detail of fault gouge from b.), showing carbonate clasts embedded in a clay-rich ground mass

Figure 15 (continued)

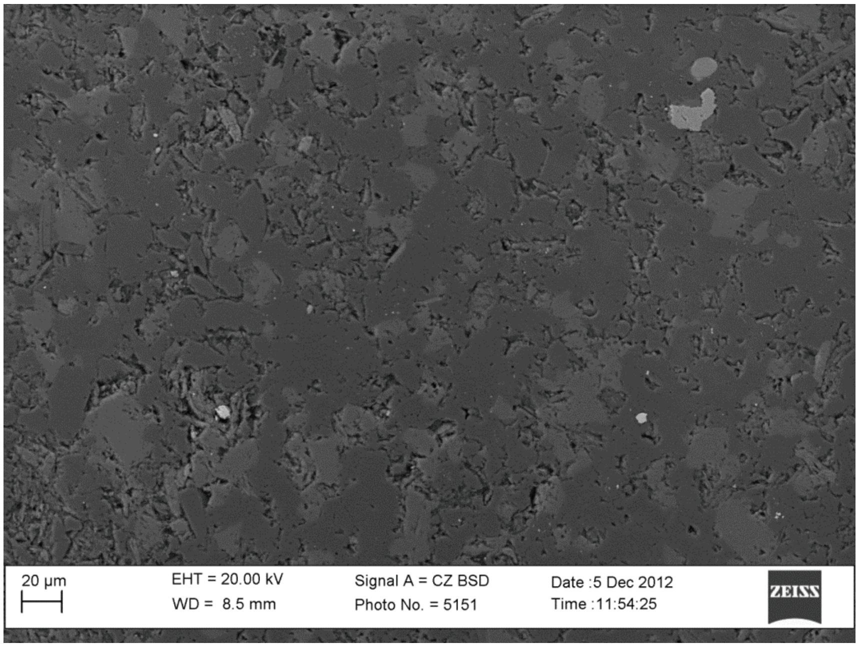
4.2.3 Sample DGR-5 225.68 (Salina F Unit)

Unsqueezed rock

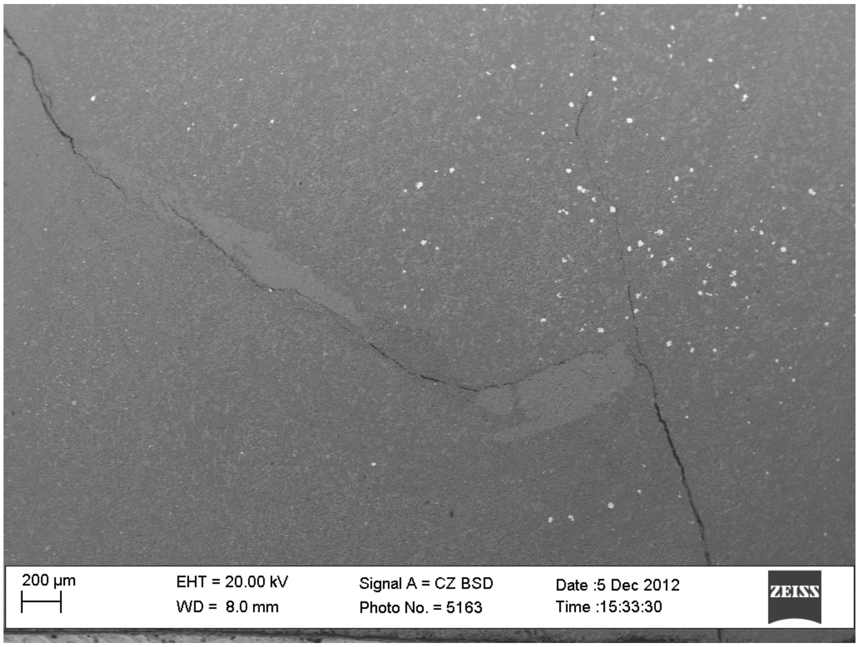
- Fine-grained, massive rock fabric (Figure 16a).
- Trace minerals identified: muscovite, pyrite, Ti-oxide.
- Trace amounts of gypsum in a natural vein.

Squeezed rock

- Highly tectonised rock with 3 sets of microfractures (conjugate system, Figure 17a).
- Partial disintegration of the matrix to fault gouge; grain-size reduction (Figure 17b).
- Veins containing gypsum are deformed, consistent with their natural origin (i.e., not a product of porewater evaporation).

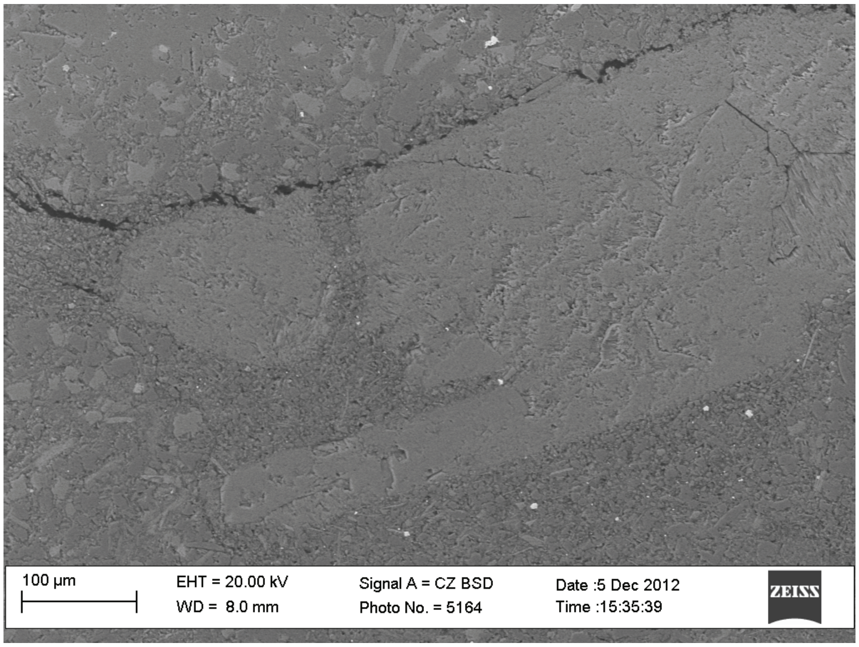


a.) Massive rock matrix



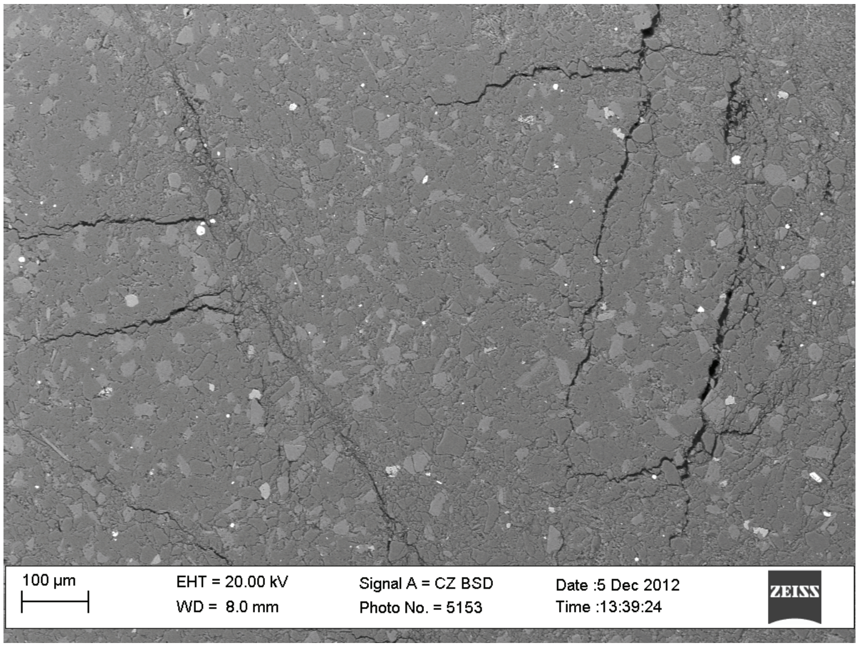
b.) Natural vein containing gypsum (lighter grey)

Figure 16: SEM Images (backscatter mode) of Unsqueezed Sample DGR-5 225.68 (Salina F Unit)

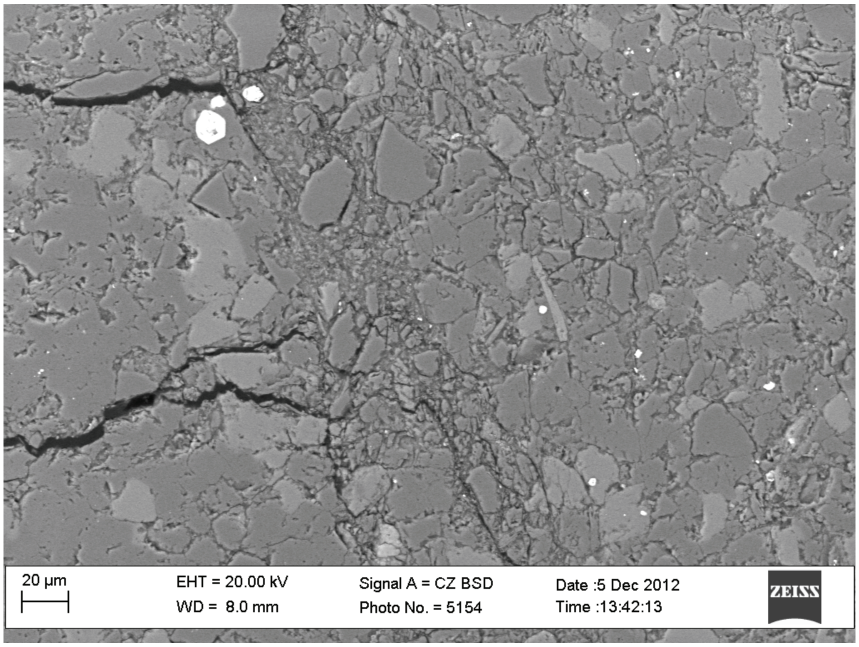


c.) Detail of b.). The shape of the gypsum crystal indicates a natural origin (i.e., not an effect of porewater evaporation)

Figure 16 (continued)



a.) Three fracture sets, partial gouge formation along them



b.) Detail of a.) showing disintegration of rock fabric and grain-size reduction

Figure 17: SEM Images (backscatter mode) of Sample DGR-5 225.68 (Salina F Unit) after Squeezing

4.3 WATER AND POREWATER CONTENTS

As presented in Section 3.3, water contents of the rock materials were measured both at CRIEPI (unsqueezed rock pieces, 15–30 g each) and at RWI (squeezed rock, 400–450 g each).

