

Porewater characterization in low-permeability geologic materials using a novel extraction method

by

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A Dissertation Submitted in Partial Fulfillment
of the Requirements for the Degree of

Doctor of Philosophy

in the Graduate Academic Unit of Earth Sciences

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This dissertation is accepted by the Dean of Graduate Studies

THE UNIVERSITY OF NEW BRUNSWICK

December 2022

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Abstract

Characterization of porewater chemistry in low-permeability sedimentary deposits provides insights into solute transport mechanisms and the origin and residence time of fluids. Recent interest in solute transport through low-permeability rocks defined by low hydraulic conductivity ($<10^{-11}$ m/s) and diffusion dominated solute transport has been prompted by requirements for long-term geological sequestration of CO₂ and isolation of various waste forms, including nuclear waste. Additionally, development of landslide potential in sensitive marine muds with low hydraulic conductivity is dependent on solute distribution through the deposit. However, representative sampling of porewater from materials with low permeability and small porewater volumes remains a challenge. The main objective of this thesis is to develop and establish a novel method for extraction and characterization of in-situ porewater by capillarity and diffusion, targeting only the water in the most interconnected pore spaces. This method uses a cellulose-based material with a low chemical background and exhibiting no preferential sorption of major porewater solutes.

The feasibility of porewater extraction by this cellulosic material from sediments and rocks with low hydraulic conductivity is demonstrated on samples from the Opalinus Clay, Switzerland, the Upper Ordovician Lorraine Group shale, Quebec, the Upper Ordovician shales of the Michigan Basin, Ontario, and the Champlain Sea mud, Ontario. Results of Cl⁻ and Br⁻ masses obtained by the paper absorption method from shale and clay-rocks produce systematically lower Cl⁻ : Br⁻ ratios than those from a crush-and-leach method. The magnitude of the difference in Cl⁻ : Br⁻ ratios is inversely related to pore throat diameters, and is attributed to size-specific anion exclusion effects.

A benchmarking experiment conducted on Champlain Sea mud demonstrated that porewater solute concentrations measured in paper-absorption and centrifuge extracts compare well. However, alkaline-earth metal concentrations are systematically lower in porewater extracted by the paper absorption method, indicating potential sorption to the absorbing paper or fractionation during centrifugation.

The results of this work highlight the fact that different porewater extraction methods yield different proportions of porewater from the mobile and bound fractions. As such, understanding the unique characteristics or biases of each method is important when assessing solute distribution and transport.

Acknowledgements

The research presented in Chapter 2 and 3 as well as ongoing work on the development of the paper absorption method is supported by the Nuclear Waste Management Organization (NWMO). Work for Chapter 4 was conducted in collaboration with the Geological Survey of Canada (GSC), City of Ottawa, and the Rideau Valley Conservation Authority.

I would like to thank my supervisor, Tom Al for sticking with me through this adventure. Your guidance, encouragement, and patience has been invaluable.

I am grateful to Jennifer McKelvie for your inspiration and support and to Sam Alpay and Marc Hinton at the GSC for your excitement and passion for all things mud.

I would like to acknowledge Smirti Singh, David Barton, and Chantal Lurette for help with laboratory work. This project benefited greatly from technical support from Chris McFarlane, Jiujiang Zhao (Geochemistry Laboratory, University of New Brunswick) Smita Mohanty and Nimal De Silva (Geochemistry Laboratory, University of Ottawa), and Jeffery Ovens (X-Ray Laboratory, University of Ottawa).

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List of Symbols, Nomenclature, or Abbreviations