As shown in Table 4, water contents obtained at CRIEPI exceed those of RWI by 0.64–1.15 wt.%. This difference corresponds to a water-mass deficit of about 2.5–5.2 g in each of the squeezed cores (see sample masses in Table 7). The following points need to be considered in this context:

- The deficit of the water mass in the squeezed samples exceeds that of the water that was previously squeezed (0–0.68 g, Table 7), so this cannot serve as an explanation.
- The deficit also exceeds the dead volume of the system (see Section 3.1). Note that for sample DGR-6 512.15, the water-mass deficit in the squeezed core amounts to 5.21 g, whereas no moisture could be identified on the filters. This means that at least for this sample the dead volume was not filled with squeezed water.
- Evaporation of water from the sample may have taken place since the time of the initial sample preparation at CRIEPI. However, the total contact time with air was limited to about 20 minutes before each experiment, and then the sample was mounted in the squeezing rig where evaporation is not an issue. During disassembly of each experiment, the samples were exposed to air for about 5 minutes only. The masses of the cores after squeezing were measured at CRIEPI and, after shipping to Switzerland, at RWI. These two measurements mostly coincide within ±0.1 g (DGR-5 225.68: 0.27 g), which shows that evaporation since the finalisation of the squeezing tests is at best minor and in any case cannot account for the water-mass deficit. Also note that the same experimental protocol was applied to squeezing tests for Mesozoic rocks from the Schlattingen borehole in northern Switzerland (Wersin et al. 2013). The stable-isotope ratios in the squeezed waters from those cores were similar or slightly more negative than those obtained from the diffusive-exchange technique. This also speaks against evaporation as a relevant process.

At this stage, the differences in the water contents cannot be satisfactorily explained. The RWI data are used for further interpretation because they refer to the same piece of rock material from which all other laboratory data were obtained, and also because the mass of the RWI samples is substantially larger than that of the adjacent rock pieces subjected to drying at CRIEPI.

Given the high salinity of the porewaters, the porewater contents (i.e., the mass fraction of water and dissolved ions in the rock) are expected to markedly exceed the water contents. They are calculated according to equations (3) and (4), which require knowledge of the total salinity of the porewater. Salinity for sample DGR-4 610.48 was taken from the total dissolved solids of the squeezed water (see below), and the same value was also applied for sample DGR-6 512.15. For the shallower sample DGR-5 225.68, a salinity of 0.05 $\mathrm{kg/kg_{porewater}}$ was roughly estimated based on the general geochemical trends (Clark et al. 2010). The resulting values for porewater contents are listed in Table 5.

Table 4: Water Contents Based on Gravimetric Water-loss Measurements at CRIEPI and at RWI

Sample ID	Unit	Gravimetric data produced at CRIEPI on unsqueezed material (immediately adjacent to core subjected to squeezing)		Gravimetric data produced at RWI on squeezed core	
		WC_{wet} [wt.%]	WC_{dry} [wt.%]	WC_{wet} [wt.%]	WC_{dry} [wt.%]
DGR-4 610.48 I	Blue Mountain Formation	3.87	4.02	2.81	2.90
DGR-4 610.48 II	Blue Mountain Formation			2.79	2.87
DGR-6 512.15	Queenston Formation	3.30	3.41	2.15	2.20
DGR-5 225.68	Salina F Unit	4.31	4.50	3.67	3.81

Table 5: Porewater Contents Based on Water-loss Measurements at CRIEPI and at RWI

Sample ID	Unit	Assumed salinity used for calculation [kg/kg$_{pw}$]	Gravimetric data produced at CRIEPI on unsqueezed material (immediately adjacent to core subjected to squeezing)		Gravimetric data produced at RWI on squeezed core	
			PWC_{wet} [wt.%]	PWC_{dry} [wt.%]	PWC_{wet} [wt.%]	PWC_{dry} [wt.%]
DGR-4 610.48 I	Blue Mountain Formation	0.2725	5.32	5.62	3.87	4.02
DGR-4 610.48 II	Blue Mountain Formation				3.84	3.99
DGR-6 512.15	Queenston Formation	0.2725	4.54	4.76	2.95	3.04
DGR-5 225.68	Salina F Unit	0.05	4.54	4.76	3.86	4.02

4.4 GRAIN DENSITY AND WATER-LOSS POROSITY

Grain density, ρ_g, was measured on materials from the squeezed core, and data are listed in Table 6. Porewater loss porosity can be calculated from porewater contents and grain density using equation (5) and the results are given in Table 6.

The porewater density, ρ_{pw}, is also needed for the calculation of porewater loss porosity. For sample DGR-4 610.48, an artificial porewater was produced with a composition close to that of the water squeezed from this sample (see Section 4.8). The density of this water was measured and used for the calculation of porewater loss porosity of sample DGR-4 610.48. The same density was also used for sample DGR-6 512.15. A lower salinity is expected for the sample from the Salina F Unit (DGR-5 225.68), and the value listed in Table 6 is a rough estimation.

Table 6: Grain Density and Water-loss Porosity Data

Sample ID	Unit	Grain density of squeezed rock [g/cm3]	Standard deviation of individual measurements [g/cm3]	Number of measurements	Assumed porewater density [g/cm^3]	Water-loss porosity based on gravimetric data produced at CRIEPI on unsqueezed material (immediately adjacent to core subjected to squeezing) [vol.%]	Water-loss porosity based on gravimetric data produced at RWI on squeezed core [vol.%]
DGR-4 610.48 I	Blue Mountain Formation	2.701	0.011	2	1.233	11.0	8.1
DGR-4 610.48 II	Blue Mountain Formation	2.703	0.018	2	1.233	11.0	8.0
DGR-6 512.15	Queenston Formation	2.682	0.002	2	1.233	9.4	6.2
DGR-5 225.68	Salina F Unit	2.713	0.002	2	1.043	11.0	9.5

4.5 RECOVERY OF WATER IN SQUEEZING TESTS

Table 7 provides an overview of the squeezed water masses. Only for sample DGR-4 610.48 could 0.68 g water be collected at the highest pressure of 500 MPa, whereas no water was obtained for the other samples. However, for sample DGR-5 225.68, the filters adjacent to the sample were wet. This means that some water was squeezed out of the sample, but its mass was insufficient to be collected in the syringes. In the case of sample DGR-6 512.15, the filters were dry. Given the success of the experiment with sample DGR-4 610.48 from the Blue Mountain Formation, a second piece from the same core was prepared and squeezed. Another 0.20 g of water was obtained at 500 MPa from this experiment.

After the squeezing experiment, sample DGR-4 610.48 was perfectly cylindrical (see Figure 18a), meaning that the rock material (initially a polygonal prism) was "pressed to shape" during the experiment. In contrast, this did not happen for the other two samples. As shown in Figure 18b and 18c, large spaces remain open between brecciated components in these samples. These spaces probably remained air-filled throughout the experiment, meaning that the squeezing pressure exerted on the rock was not fully transmitted to the pore fluid, at least not throughout the sample.

The successful sample, DGR-4 610.48, is the one with the highest clay-mineral content (Table 3), i.e., with the lowest mechanical strength. It is worth noting that sample DGR-5 225.68 (Salina F Unit) has a slightly higher porosity (Table 6) but did not yield any water during squeezing due to its high carbonate content and related high mechanical strength. For future campaigns, selection criteria should include high water content, as well as high clay-mineral and low carbonate contents.

4.6 CHEMICAL COMPOSITION OF SQUEEZED WATER

Chemical analyses of the porewaters squeezed from two pieces of sample DGR-4 610.48 (Blue Mountain Formation) are listed in Table 8. The results are near-identical and yield <u>Ca</u>-Na-<u>Cl</u> brines with TDS = 272.5 g/kg$_{pw}$. SO_4^{2-}, F^- and NO_3^- concentrations are below the detection limit of 160 mg/kg$_{pw}$[1]. The Cl^-/Br^- ratio around 80 is much lower than that of modern sea water (290 in mass units). Due to the small masses of the squeezed waters, alkalinity and pH could not be measured. The low SO_4^{2-} contents indicate that pyrite oxidation and/or sulphate dissolution have not been relevant processes since the cores were collected, sealed and stored.

Table 7: Overview of Water Masses Collected During Squeezing

Depth [m]	Unit	Core mass before squeezing [g]	Mass squeezed at 200 MPa [g]	Mass squeezed at 300 MPa [g]	Mass squeezed at 400 MPa [g]	Mass squeezed at 500 MPa [g]	Total mass squeezed [g]
DGR-4 610.48 I	Blue Mountain Formation	429.06	0	0	0	0.68	0.68
DGR-4 610.48 II	Blue Mountain Formation	393.08	0	0	0	0.20	0.20
DGR-6 512.15	Queenston Formation	453.11	0	0	0	0	0
DGR-5 225.68	Salina F Unit	398.14	0	0	0	0	0*

* Filters on both sides of the sample were wet

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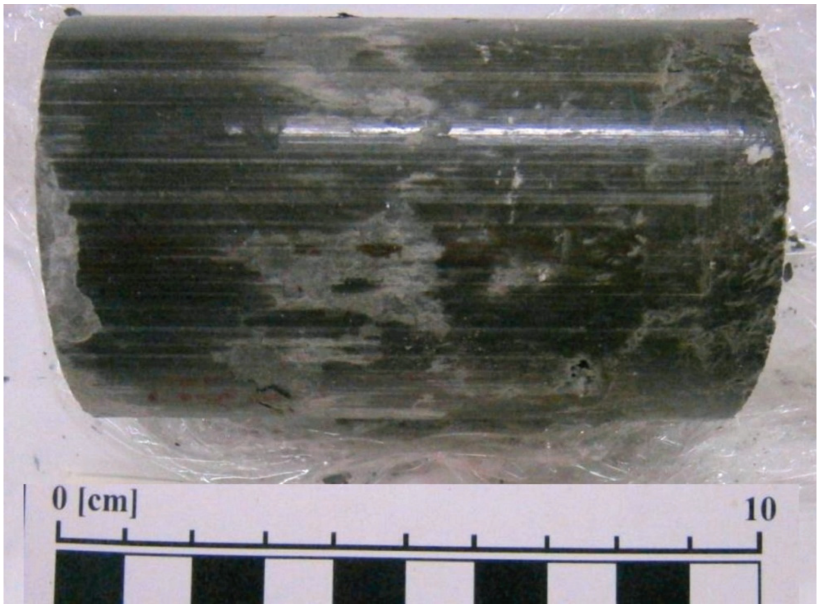
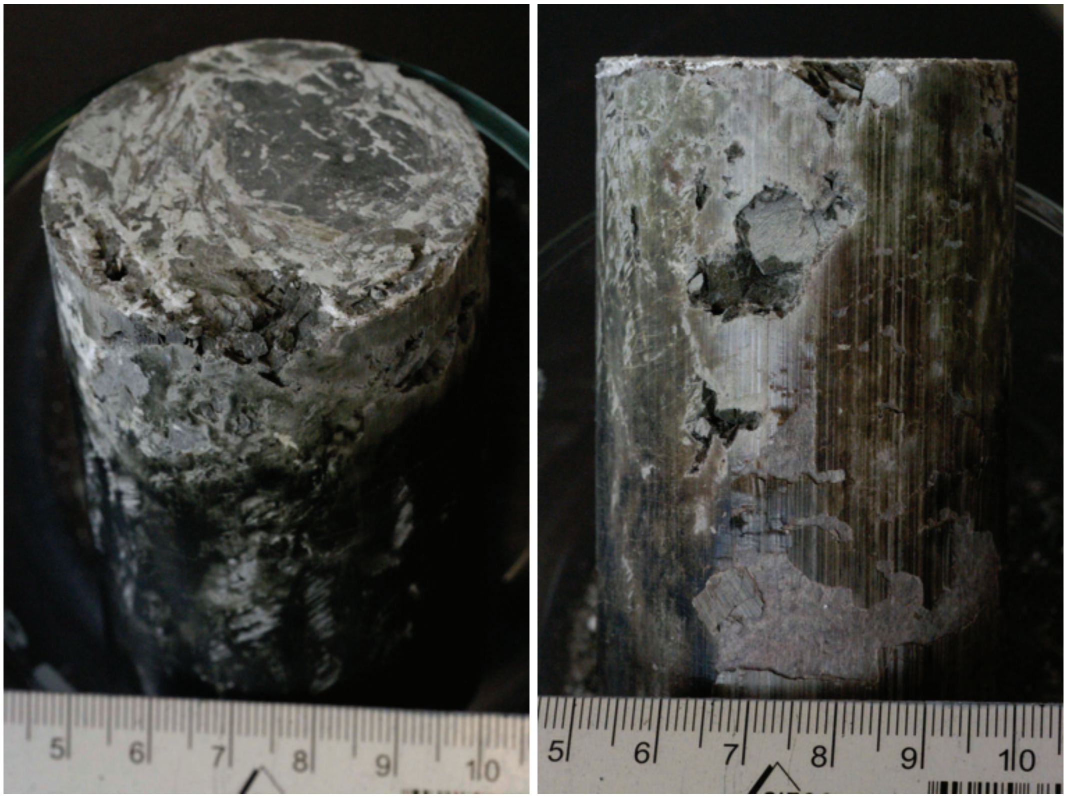
[1] Detection limit is 0.016 mg/L (Section 3.5) multiplied by the dilution factor of 10,000



a.) Sample DGR-4 610.48 I



b.) Sample DGR-5 225.68

c.) Sample DGR-6 512.15

Figure 18: Sample Materials After Removal from the Squeezing Rig

Table 8: Chemical Composition of Waters Squeezed at 500 MPa

Sample ID	Unit	Na^+ [mg/kg$_{pw}$]	K^+ [mg/kg$_{pw}$]	Ca^{2+} [mg/kg$_{pw}$]	Mg^{2+} [mg/kg$_{pw}$]	Sr^{2+} [mg/kg$_{pw}$]	F^- [mg/kg$_{pw}$]	Cl^- [mg/kg$_{pw}$]	Br^- [mg/kg$_{pw}$]	NO_3^- [mg/kg$_{pw}$]	SO_4^{2-} [mg/kg$_{pw}$]	Cl/Br
DGR-4 610.48 I	Blue Mountain Formation	38191	2259	55725	4741	1828	<160	167591	2083	<160	<160	80.5
DGR-4 610.48 II	Blue Mountain Formation	38020	2264	55545	5001	1850	<160	167922	2082	<160	<160	80.7

4.7 CHEMICAL COMPOSITION OF AQUEOUS EXTRACTS OF SQUEEZED CORE MATERIAL

Squeezed cores were subjected to aqueous extraction at a S:L ratio of 1, and the chemical composition of the extract solutions are listed in Table 9. The water types differ between the samples and are Ca-Na-(Mg)-Cl-(SO_4) for sample DGR-4 610.48 (Blue Mountain Formation), Ca-Na-(K)-(Mg)-Cl-SO_4 for sample DGR-6 512.15 (Queenston Formation) and Ca-Mg-(Na)-(K)-SO_4-(Cl) for sample DGR-5 225.68 (Salina F Unit). The ion ratios in the aqueous extracts and in the squeezed waters of sample DGR-4 610.48 differ substantially, indicating that 1) water/rock interactions (such as mineral dissolution and ion exchange) took place during aqueous extraction, and 2) that recalculation of aqueous-extract data to porewater concentrations (using the porewater content) is not feasible, at least for any reactive components.

Aliquots of the two cores from sample DGR-4 610.48 were both subjected to aqueous extraction for 10 minutes and for 24 hours. As shown in Table 9, the resulting concentrations in the extracts are identical, within analytical error (±5 %), for the two extraction times. Exceptions are Mg^{2+} and alkalinity, whose concentrations increase with extraction time, most probably reflecting ongoing dissolution of carbonate minerals. SO_4^{2-} concentrations also increase, and this is most likely due to the dissolution of pyrite (note that extraction was performed under atmospheric conditions).

Table 9: Chemical Composition of Aqueous Extracts of Squeezed Cores

Sample ID	Unit	Extraction time	Na^+ [mg/kg$_{pw}$]	K^+ [mg/kg$_{pw}$]	Ca^{2+} [mg/kg$_{pw}$]	Mg^{2+} [mg/kg$_{pw}$]	Sr^{2+} [mg/kg$_{pw}$]	F^- [mg/kg$_{pw}$]	Cl^- [mg/kg$_{pw}$]	Br^- [mg/kg$_{pw}$]	NO_3^- [mg/kg$_{pw}$]	SO_4^{2-} [mg/kg$_{pw}$]	Total alkalinity [meq/kg$_{pw}$]	Total alkalinity as HCO_3^-[mg/kg$_{pw}$]	Cl/Br
DGR-4 610.48 I	Blue Mountain Formation	10 min	1514	870	1555	189	37.2	<1.6	5774	55.8	<1.6	769	1.28	78.1	103.5
		24 h	1524	844	1571	224	38.1	<1.6	5763	56.9	<1.6	871	1.39	84.8	101.3
DGR-4 610.48 II	Blue Mountain Formation	10 min	1553	824	1591	168	40.3	<1.6	5733	56.6	<1.6	804	1.27	77.5	101.4
		24 h	1529	795	1609	201	41.1	<1.6	5754	57.2	<1.6	897	1.41	86.0	100.7
DGR-6 512.15	Queenston Formation	24 h	1005	1025	1469	289	19.8	<1.6	4603	53.7	<1.6	1755	0.93	56.7	85.7
DGR-5 225.68	Salina F Unit	24 h	359	582	582	282	<10	11.0	589	2.53	<1.6	3165	2.56	156.2	232.8

4.8 ISOTOPIC ANALYSIS OF SQUEEZED WATER

In order to reduce the uncertainties related to the measurement of water-isotope ratios in brines, a two-step procedure was adopted.

4.8.1 First Step

In the first step, the potential effect of high salinity on the measurement of the isotope ratios was tested. For this purpose, Suprapur water was used to prepare an artificial porewater whose composition closely approaches that of the squeezed water. Table 10 shows both the recipe and the ion-chromatographic analysis of the artificial porewater (APW). In total, 1 kg solution was prepared from Suprapur water, NaCl, NaBr, KCl, $CaCl_2$ and $MgCl_2$. The hygroscopic salts $CaCl_2$ and $MgCl_2$ were dried at 105 °C for 4 h and added to the solution in a glovebox in order to minimise the amount of hydration water on these salts.

The Suprapur water and the APW were then analysed with a Picarro CRDS isotope analyser at Hydroisotop GmbH (Schweitenkirchen, Germany). The same waters were also sent to the University of Lausanne (Switzerland) for a mass-spectrometric analysis. While the Suprapur water was analysed directly, the APW was treated with NaF and then distilled at 120°C (method described in De Haller et al. 2014; *in preparation*).

All results are listed in Table 11 and shown in Figure 19. The following conclusions can be drawn:

- When comparing the results of Suprapur water and APW in separation, it is evident that the data obtained from the two laboratories are near-identical. In particular, it is encouraging that the analysis of the brine is so consistent in both samples, given that different techniques were used.
- For both laboratories, the isotope ratios obtained for the APW are near-identical to those obtained for the Suprapur water from which it was prepared. This means that the addition of salt does not affect the analysis of the isotope ratios for either of the methods.

Table 10: Components of the Artificial Porewater (APW) Based on the Composition of Water Squeezed from Sample DGR-4 610.48

Ion	Analysis of squeezed water (average of DGR-4 610.48 I and DGR-4 610.48 II)		APW recipe: components in molar units						APW recipe: components in mass units						IC analysis of APW
	[mg/kg$_{sol}$]	[mmol/kg$_{sol}$]	NaBr [mmol/kg$_{sol}$]	KCl [mmol/kg$_{sol}$]	CaCl$_2$ [mmol/kg$_{sol}$]	MgCl$_2$ [mmol/kg$_{sol}$]	NaCl [mmol/kg$_{sol}$]	Sum ions [mmol/kg$_{sol}$]	NaBr [mg/kg$_{sol}$]	KCl [mg/kg$_{sol}$]	CaCl$_2$ [mg/kg$_{sol}$]	MgCl$_2$ [mg/kg$_{sol}$]	NaCl [mg/kg$_{sol}$]	Sum ions [mg/kg$_{sol}$]	[mg/kg$_{sol}$]
Na^+	38105	1657	26				1631	1657	599				37506	38105	37742
K^+	2261	58		58				58		2261				2261	2294
Ca^{2+}	55635	1388			1388			1388			55635			55635	52253
Mg^{2+}	4871	200				200		200				4871		4871	5066
Sr^{2+}	1839	21													<1000
F^-	<160	<8													<160
Cl^-	167756	4732		58	2776	401	1631	4866		2051	98427	14211	57840	172528	167513
Br^-	2082	26	26					26	2082					2082	2588
NO_3^-	<160	<3													<160
SO_4^{2-}	<160	<2													<160
Sum ions									2682	4312	154062	19082	95346	275484	

Table 11: Results of Water-isotope Analyses of Suprapur Water and Artificial Porewater (APW)