3D	Three dimensional
C^*	Mass of sorbed solute per mass of paper
C_i	Initial solute concentration
CI	Confidence interval
CEC	Cation exchange capacity
C_f	Final solute concentration
CRDS	Cavity ring down spectrometer
CT	Computed tomography
DDL	Diffuse double layer
Δ	Change in
DGR	Deep geological repository
DI	Distilled water
FEP	Fluorinated ethylene propylene
γ	Surface tension
G_f	Geometric factor
GSC	Geologic Survey of Canada
I	Ionic strength
IAEA	International Atomic Energy Agency
ICP-MS	Inductively coupled mass spectrometry
ICP-OES	Inductively coupled optic emission spectrometry
κ^{-1}	Debye length (nm)
K_{assoc}	Ion-association coefficients
kgw	Kilogram water
ICP-MS	Inductively coupled plasma mass spectrometry
LOD	Limit of detection
$mass_{X\ CENT}$	Mass of solute “x” extracted by the centrifuge method
$mass_{X\ PAM}$	Mass of solute “x” extracted by the paper absorption method
mBGS	Meters below ground surface
MIP	Mercury intrusion porosimetry
m_s	Mass of paper
N	Anion-accessible porosity
NSERC	Canadian Natural Sciences and Engineering Research Council
Ni-et	Nickel-ethylenediamine
NIR	Near infrared
NWMO	Nuclear water management organization
σ	Standard deviation
θ	Wetting angle
p	p-value
P_{ae}	Air entry pressure
P_c	Capillary pressure
pH	Logarithm of the reciprocal of the hydrogen ion activity
pXRD	Powder x-ray diffraction
r_1	Hydrated radius of ion 1
r_2	Hydrated radius of ion 2

r	Pore radius
R ²	Coefficient of determination
RH	Relative humidity
RSD	Relative standard deviation
RMSE	Root mean square error
SA	Area of the absorbing paper
SEM	Scanning electron microscopy
δ	Constrictivity
SPW	Synthetic porewater
τ	Tortuosity
US EPA	United States Environmental Protection Agency
V _{H2O}	Volume of porewater extracted
wt. %	Weight percent
x	Cation species
XRF	X-ray fluorescence

1.0. Introduction

Characterization of porewater chemistry in geological formations can provide insight into the origin and residence time of porewater as well as mechanisms driving solute transport and reaction processes. Understanding the distribution of porewater solutes through geologic formations is important for predicting and solving anthropogenically and naturally caused environmental, hydrogeochemical, and geotechnical problems (Benson and Cole, 2008; Cherry et al., 2014; Hendry et al., 2015; Lackner, 2003; Russell and Gale, 1982). Porewater chemistry characterization requires extraction techniques, several of which are available for a range of rock types and soils (Altinier et al., 2007; Cyr and Daidié, 2007; Fernández et al., 2003, 2014; Gascoyne, 2004; Mader et al., 2004; Mazurek et al., 2011; Savoye et al., 2006; Waber and Smellie, 2008; Yang et al., 2003). However, the solute compositions these methods provide can be affected by ion exchange processes and mineral dissolution and may require independent measurements of porosity and bulk density of rock samples (Anovitz and Cole, 2015; Mazurek et al., 2009; Reeder et al., 1998; Sacchi et al., 2001). Porewater is the portion of groundwater found in the interstitial spaces of sediments deposited in aquatic environments. In low-permeability samples extraction and characterization of porewater has proven to be especially challenging due to the small volumes available and the difficulty in extracting a representative sample.

The main motivation for this work was to extract and characterize representative samples of porewater chemistry in low-permeability rocks to gain a better understanding of solute transport through geological formations in the context of deep geologic repository (DGR) development for long-term sequestration of nuclear waste. The use of

nuclear energy generates various forms of waste; used fuel, commonly referred to as high-level waste, as well as intermediate- and low-level wastes generated during operation, maintenance, and decommissioning of reactors. Many countries that use nuclear power have organizations dedicated to radioactive waste management and are actively developing DGRs tailored to their local geologies. The DGR concept requires a tectonically stable geologic system with rocks of low hydraulic conductivity ($K < 10^{-10}$ m/s) such that solute transport is dominated by diffusion (IAEA, 2009). This system could be crystalline igneous or metamorphic rock, as is the case in Sweden (SKB, 2019), Finland (Posiva Oy, 2021), and Canada (NWMO, 2021), or sedimentary as for sites of interest in Switzerland (NAGRA, 2021) and Canada (NWMO, 2021).