Suprapur water		Artificial porewater			Analytical errors	
δ^{18}O [‰$_{V\text{-}SMOW}$]	δ^{2}H [‰$_{V\text{-}SMOW}$]	δ^{18}O [‰$_{V\text{-}SMOW}$]	δ^{2}H [‰$_{V\text{-}SMOW}$]	Remarks	δ^{18}O [‰$_{V\text{-}SMOW}$]	δ^{2}H [‰$_{V\text{-}SMOW}$]
Picarro CRDS analysis at Hydroisotop (Germany)						
-11.45	-81.9	-11.52	-80.8	Automatic injection, 30 µL	±0.1	±1
-11.44 -11.40	-80.1 -80.8	-11.36	-80.2	Manual injection, 2 µL	±0.1	±1
Mass-spectrometric analysis at Uni. Lausanne (Switzerland)						
-11.5 -11.7 -11.5	-80.6 -80.3 -80.6	-11.6 -11.3 -11.5	-79.2 -79.6 -80.0	Direct analysis of Suprapur water, APW distilled at 120 °C	±0.08	±0.5

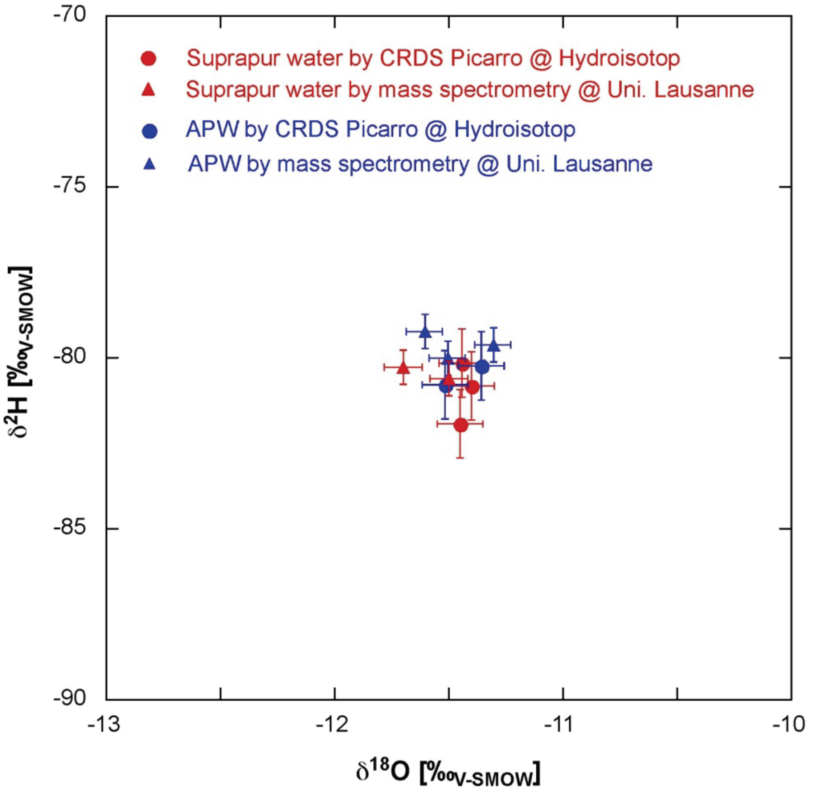


Figure 19: Comparison of Isotope Analyses of APW and the Suprapur Water

4.8.2 Second Step

Given the positive outcome of the tests with the Suprapur water and the APW, the squeezed waters were subsequently analysed at Hydroisotop using the Picarro CRDS instrument and adopting strictly the identical analytical protocol as that for the analysis of the APW. The results are listed in Table 12. Whereas the δ^{2}H values are fully consistent for the two subsamples, some variability is observed for δ^{18}O. This variability is not fully understood but may be related to the small sample mass (0.2 mL) that was available for sample DGR-4 610.48 II, in comparison to 0.5 mL available for DGR-4 610.48 I. Therefore, a stronger weighting is placed on the values determined for DGR-4 610.48 I.

Table 12: Stable-isotope Composition of Porewater Squeezed from Sample DGR-4 610.48 (Blue Mountain Formation)

Sample	$\delta^{18}O$ [‰$_{V\text{-}SMOW}$]	$\delta^{2}H$ [‰$_{V\text{-}SMOW}$]	Remarks
DGR-4 610.48 I	1.39	-35.6	Manual injection, 2 µL
DGR-4 610.48 II	3.32	-35.3	Manual injection, 2 µL

In order to build further confidence in the measurements of the stable-isotope ratios of the squeezed waters, two further actions were taken by Hydroisotop, as indicated below.

- Small volumes of the squeezed waters were diluted using Antarctic ice water (with a highly contrasting isotopic signature) and then analysed on the Picarro instrument. The motivation for the dilution included the following: 1) to gain more mass for isotope analysis, and 2) to analyse water mixtures with a lower salinity when compared to the squeezed waters. Results are documented in Table 13. Given the fact that the values listed for the extrapolated values for the squeezed waters include analytical errors on the analyses of the pure Antarctic ice water and the mixture plus an error on the dilution, the respective error margins are estimated at *ca.* ±0.4 ‰ for $\delta^{18}O$ and ±4 for $\delta^{2}H$. Three out of the 4 extrapolated data are identical, within error, to the data obtained for the undiluted samples. This adds further confidence to the measurements.

- An attempt was made to measure the remaining mass of water from DGR-4 610.48 I by mass spectrometry, applying a long (72 h) equilibration time. Unfortunately, reliable results could not be obtained due to the low sample volume, which was only 0.3 mL.

Table 13: Results of Water-isotope Analyses of Samples DGR-4 610.48 I and II Diluted with Antarctic Ice Water

Sample	V_{sample} [mL]	$V_{Ant.\ ice\ water}$ [mL]	Dilution ratio [mL/mL]	$\delta^{18}O_{Ant.\ ice\ water\ +\ sample}$ [‰V-SMOW]	$\delta^{2}H_{Ant.\ ice\ water\ +\ sample}$ [‰V-SMOW]	Extrapolated $\delta^{18}O_{sample}$ [‰V-SMOW]	Extrapolated $\delta^{2}H_{sample}$ [‰V-SMOW]
Antarctic ice water	0.25					-25.4	-189.8
	1.5					-25.58	-191.1
	0.25					-25.09	-188.4
	0.25					-25.26	-190.5
	1.5					-25.26	-186.6
Average Ant. ice water						-25.32	-189.3
DGR-4 610.48 I + Ant. ice water	0.0525	0.2024	1 : 3.855	-19.86	-156.9	1.18	-32.1
DGR-4 610.48 II + Ant. ice water	0.0670	0.2643	1 : 3.945	-19.22	-158.8	4.84	-38.6

5. DISCUSSION

5.1 GEOCHEMICAL MODELLING OF SQUEEZED WATER

The geochemical modelling code PHREEQC (Parkhurst & Appelo 1999) was used in conjunction with the pitzer.dat thermodynamic database to speciate the squeezed water from the Blue Mountain Formation and to provide predictions of saturation indices of soluble salts. Halite is only slightly undersaturated (SI = -0.11), consistent with the interpretation of SEM images that observed halite is due to the evaporation of porewater and is not present *in situ*. Because SO_4^{2-} in squeezed water is below detection, only maximum SI values can be calculated for sulphate minerals. When setting SO_4^{2-} contents to the value of the detection limit (160 $mg/kg_{porewater}$) for the sake of thermodynamic modelling, calculated SI is +0.1 for gypsum, +0.17 for anhydrite and +0.46 for celestite. These results are inconclusive because *in-situ* SO_4^{2-} concentrations substantially lower than the detection limit cannot be excluded and could result in lower, possibly negative saturation indices for sulphate minerals. A suite of further salts was also considered in the calculation, but all of these are strongly undersaturated.

5.2 RECALCULATION OF AQUESOUS EXTRACTION DATA TO POREWATER CONCENTRATIONS

Data from aqueous extraction of squeezed core can be recalculated to porewater concentrations provided: 1) the ion concentrations in the aqueous extract originate only from porewater (i.e., rock-water interactions before and during the experiment, such as ion exchange or mineral dissolution, are negligible), and 2) the whole water-accessible porosity is accessible to the ions. If these conditions are fulfilled, recalculation can be made using

$$C\left[\frac{mg}{kg_{pw}}\right]=\frac{C\left[\frac{mg}{kg_{rock}}\right]}{PWC_{dry}\left[\frac{kg_{pw}}{kg_{rock}}\right]} \tag{6}$$

with C = ion concentration and PWC_{dry} = gravimetric porewater content relative to the dry rock mass. The mass of the rock (kg_{rock}) includes the mass of salts precipitated from porewater during drying. As discussed in Section 4.3, porewater contents obtained at CRIEPI and at RWI differ considerably. Here, the data of RWI are used because they refer exactly to the same rock materials that have been subjected to aqueous extraction, and because the rock mass used for the measurement by far exceeds that used at CRIEPI. For the calculation, the porewater contents obtained on squeezed samples were corrected to account for the water lost during the squeezing process (including the sampled water and an assumed porewater mass in the dead volume of the squeezing apparatus). The recalculated porewater concentrations are given in Table 14. Note that equation (6) above only applies to conservative species, i.e., to halogens and possibly Na^+. For all other constituents, rock/water interaction may affect the aqueous extraction to some degree, so for these, the recalculation serves an illustrative purpose only, with limited relevance for the porewater.

Table 14: Compositions of Aqueous Extracts (extraction time of 24 h) Recalculated to Porewater Content (RWI data set); Data in Italics are Shown for Illustrative Purposes Only and Do Not Necessarily Reflect *In-situ* Concentrations (see text). Compositions of Waters Squeezed From Sample DGR-4 610.48 are Shown for Comparison, Followed by the Ion Ratios Based on the Two Methods

Sample ID	Unit		Na^+ [mg/kg$_{pw}$]	K^+ [mg/kg$_{pw}$]	Ca^{2+} [mg/kg$_{pw}$]	Mg^{2+} [mg/kg$_{pw}$]	Sr^{2+} [mg/kg$_{pw}$]	F^- [mg/kg$_{pw}$]	Cl^- [mg/kg$_{pw}$]	Br^- [mg/kg$_{pw}$]	NO_3^- [mg/kg$_{pw}$]	SO_4^{2-} [mg/kg$_{pw}$]	Total alkalinity [meq/kg$_{pw}$]	Total alkalinity as HCO_3^- [mg/kg$_{pw}$]
DGR-4 610.48 I	Blue Mountain Fm.	Aqueous extraction data recalculated to porewater content	37871	*20973*	*39039*	*5566*	*947*	*<40*	143208	1414	*<40*	*21644*	*34.5*	*2107*
DGR-4 610.48 II	Blue Mountain Fm.		38329	*19929*	*40334*	*5039*	*1030*	*<40*	144241	1434	*<40*	*22486*	*35.3*	*2156*
DGR-6 512.15	Queenston Fm.		33039	*33696*	*48293*	*9501*	*651*	*<40*	151321	1765	*<40*	*57695*	*30.6*	*1864*
DGR-5 225.68	Salina F Unit		8936	*14487*	*14487*	*7020*	*<249*	*274*	14661	63	*<40*	*78783*	*63.7*	*3888*
DGR-4 610.48 I	Blue Mountain Fm.	Squeezing data	38191	2259	55725	4741	1828	<160	167591	2083	<160	<160		
DGR-4 610.48 II	Blue Mountain Fm.		38020	2264	55545	5001	1850	<160	167922	2082	<160	<160		
DGR-4 610.48 I	Blue Mountain Fm.	Recalculated aqueous extraction data / squeezing data	0.99	*9.28*	*0.70*	*1.17*	*0.52*		0.85	0.68		large		
DGR-4 610.48 II	Blue Mountain Fm.		1.01	*8.80*	*0.73*	*1.01*	*0.56*		0.86	0.69		large		

5.3 COMPARISON OF RECALCULATED AQUEOUS EXTRACTION AND SQUEEZING DATA

In this section, the recalculated aqueous-leaching data are compared with the compositions obtained from squeezing of sample DGR-4 610.48 (see Table 14).