A secondary focus of this research aims to understand effect that porewater and exchangeable cation composition have on the geotechnical stability of sensitive marine muds like the Champlain Sea mud, which occupies much of the St. Lawrence valley (Bogaard et al., 2007; Thakur et al., 2017). Sensitive marine muds are composed of clay- and silt-sized detrital sediments deposited in a marine environment (Gillott, 1970; Locat and St-Gelais, 2014). Over time, weathering reactions and freshening can alter the chemistry of the porewater and cation exchange sites resulting in changes to mud sensitivity (Torrance, 1999). Understanding these changes can play a role in future land development policies.

1.1. Porewater chemistry and water-rock interactions

Conservative natural tracers, such as stable water isotopes (^{18}O and ^2H) and Br^- , Cl^- are important in investigations of fluid movement and origin (Armstrong et al., 1998; Clark et al., 2013; Hendry and Wassenaar, 2000, 2011; Mazurek et al., 2011; Rübel et al.,

2002). Figure 1.1 shows the distribution of Cl^- concentrations in porewater from the Couche Silteuse de Marcoule, in France, which is flanked by low salinity aquifers (Mazurek et al., 2011). Mazurek et al. (2011) attribute the symmetric distribution of Cl^- concentrations between the aquifers to diffusion dominated transport. Such tracer data in conjunction with major ion (Cl^- , Na^+ , K^+ , Br^- , Sr^{2+} , Ca^{2+} , and Mg^{2+}) concentrations can assist in determining the origin of porewater and solute transport (Clark et al., 2013; Desaulniers et al., 1981; Hanor, 1994; Hendry and Wassenaar, 2000). The information obtained from porewater chemistry is important for providing constraints on the processes and timing of solute transport, modeling potential movement of radiogenic contaminants released from DGRs, and determining the hydraulic stability of a geologic system (Al et al., 2011, 2015; Bensenouci et al., 2013; Clark et al., 2013; Mazurek et al., 2011; Nakata et al., 2015; Van Loon et al., 2003, 2005).

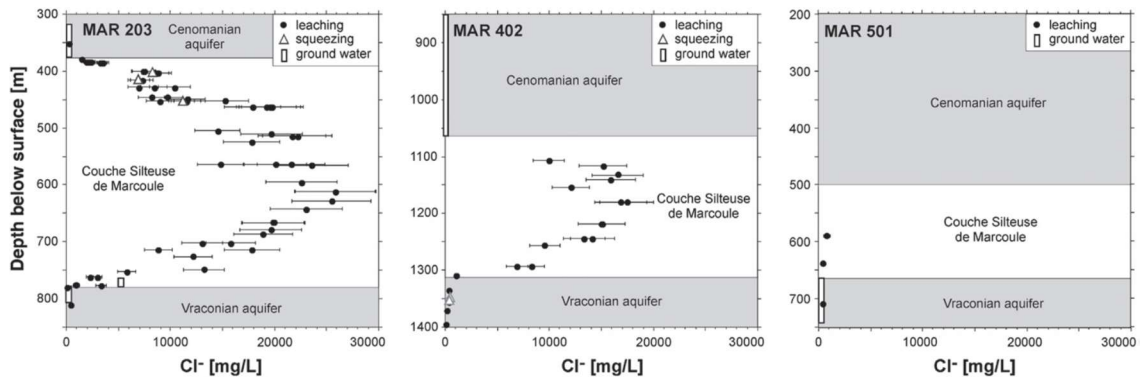


Figure 1.1. Distribution of Cl^- contents in porewaters of boreholes MAR203, MAR402 and MAR501 penetrating the Couche Silteuse de Marcoule, France. Grey areas indicate aquifers (adapted from Mazurek et al. 2011).

Quantification of porewater chemistry requires extraction of representative samples of porewater, which has proven to be a complicated task (Edmunds and Bath,