- Cl^- and Br^- concentrations based on aqueous extraction data recalculated to porewater content are below those obtained from squeezing. This is usually interpreted as due to an anion-exclusion effect, i.e., concentrations near negatively charged clay-mineral surfaces are lower than in the "free" porewater.

- The discrepancy between the porewater concentrations based on aqueous extraction and squeezing is stronger for Br^- than for Cl^-. If it is assumed that Br^- is conservative and that the exclusion effect is similar for both anions, then some Cl^- must have been added to the aqueous extract by dissolution of a mineral. There is no independent evidence for this, given the fact that the halite observed under the SEM in sample DGR-4 610.48 is considered to be due to porewater evaporation in the laboratory and not an *in-situ* phase. Moreover, halite is slightly undersaturated in the squeezed water (see Section 5.1). Alternatively, the difference could be due to differences in the mobility of Cl^- and Br^- during squeezing. This remains a hypothesis not supported by independent experience at this stage. In European studies, porewater salinities are always much lower, and Br^- concentrations are frequently close to or below detection limits.

- The ratios of the Cl^- and Br^- concentrations determined using the two methods (i.e., $Cl^-_{\text{aq. extraction}}/Cl^-_{\text{squeezing}}$ and $Br^-_{\text{aq. extraction}}/Br^-_{\text{squeezing}}$) are given at the bottom of Table 14 and are in the range 0.68–0.86. This is higher than the anion-accessible porosity fractions of around 0.5 that are typical for European shales with low-salinity porewaters (Mazurek et al. 2009, 2011). In brine systems, anion exclusion effects would be expected to be reduced because the electric double layer collapses at high salinity. Therefore, the range appears plausible for a shale containing brine. While the interpretation of the data is admittedly affected by uncertainties, it appears that some degree of anion exclusion may be present, even at the high salinities of the deep DGR porewaters. This conclusion affects, among others, the recalculation of porewater concentrations on the basis of aqueous extraction data, as done, for example, by Clark et al. (2010) and Hobbs et al. (2011). If an anion-exclusion effect were included in those calculations, the resulting porewater concentrations of anions would become higher.

- No exclusion effect is observed for Na^+, which is consistent with the fact that cations can access the whole water-accessible porosity, i.e., including the internal surfaces of clay minerals and the electric double layer.

- K^+ concentrations obtained from recalculation of aqueous extraction data are about an order of magnitude higher than those in squeezed waters. This can be interpreted as an indication that a K-bearing phase dissolved during extraction, or other processes during aqueous extraction. From general experience, K^+ data based on aqueous extraction tend to be unreliable, possibly due to the effects of rock-water interactions (e.g., cation exchange).

  Alternatively, the discrepancy may be related to currently not well understood phenomena of K^+ transport during squeezing. In a squeezing campaign targeted at Swiss Mesozoic sedimentary rocks (Wersin et al. 2013), water was collected at 200, 300, 400 and 500 MPa pressure. There are arguments supporting the hypothesis that the water squeezed at 200 MPa closely represents porewater. With increasing pressure, the concentrations of anions and alkali metals in squeezed waters decreased. This decrease was moderate for Cl^- and Na^+, whereas K^+ decreased by about 60 % between 200 and 500 MPa. The mechanisms related to this decrease are not understood but are likely related to differences in the mobility of ion species. A similar effect may play a role for the sample from the Blue Mountain Formation (where water was only obtained at 500 MPa), even though the discrepancy with the aqueous extraction data is much larger than 60%. This means that, in the case of K^+, highest-pressure squeezing data may be unreliable, or, at least, requires better understanding.

In conclusion, K^+ data, based both on squeezing and on aqueous extraction, are uncertain, and it is difficult at this stage to judge which of the methods is a better approximation of porewater concentrations.

- The Ca^{2+} concentrations based on recalculated aqueous extraction data are much lower than those in squeezed waters. In the mentioned Swiss squeezing campaign of Wersin et al. (2013), an increase of Ca^{2+} of up to 15% was observed between water squeezed at 200 and 500 MPa, and it was tentatively attributed to pressure solution of carbonate minerals during the experiment. The extent to which pressure solution may have affected the measured Ca^{2+} concentration in the sample from the Blue Mountain Formation is unknown, but it appears unlikely that this process could fully explain the discrepancy. The reason for the observed discrepancy is not fully understood at this stage. Similarly, the behaviour of Mg^{2+} and Sr^{2+} is not clear.

- The fact that SO_4^{2-} in squeezed waters is below detection is taken as evidence that oxidation of sulphide minerals did not play a role during squeezing experiments. On the other hand, the high SO_4^{2-} concentrations obtained from aqueous extraction are affected by dissolution of minerals, such as pyrite (the aqueous extraction experiments were performed under atmospheric conditions) or sulphate phases.

5.4 COMPARISON WITH LITERATURE DATA

Porewater data are available from boreholes DGR-3 and DGR-4 from Hobbs et al. (2011) and Clark et al. (2010). Ion data from both laboratories are based on the recalculation of aqueous extraction data to water contents and are given in molality units ($mmol/kg_{H2O}$). The data produced in this report (both analyses of squeezed water and data based on aqueous extraction) were, therefore, recalculated from units of mg/kg_{pw} to molalities for the sake of comparison with the existing data.

Chloride and bromide

As shown in Figure 20, both Cl^- and Br^- concentrations obtained here are within the respective ranges at the base of the Ordovician shales reported by Hobbs et al. (2011), even though the scatter of the data is considerable in the depth interval 600–700 m. Figure 21 shows that a similar consistency is obtained with Cl^- contents reported by Clark et al. (2010), even though the Cl^- concentration based on squeezing is slightly above the general trend. Br^- in squeezed water (36 $mmol/kg_{H2O}$) is slightly above the concentrations obtained by Clark et al. (2010) (not shown; range in the interval 600–700 m in DGR-4 is 17–33 $mmol/kg_{H2O}$). It is concluded that Cl^- and Br^- concentrations based on aqueous extraction are within the ranges of the literature data, whereas the values from squeezing are slightly higher when compared with the data set of Clark et al. (2010). Note that the recalculation of the aqueous extraction data from all sources implicitly assumes that anions can access the entire pore space. Inclusion of a limited anion-exclusion effect in the calculations would improve the consistency between these data and the concentration derived from squeezing.

Sodium

Figure 21 and Figure 22 show that the Na^+ concentration in squeezed water is consistent with that of both pre-existing data sets. This is in line with the fact that exclusion effects play no role for cations.

Potassium

The concentration of K^+ in squeezed water is about one order of magnitude lower than indicated in both data sets based on aqueous leaching (Figure 22 and Figure 23), and also is of lower magnitude than the value based on aqueous leaching of the squeezed sample itself. This discrepancy is currently not understood, and a short discussion is provided in Section 5.3.

Calcium

Ca^{2+} contents in the squeezed water are substantially higher than those based on aqueous extraction, including aqueous extraction of the squeezed sample itself (Figure 24 and Figure 25). A discussion of this observation is provided in Section 5.3.

Sulphate

SO_4^{2-} contents in the squeezed water are below the detection limit of 160 mg/kg$_{pw}$ (<2.3 mmol/kg$_{H2O}$). In the interval 600–700 m in DGR-4, Clark et al. (2010) report a range of 144–854 mmol/kg$_{H2O}$ (one sample with up to 8107 mmol/kg$_{H2O}$; Figure 25). Given the fact that SO_4^{2-} can be added to the solution during aqueous extraction experiments by dissolution of sulphate minerals or by sulphide oxidation, it is likely that the low value indicated by the squeezing value is a better proxy for porewater. Note that, given the fact that aqueous extraction of the squeezed sample was performed under atmospheric conditions, SO_4^{2-} contents are affected, at least, by oxidation and so provide overestimates of porewater concentrations.

Stable Isotopes of Water

Data from Hobbs et al. (2011), based on the diffusive-exchange method, as well as the vacuum-distillation data of Clark et al. (2010), are shown in Figure 26, in addition to the values of the squeezed water from the Blue Mountain Formation. The positive $\delta^{18}O$ values in the squeezed sample fit well into the trend indicated by the diffusive-exchange data of Hobbs et al. (2011), but are ≥6 per mil higher than the vacuum distillation data. Similarly, the δ^2H values are in line with the data of Hobbs et al. (2011) but clearly are higher relative to the trend of Clark et al. (2010) determined by vacuum distillation.

In a plot of $\delta^{18}O$ *vs.* δ^2H (Figure 27), the squeezed waters lie far right from the Global Meteoric Water Line, which is interpreted as a result of long residence time and water-rock interaction over geological time periods.