1976; Mazurek et al., 2009; Reeder et al., 1998; Sacchi et al., 2001). Figure 1.2 depicts the small scale heterogeneity of porewater that must be considered when investigating porewater chemistry (Appelo et al., 2008). Two types of porewater, at equilibrium with each other, have been designated in these systems: mobile and bound (Sposito and Prost, 1982; van Olphen, 1965). Mobile water is found toward the center of pore spaces and solute transport in this fraction of porewater can occur by diffusion and advection. Solute transport in bound water is diffusion dominated. This water fraction includes both water in the diffuse double layer (DDL), the layer of water directly in contact with mineral surfaces, and interlayer water, found between layers of swelling clay minerals (Leroy et al., 2007; Ochs et al., 2004). The interlayer water is a single layer of cations confined between the clay mineral sheets, and contribute to the swelling properties of these minerals. The DDL is an exchangeable, diffuse, cation-rich, charge-balancing layer (Figure 1.2) with the number of cations dictated by the total mineral surface charge, represented by the cation exchange capacity (CEC). The composition and thickness is dependent upon porewater chemistry (Appelo and Postma, 2005; Sparks, 2003). The existence and properties of the DDL are important for understanding solute transport and distribution within geologic formations, especially in low-permeability rocks with tight pore spaces where the ratio of bound to mobile water is high (Birkholzer et al., 2012; Hendry et al., 2009; Neuzil, 1986).

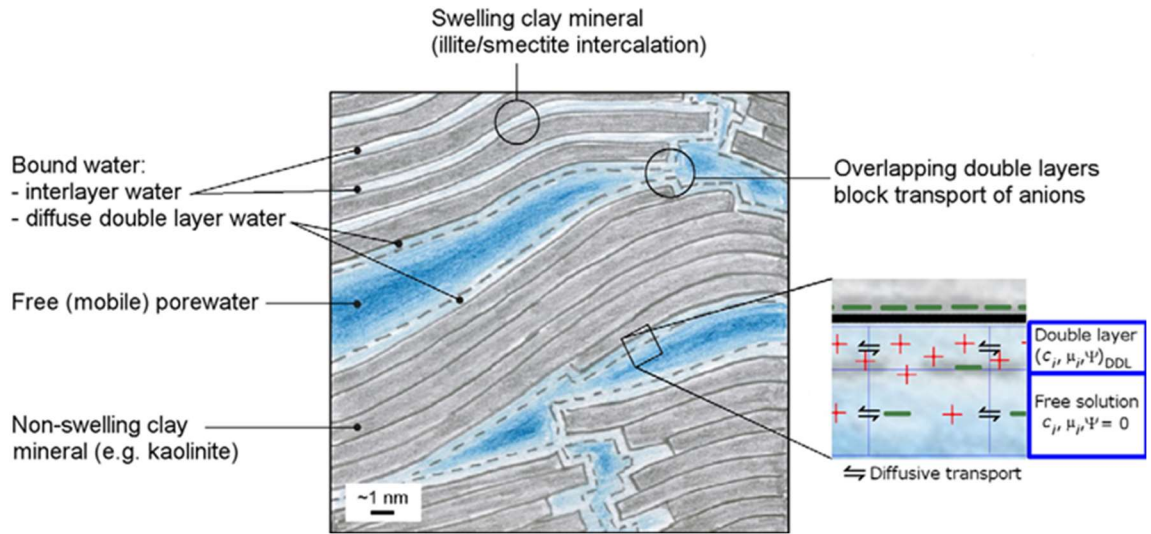


Figure 1.2. Schematic of clay rock on the nanometer scale, showing water types associated with clay minerals (adapted from Appelo et al., 2008).

Porewater solute transport is affected both by exchange reactions that occur between the mobile and bound waters and pore geometry. Exchange reactions can occur when the equilibrium between mobile and bound water fractions is disrupted and can result in mobilization or retardation of specific solutes. Changes to porewater chemistry can also alter the ionic strength which is inversely related to the DDL thickness (Appelo et al., 2008; Appelo and Postma, 2005), and in pore throats and channels that are small enough the cation-rich layers approach each other or overlap resulting in total or size-specific anion exclusion (Lavoie et al., 2014). Additionally, pore geometry can influence solute movement through variations in constrictivity, connectivity and tortuosity of pore channels (Keller et al., 2013). This can result in solute-specific accessible porosities (Pearson, 1999), and measurement of these porosities can be method dependent (Anovitz and Cole, 2015).