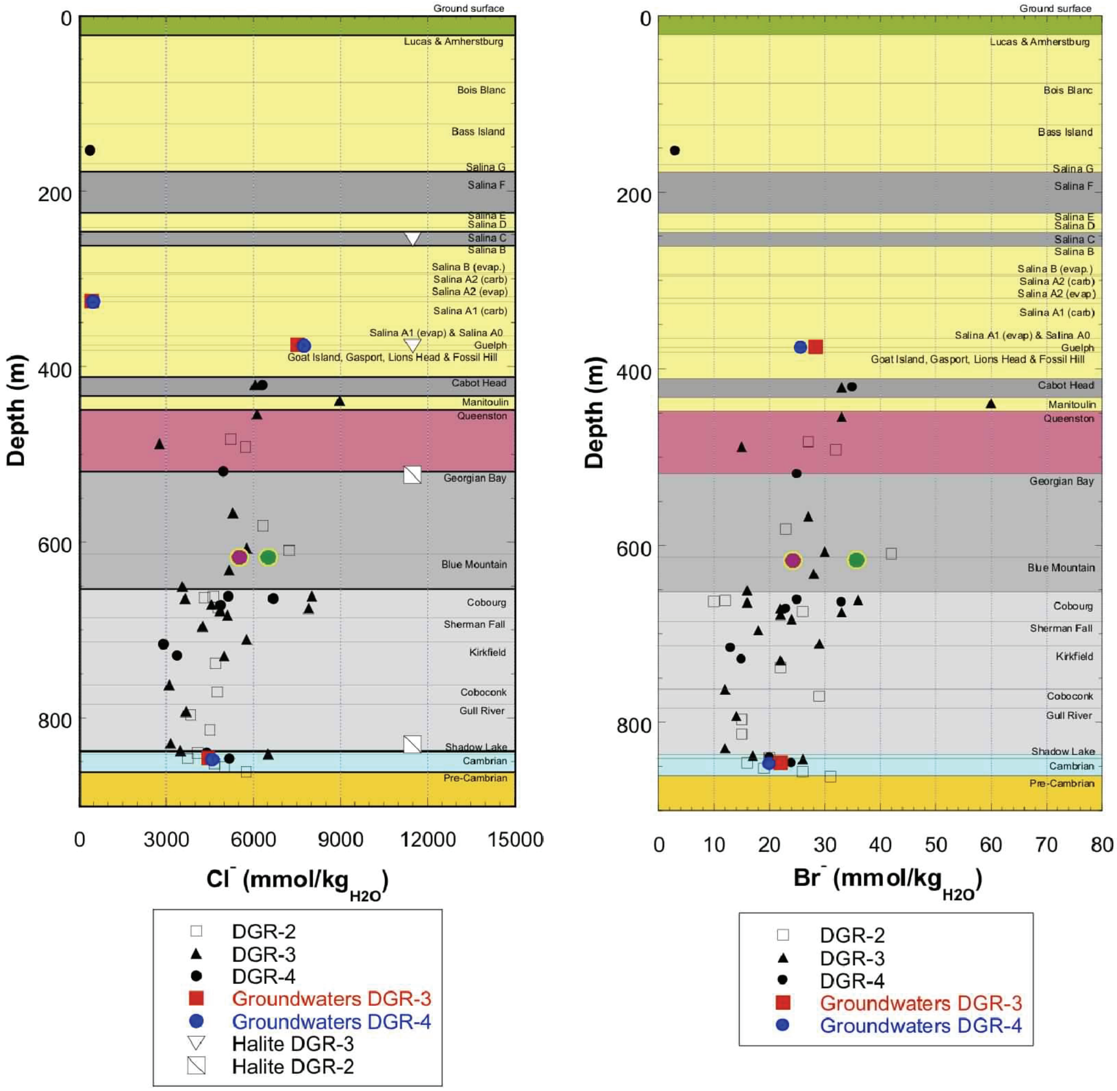


Figure 20: Cl$^-$ and Br$^-$ Concentrations in Porewater of Sample DGR-4 610.48 Based on Squeezing (large green circle) and Aqueous Extraction (large purple circle) in Comparison With Pre-existing Aqueous Extraction Data of Hobbs et al. (2011); Adapted from Hobbs et al. (2011)

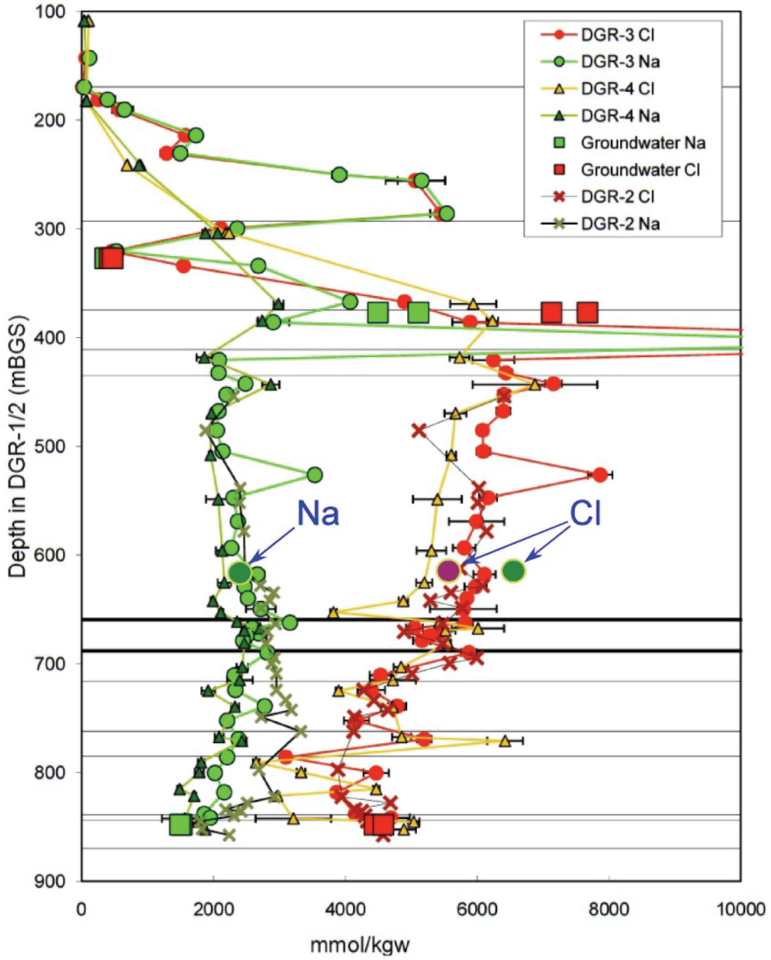


Figure 21: Na$^+$ and Cl$^-$ Concentrations in Porewater of Sample DGR-4 610.48 Based on Squeezing (large green circle) and Aqueous Extraction (large purple circle - not visible because of a complete overlap with the point for Na$^+$ from squeezing) in Comparison With Pre-existing Aqueous Extraction data of Clark et al. (2010); Adapted from Clark et al. (2010)

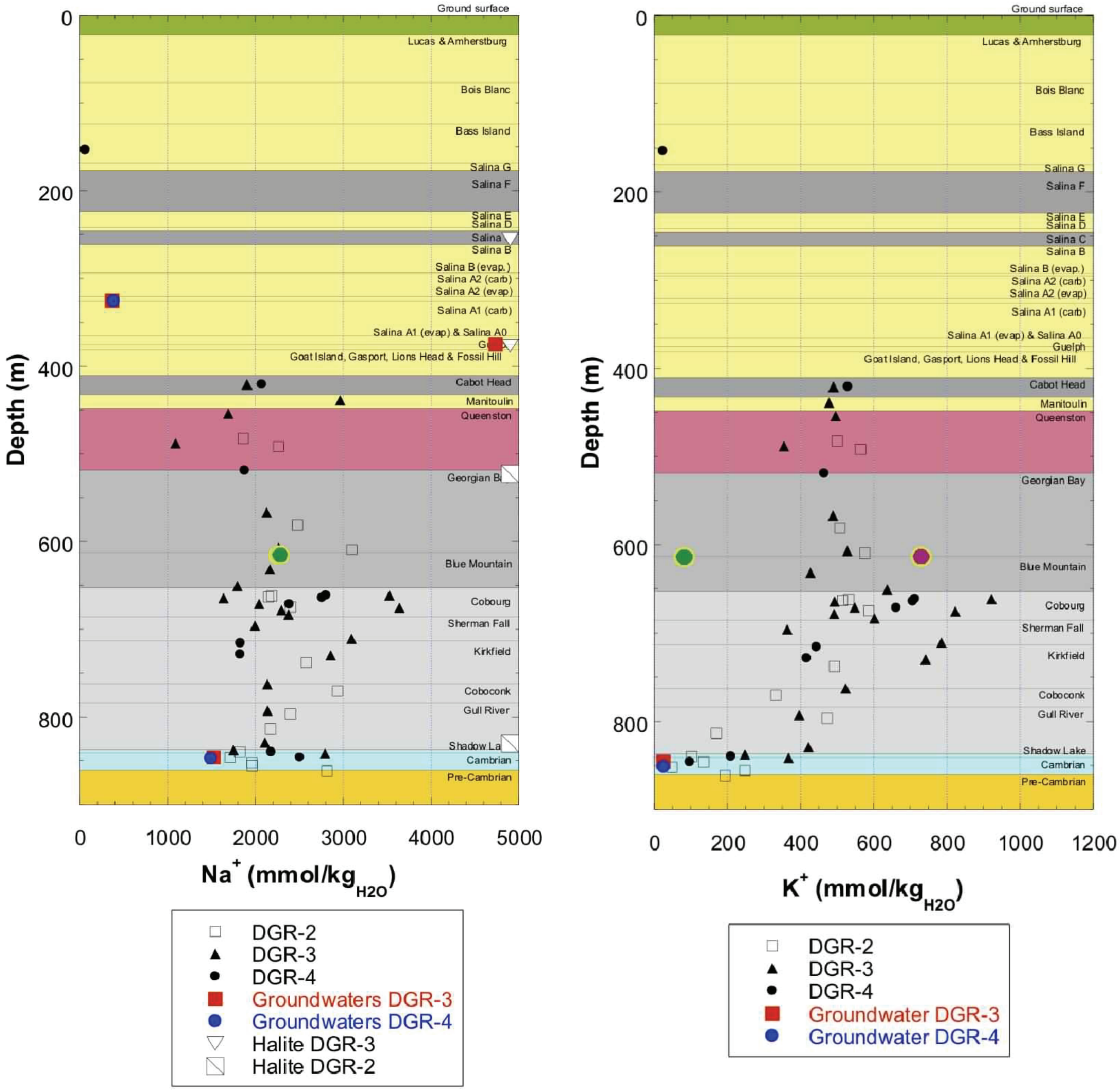


Figure 22: Na+ and K+ Concentrations in Porewater of Sample DGR-4 610.48 Based on Squeezing (large green circle) and Aqueous Extraction (large purple circle) in Comparison With Pre-existing Aqueous Extraction Data of Hobbs et al. (2011); In Graph for Na+, the Point Obtained from Aqueous Extraction is Not Visible Because of a Complete Overlap With the Point from Squeezing; Adapted from Hobbs et al. (2011)

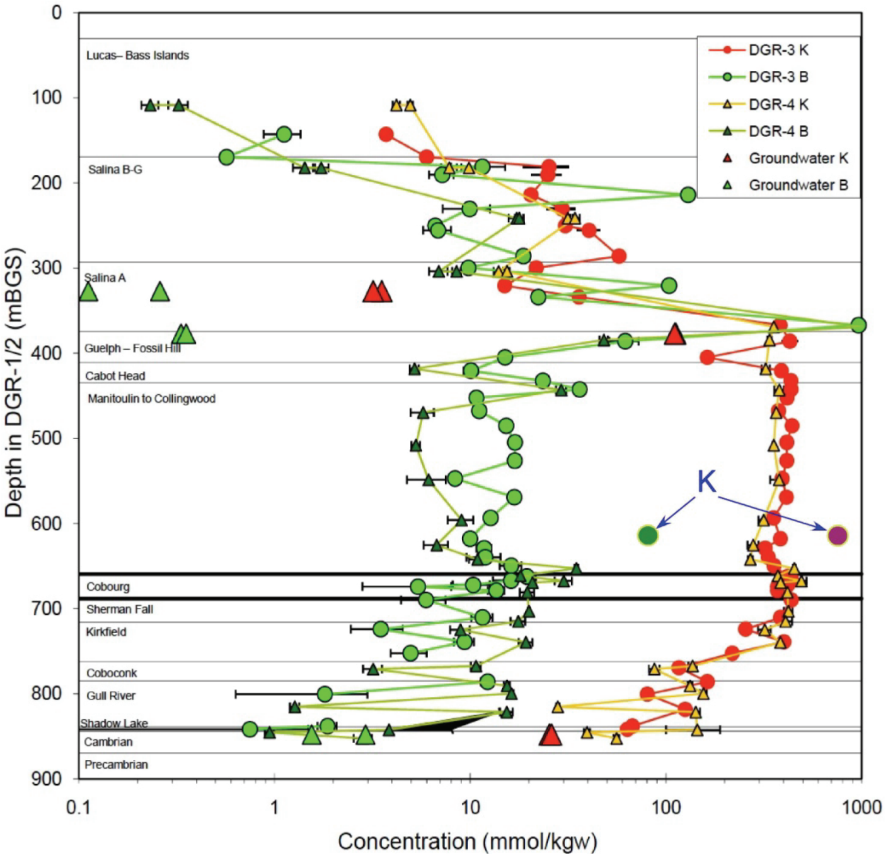


Figure 23: K^+ Concentration in Porewater of Sample DGR-4 610.48 Based on Squeezing (large green circle) and Aqueous Extraction (large purple circle) in Comparison With Pre-existing Aqueous Extraction Data of Clark et al*.* (2010); Adapted from Clark et al*.* (2010)

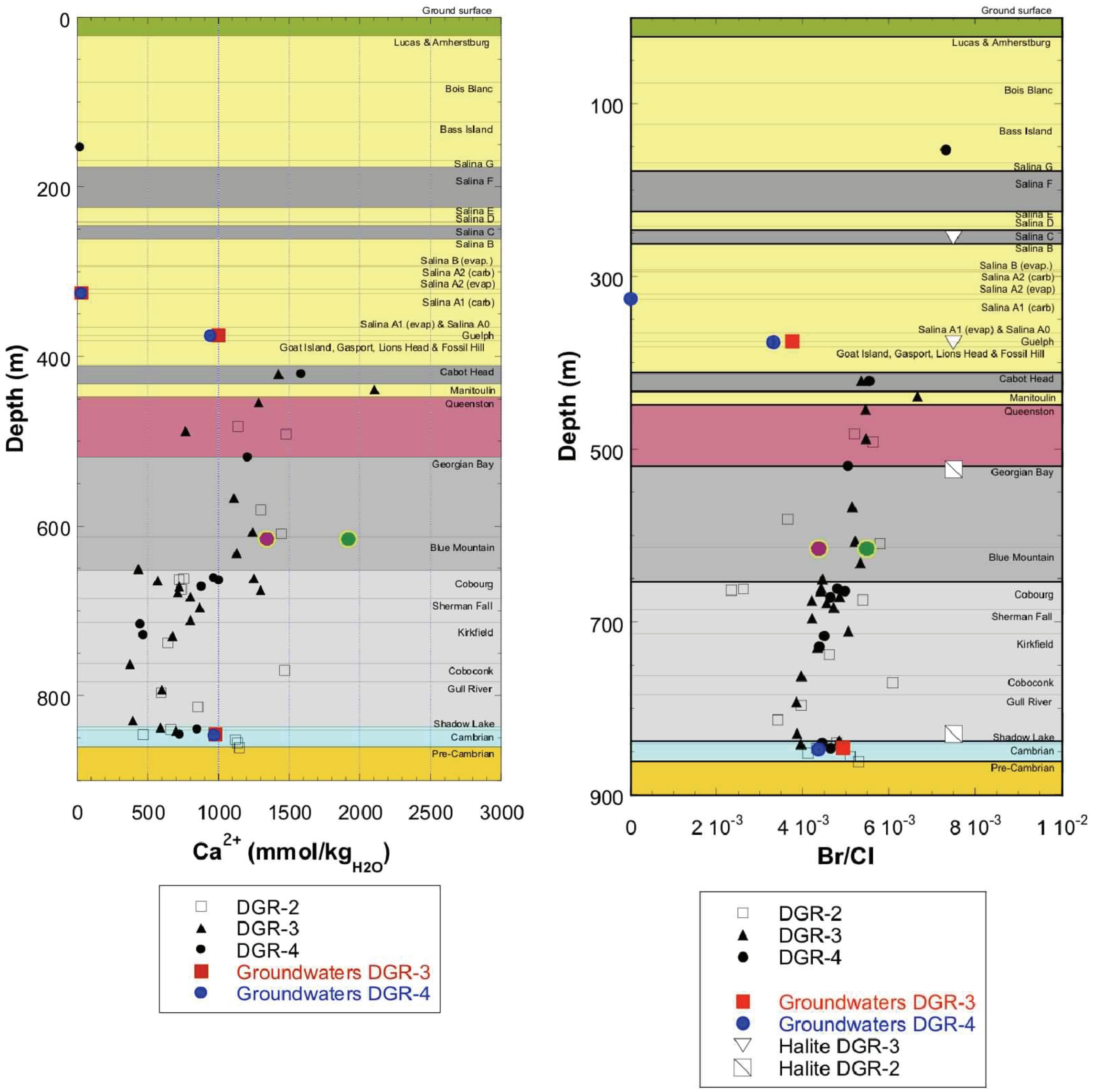


Figure 24: Ca^{2+} Concentrations and Molar Br/Cl ratio in Porewater of Sample DGR-4 610.48 Based on Squeezing (large green circle) and Aqueous Extraction (large purple circle) in Comparison With Pre-existing Aqueous Extraction Data of Hobbs et al. (2011); Adapted from Hobbs et al. (2011)

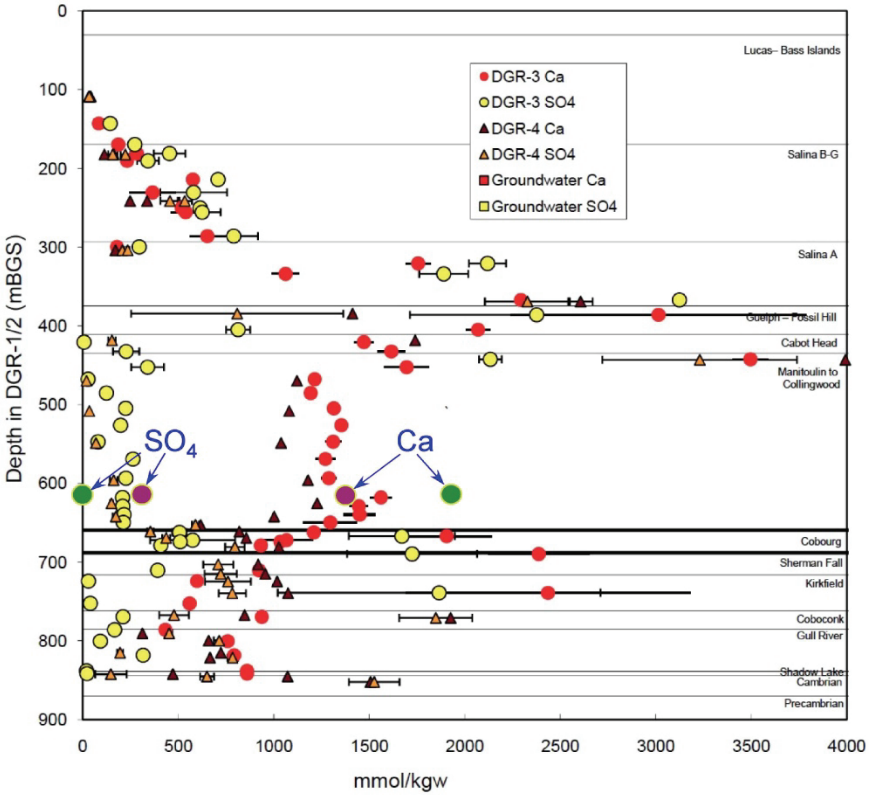


Figure 25: Ca^{2+} and SO_4^{2-} Concentrations in Porewater of Sample DGR-4 610.48 Based on Squeezing (large green circle) and Aqueous Extraction (large purple circle) in Comparison With Pre-existing Aqueous Extraction Data of Clark et al. (2010); Adapted from Clark et al. (2010)