Determination of the chemical composition of porewater from low-permeability rocks has been achieved using several different methods, including direct sampling

(Gascoyne 2004; Waber and Smellie 2008), ultracentrifugation (Yang et al. 2003), squeezing (Cyr and Daidié 2007; Fernandez et al. 2003; Yang et al., 2003), diffusive exchange (Savoye et al. 2006; Waber and Smellie 2008; Waber et al. 2011), crush-and-leach (Clark et al. 2010) and advective displacement (Mäder et al. 2004; Mazurek et al. 2011). Each method is associated with a distinct set of challenges and chemical artefacts (Sacchi et al., 2001). Direct sampling of porewater is commonly not feasible in low permeability rocks, and where it is possible sample collection can take months or years (Waber and Smellie, 2008). Both ultracentrifugation and crush-and-leach techniques require the disaggregation of samples, which exposes additional rock surfaces and may promote dissolution of minerals. Ion exchange has also been found to be problematic with high pressures required during squeezing (Yang et al, 2003). Both crush-and-leach and out-diffusion attempt to characterize porewater composition by altering the chemical environment of the solutes leading to ion exchange. Correcting for mineral dissolution and ion exchange artefacts is difficult since both processes are dependent on individual samples. These methods also require measurements of total pore volume. Pore volumes can be estimated from water volumes extracted during vacuum distillation (Clark et al. 2010) or with conventional porosity measurements (Withjack and Durham, 2001). Accurate porosity measurements in low-permeability rocks are difficult and can introduce a significant amount of error in the calculated porewater ion concentrations. Incomplete water extraction with vacuum distillation will lead to inaccurate concentration calculations and fractionation of stable water isotopes (Altinier et al., 2007; Gimmi et al., 2007).

Since mobile porewater solute concentrations will differ from total porewater concentrations, understanding the fractions of each porewater, mobile or bound, extracted by individual sampling techniques is important. The importance of accurate porewater chemistry measurements becomes obvious when using these results to make predictions about solute transport, which may be implemented in waste disposal and land development policies.

1.2. Thesis objectives

The goal of this work is to develop a method for porewater extraction that produces representative samples of in-situ porewater from low-permeability rocks for hydrogeochemical characterization. The idea is to extract porewater and associated solutes into an absorbent paper material in direct contact with the rock using capillarity and diffusion. Solute concentrations will be calculated from discrete measurements of extracted solute masses and water mass, independent of additional porosity and bulk density measurements.

Four primary objectives were set to meet this goal. The first objective was to select an absorbent material for porewater extraction and characterize its properties including chemical background and the extent of ion adsorption and desorption to the paper. The second objective was to establish a method for quantification of porewater solute concentrations from separate measurements of water and solute masses extracted by paper absorption. The third objective was to verify the accuracy of extracted solute concentration measurements by sampling cores saturated with a known synthetic porewater, producing core samples with known porewater chemistry. The final objective

was to benchmark the paper absorption method against other established porewater extraction techniques on preserved core samples containing formation water.

1.3. Thesis outline

This thesis consists of five chapters beginning with this introductory Chapter 1, which describes the motivation and overall objectives for this work. Chapters 2 and 3 are published in *Applied Geochemistry* and *Geofluids* respectively and Chapter 4 has been written as a journal article and will be submitted to *Hydrogeology Journal* for review. The thesis ends with a concluding chapter (Chapter 5) that outlines recommendations for future work and the current implementation of the paper absorption method.

The first article (Chapter 2, Celejewski et al., 2014) describes the development of a novel technique, the paper absorption method, for extraction of representative samples of porewater from low-permeability rocks with the aim to accurately quantify solute concentrations. It provides a detailed characterization of the material used for porewater extraction, the development of a spectrometric method for quantifying extracted water masses, and a method for the measurement of porewater solutes. This work presents data verifying the analytical precision of solute concentrations quantified in porewater samples extracted by the paper absorption method and establishes the feasibility of this method to extract water from a low-permeability shale (Georgian Bay Formation, Michigan Basin, Ontario, Canada).

The second article (Chapter 3, Celejewski et al., 2018) presents a comparison of $\text{Cl}^- : \text{Br}^-$ ratios quantified in porewater samples extracted by crush and leach and paper absorption methods from low-permeability rock samples obtained from Upper Ordovician shales in the Michigan Basin in Ontario, the Opalinus Clay at the Mont Terri

Rock Laboratory in Switzerland, and the Upper Ordovician Lorraine Group shale in southern Quebec. This work presents evidence for the sensitivity of individual porewater extraction methods to anion exclusion effects in samples with low porosity values and provides arguments for using multiple extraction techniques when characterizing porewater chemistry in low permeability rock samples.

The third article (Chapter 4) benchmarks Champlain Sea mud porewater concentrations obtained using the paper absorption method against two established porewater extraction methods: centrifugation and crush and leach. The importance of using multiple porewater extraction techniques targeting different fractions of mobile and bound porewaters to gain a better understanding of mobile water-bound water-rock equilibria is emphasized. This work is part of a larger project that aims to understand the hydrogeochemical impact on geotechnical properties of the Champlain Sea mud.

The work presented in this thesis involves the development of the paper absorption method for porewater extraction. Method development is an iterative process involving a trial-and-error approach. Through this process three major issues were identified over the span of the project: 1) the inaccuracy of the reflectance NIR for small water mass measurements (< 30 mg), 2) evaporation during paper insertion and removal, and 3) particulate transfer from the core sample to the paper (Figure 1.3). The first issue was addressed, prior to extracting porewater from core samples, by developing a transmission NIR spectrometry method with an effective range of 0 to 35 mg water. Issues 2 and 3 were addressed over the course of multiple porewater extraction experiments from Michigan Basin shales, Opalinus clay, and Lorraine Group shales. Due to the presence of evaporation and particulate transfer during these extractions porewater

concentrations are not reported in Chapter 3. Instead, Chapter 3 focuses on $\text{Cl}^- : \text{Br}^-$ mass ratios, which are not affected by these issues. The work presented in Chapter 4 used the paper absorption method in its most developed state to extract porewaters from Champlain Sea mud samples. In this chapter porewater solute concentrations are reported and compared to results of other extraction methods.

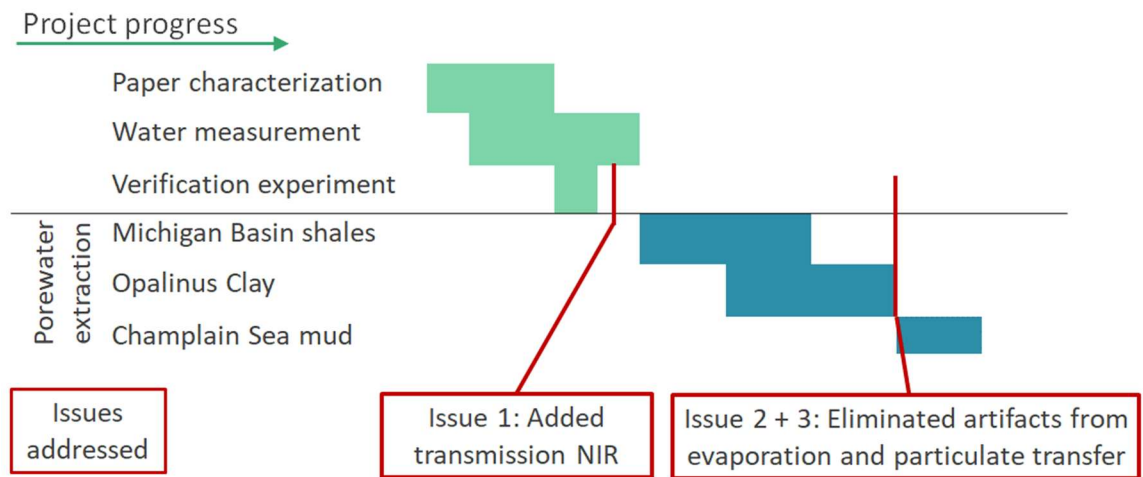


Figure 1.3. Development of the paper absorption method. Time of resolution of major issues is highlighted.