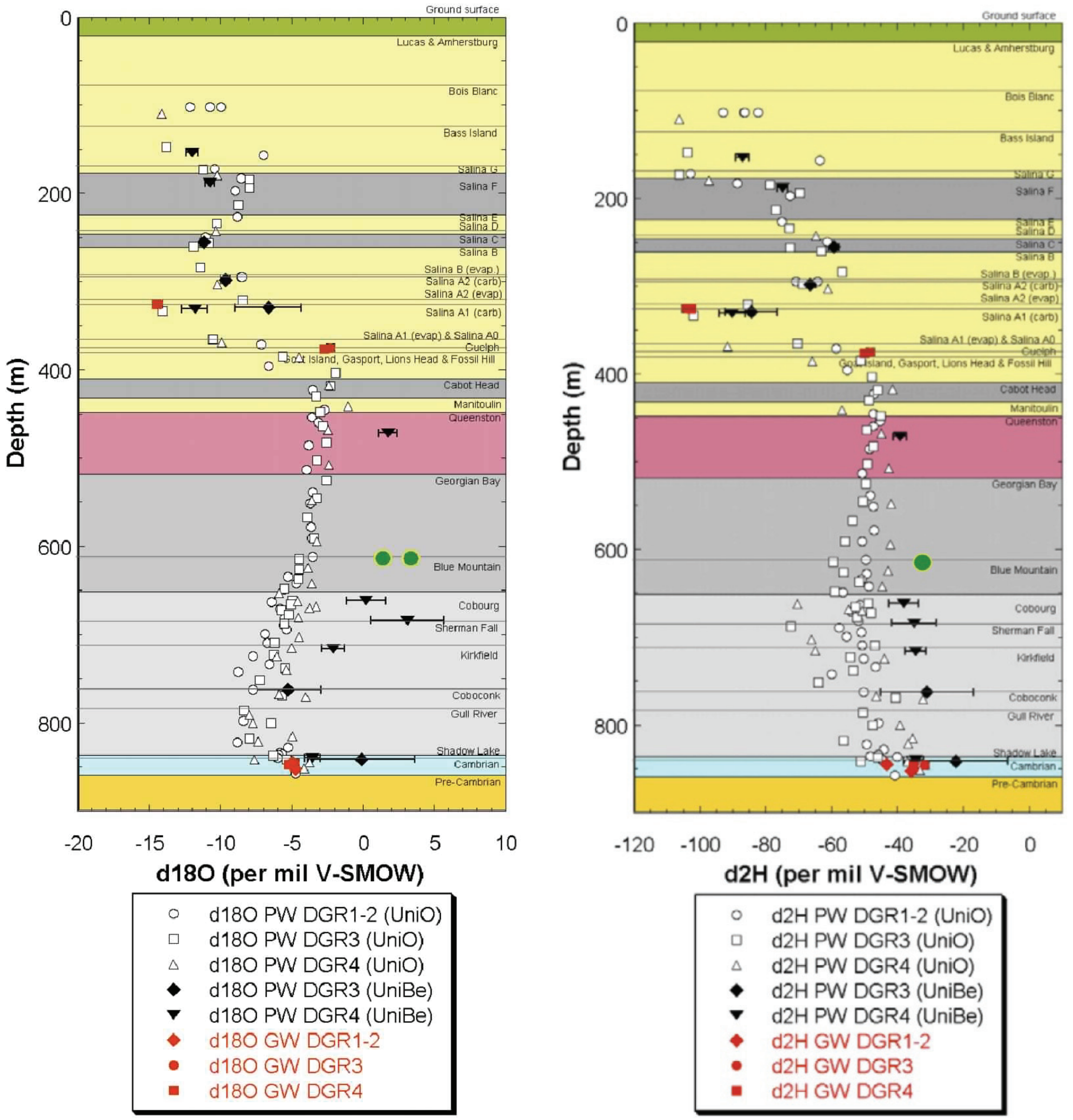


Figure 26: Isotopic Composition of Porewater of Sample DGR-4 610.48 Based on Squeezing (large green circle) in Comparison With Pre-existing Aqueous Extraction Data of Hobbs et al. (2011) and Clark et al. (2010); Adapted from Hobbs et al. (2011)

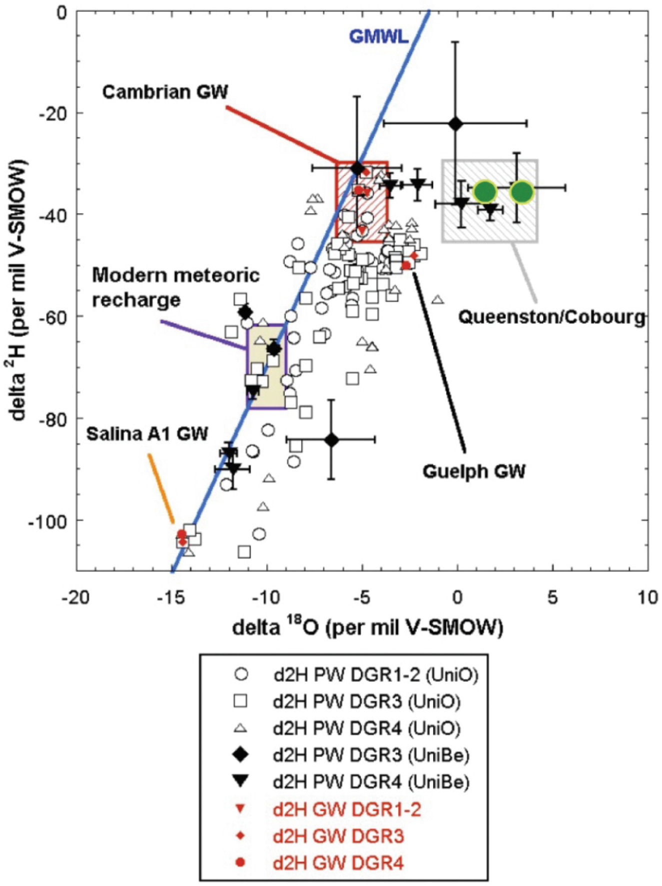


Figure 27: δ^{18}O *vs.* δ^{2}H of Pore and Ground Waters from DGR Boreholes (compilation from Hobbs et al. 2011) and Data Points for the Squeezed Water from Sample DGR-4 610.48 (large green circles); Closed Black Symbols are Data based on Diffusive Exchange (University of Bern), Open Black Symbols are Data Based on Vacuum Distillation (University of Ottawa, Clark et al. 2010); Adapted from Hobbs et al. (2011)

6. SUMMARY AND CONCLUSIONS

The chemical and isotopic composition of pore water in aquitards is an archive of fluid transport and fluid-rock interaction in the past and, therefore, is an important element contributing to the understanding of the long-term evolution of the system. However, due to the low permeabilities and water contents in the Paleozoic rocks of southern Ontario, the chemical characterisation of pore waters is a non-trivial task. This report describes high-pressure squeezing as a new method that, to-date, has not been applied to rocks of comparably low water contents. It could be demonstrated that water can be squeezed from clay-rich lithologies from the sedimentary sequence at the proposed site for the L&ILW DGR, but water could not be squeezed from carbonate-rich units. Given recent analytical developments, only 0.5 mL water is sufficient for a major-element chemical analysis and for the measurement of the stable-isotopic composition of the porewater. If dedicated clay-rich samples are taken in the frame of future drilling campaigns, the opportunity becomes available to obtain vertical profiles of porewater data based on squeezing that can be compared with the results of other methods and used for an improved understanding of the paleohydrogeological evolution. In detail, the following conclusions can be drawn based on the work to-date:

- The availability of samples suited for the present study was limited, and two out of the three samples did not fully fulfill the selection criteria. Nevertheless, squeezing of one of three tested samples was successful and yielded sufficient water for chemical and isotopic analysis at a squeezing pressure of 500 MPa. The sample originates from the Blue Mountain Formation in borehole DGR-4 and has a porewater content of 3.9 wt.% relative to the wet mass, corresponding to a water-loss porosity of 8 vol.%.

- The successful sample from the Blue Mountain Formation has a clay-mineral content of 66 wt.%, compared to 41–45 wt.% for the Queenston Formation and Salina F Unit samples that were also attempted without success. The high carbonate contents of 38–47 wt.% (and related cementation) of the latter samples resulted in a stiff, competent fabric that was not completely destroyed even at the highest squeezing pressure. These samples were not perfectly pressed into shape in the squeezing apparatus and displayed macroscopic openings even after squeezing. In contrast, the squeezed sample from the Blue Mountain Formation had a perfect cylindrical shape.

- SEM investigations indicate the extensive formation of fault gouge in the clay-rich sample from the Blue Mountain Formation during squeezing, indicating a rearrangement of the pore space that led to expulsion of porewater; less gouge was produced in the other two samples.

- The successful core from the Blue Mountain Formation was drilled in late 2008. It is remarkable that the sample remained water-saturated even after a storage period of almost 4 years. It follows that if core samples are packed properly and stored cool, they may remain essentially undisturbed even over extended periods of time.

- The squeezed water is of the <u>Ca</u>-Na-<u>Cl</u> type, with a salinity of about 270 g/kg_{pw}. Sulphate concentration is below the detection limit of 160 mg/kg_{pw}. The water is slightly undersaturated with respect to halite (SI = -0.11), whereas gypsum saturation cannot be constrained because SO_4^{2-} is below detection (at the detection limit of SO_4^{2-}, gypsum, anhydrite and celestite would be oversaturated).

- The isotopic composition of the squeezed water ($\delta^{18}O$ = +1.4, δ^2H = -35) is far on the right side of the global meteoric water line in a diagram $\delta^{18}O$ vs. δ^2H, indicative of an old water affected by rock/water interaction over geological periods of time. The values fit well with those previously obtained by the modified diffusive-exchange technique (Hobbs et al*.* 2011), but are higher than those obtained by vacuum distillation (Clark et al*.* 2010).

- The total inventory of conservative ions (i.e*.,* Cl^- and Br^-, possibly Na^+) was quantified by aqueous extraction of the previously squeezed core materials, and the data were recalculated to porewater concentrations using the known porewater content. The resulting Br^- and Cl^- concentrations are about 0.68–0.86 times those obtained by squeezing. This ratio could be tentatively interpreted in terms of an anion-exclusion effect. For Na^+, this ratio is around 1, consistent with full accessibility of cations to the entire pore space.

- Concentrations of K^+, Ca^{2+}, Sr^{2+} and SO_4^{2-} in squeezed water differ substantially from those obtained by the recalculation of aqueous-leaching data to porewater concentrations. This is the case for both the leaching data obtained from the squeezed cores themselves, as well as for existing literature data (Clark et al*.* 2010). The reasons are not fully understood, at least not quantitatively. At this stage, it is difficult to judge which data set approaches porewater concentrations more closely. Potential artefacts in the aqueous extraction data include mineral dissolution (sulphate or carbonate minerals) and ion exchange. In the squeezed waters, the known dependence of ion concentrations on squeezing pressure indicates that ion-transport processes in the core during squeezing may be an issue that is not fully understood.

7. PERSPECTIVES FOR FUTURE WORK

- The probability of successful porewater squeezing would be increased by sampling of dedicated core materials from a new borehole.

- Ideally, porewater studies performed by different methods and laboratories should be co-ordinated such that all types of analyses would be accomplished on adjacent core materials of similar lithology, in order to provide directly comparable results.

- Core materials from squeezing tests should also be taken from suited lithologies in the vicinity of zones from which ground water could be extracted and analysed.

- Sample-selection criteria should include, apart from high water content, high clay-mineral and low carbonate contents because such lithologies have lower shear strength and deform more readily during squeezing.

- In order to explore the possible pressure dependence of the chemical and isotopic compositions of squeezed waters, the attempt should be made to sample squeezed waters over a range of pressures. If the core-sampling criteria are respected, waters might be squeezed at pressures below 500 MPa. On the other hand, it would be possible to increase the maximum pressure to 750 MPa in the same squeezing rig. This would be achieved by using a smaller sample chamber (diameter of 4 cm instead of 5 cm), so the force of the piston would be applied to a smaller area.

- In order to improve the control of the total mass balance, small rock pieces that are peeled off from the squeezed core during disassembly should be quantitatively collected and weighed. Also, parts of the fiberglass filters that may stick to the pedestals should be scraped off and weighed.

- Given the fact that oxidation is a negligible issue during sample preparation and squeezing, all subsequent laboratory work (drying, crushing, aqueous extraction) should also be performed under controlled atmosphere conditions. In particular, this would minimise the oxidation of pyrite, a process that has been shown to affect SO_4^{2-} concentrations in the extracts, pH and, therefore, equilibria in the carbonate system also.

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