1.4. Statement on co-authorship

In the research presented in this thesis, I was responsible for experimental design, data acquisition, and chemical data analysis with some exceptions. Tom Al aided in study design, and data interpretation and was responsible for funding acquisition and manuscript review. Lisa Scott conducted the preliminary tests reported in Chapter 2 and David Barton collected and processed data for the Lorraine Group shale porewaters presented in Chapter 3. Geofirma collected Michigan Basin samples for the Nuclear Waste Management Organization (NWMO) and the DB-A borehole in Mont Terri was drilled as part of an international porewater extraction method comparison study

published by Mazurek et al., (2017). The Mont Terri samples presented in Chapter 3 were not part of the data set published by Mazurek et al., (2017), but came from extra samples that had been preserved and stored for additional studies. The Champlain Sea mud samples analyzed in Chapter 4 are part of a larger study with the Geological Survey of Canada (GSC), City of Ottawa, and Rideau Valley Conservation Authority examining the geotechnical stability of the formation as well as a comprehensive study of porewater composition, lithology, and mineralogy. Core collection and storage, and porewater extraction by centrifugation was conducted by Sam Alpay and Marc Hinton at the GSC with help from the sedimentology laboratory team: Shauna Madore, Miriam Wygergangs, Claudia Moore, and Alain Grenier.

1.5. References

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2.0. An absorption method for extraction and characterization of porewater from low-permeability rocks using cellulosic sheets

This chapter was originally published in Applied Geochemistry:

Celejewski, M., Scott, L., Al, T. 2014, An absorption method for extraction and characterization of porewater from low-permeability rocks using cellulosic sheets.

Applied Geochemistry, 49, 22-30. doi: [10.1016/j.apgeochem.2014.06.010](https://doi.org/10.1016/j.apgeochem.2014.06.010)

2.1. Abstract

Characterization of porewater chemistry in low-permeability rocks can provide insight into the origin and residence time of porewater, the history of fluid movement and the nature of transport and reaction processes. However, the measurement of porewater chemistry in low-permeability rocks is challenging because of the small fluid volume and the difficulty of extracting representative samples. Several techniques are available, but the results they provide can be affected by ion exchange and mineral dissolution, and they may require independent porosity measurements. The objective of this work is to develop a method of extracting representative samples of *in situ* porewater from low-permeability rocks and accurately quantify solute concentrations in the extracted porewater. A preliminary trial demonstrated the feasibility of extracting porewater by absorption into hydrophilic cellulosic membranes from low-permeability shale (Georgian Bay Formation, Michigan Basin, southwest Ontario, Canada). Solute concentrations are calculated from independent measurements of solute mass quantified by Inductively-Coupled-Plasma Mass Spectrometry (ICP-MS) and water-content quantified by Near Infrared (NIR) spectrometry. Sorption experiments indicate that there is no preferential sorption of solutes (Na^+ , Cl^- , Mg^{2+} , Ca^{2+} , K^+ , Sr^{2+} , and Br^-) to the cellulosic membrane. The results indicate that the method is capable of determining solute concentrations of absorbed porewater with analytical precision that is within the margins of error recommended by EPA Method 6020a for analysis of saline water samples.

Keywords: Deep geological repository; Low permeability; Porewater extraction; Pore fluids; Sedimentary formations

2.2. Introduction

Low permeability sedimentary formations are under consideration as potential host rocks for a deep geological repository (DGR) for long-term sequestration of nuclear waste in Canada. The DGR concept requires a tectonically stable geologic system with rocks of low hydraulic conductivity ($K < 10^{-10}$ m/s) such that solute transport is dominated by diffusion (International Atomic Energy Agency (IAEA), 2009). Studies of groundwater and porewater geochemistry provide important contributions to the multiple lines of evidence that are necessary to demonstrate long-term diffusion control of solute transport. Porewater chemistry can provide insight into the origin, residence time and history of fluid movement (Clark et al., 2013; Desaulniers et al., 1981; Desaulniers and Cherry, 1989; Gimmi et al., 2007; Hendry and Wassenaar, 2011; Hendry et al., 2013; Mazurek et al., 2011; Rübel et al., 2002), microbial activity (Doig et al., 1995; Onstott et al., 2009; Stroes-Gascoyne et al., 2006), and the reaction processes affecting solute distributions (Appelo et al., 2008; Armstrong et al., 1998; Savoye et al., 2006; Savoye et al., 2012; Waber et al., 2012). Conservative natural tracers, such as stable water isotopes (^{18}O and ^2H), He, Br^- and Cl^- concentrations are of great importance in investigations of large scale and long-term transport properties (Hendry et al. 2000; Hendry and Wassenaar, 2011; Mazurek et al., 2011; Rübel et al. 2002). For example, Mazurek et al. (2011) compiled measurements of natural conservative tracers in the Opalinus Clay at Mont Terri, Switzerland, the Boom Clay at Essen, Belgium, and the Couche Silteuse at Marcoule, France; establishing spatial profiles of tracers across the formations and analyzing them to determine transport processes and porewater residence times. In addition to the conservative species, major and minor ion concentrations (Na^+ , K^+ , Mg^{2+} , Ca^{2+} and Sr^{2+}) have also been used to investigate groundwater and porewater residence

times (Desaulniers et al. 1981; Desaulniers and Cherry, 1989; Hendry and Wassenaar, 2011).

The characterization of in situ porewater chemistry in low-permeability rocks is an ongoing challenge, partly because of the complexity of the porewater distribution in clay-rich rocks. There are two main types of porewater in low-permeability clay-containing sedimentary rocks: bound water and mobile water. Bound water includes both interlayer water, which is water found between layers of swelling clay minerals, and water within the diffuse double layer. These waters generally contain relatively high cation concentrations to balance the charge from negatively charged surfaces (van Olphen, 1965; Sposito and Prost, 1982). Mobile water is the portion of porewater contained in the larger pore spaces and given sufficient pressure gradients it may be subject to advection. Solutes in both the bound and mobile water are transported by diffusion. Although the chemical composition of the bound water may differ from the mobile water, there is an equilibrium established between them, and methods of porewater or solute extraction that perturb the composition of one or the other will result in ion exchange as the system attempts to re-equilibrate.

There are several established methods to determine the chemical and isotopic composition of porewater from low-permeability rocks, including direct sampling (Gascoyne, 2004; Waber and Smellie, 2008) ultracentrifugation (Yang et al. 2003), squeezing (Cyr and Daidié, 2007; Fernández et al., 2003; Fernández et al., 2013; Yang et al., 2003), diffusive exchange (Altinier et al., 2007; Savoye et al., 2006; Waber and Smellie, 2008; Waber et al. 2011;), crush-and-leach (Clark et al. 2013) and advective displacement (Mader et al. 2004; Mazurek et al. 2011). Each method is associated with

distinct challenges and most are subject to chemical artefacts (Mazurek et al., 2009; Reeder et al., 1998; Sacchi et al., 2001). Direct sampling of in situ porewater is commonly not feasible in low-permeability rocks, and where it is possible, sample collection may require time periods of months or years (Waber and Smellie, 2008). Indirect methods require core preparation prior to porewater characterization, which may introduce error to measured solute concentrations. Ultracentrifugation and crush-and-leach techniques require sample disaggregation, which exposes fresh mineral surfaces and may promote ion exchange and dissolution of minerals. Crush-and-leach and out-diffusion alter the chemical composition of the porewater leading to ion exchange and the potential for mineral precipitation and dissolution reactions. High-pressure squeezing may provide porewater compositional data that are correlated to the applied pressure due to variable contributions of mobile and bound water (Edmunds and Bath, 1976). Corrections may be made for mineral dissolution and ion exchange artefacts but lead to greater uncertainty in the measurements. Both crush and leach and out diffusion methods also require measurements of total pore volume, which can be estimated from water volumes extracted by vacuum distillation (Clark et al., 2013) or with conventional porosity measurements (Withjack and Durham, 2001). Accurate porosity measurements in low-permeability rocks are difficult and introduce error in the calculated porewater ion concentrations and stable water isotope measurements (Altinier et al., 2007; Gimmi, et al. 2007).

The purpose of this work is to conduct laboratory-based experiments toward developing a method for porewater extraction that provides representative samples of in situ porewater from low-permeability rocks for hydrogeochemical characterization and

does not require independent porosity measurements. The method will focus on the placement of absorbent paper in direct contact with rock samples allowing for porewater and solute extraction by capillarity and diffusion (Figure 2.1).

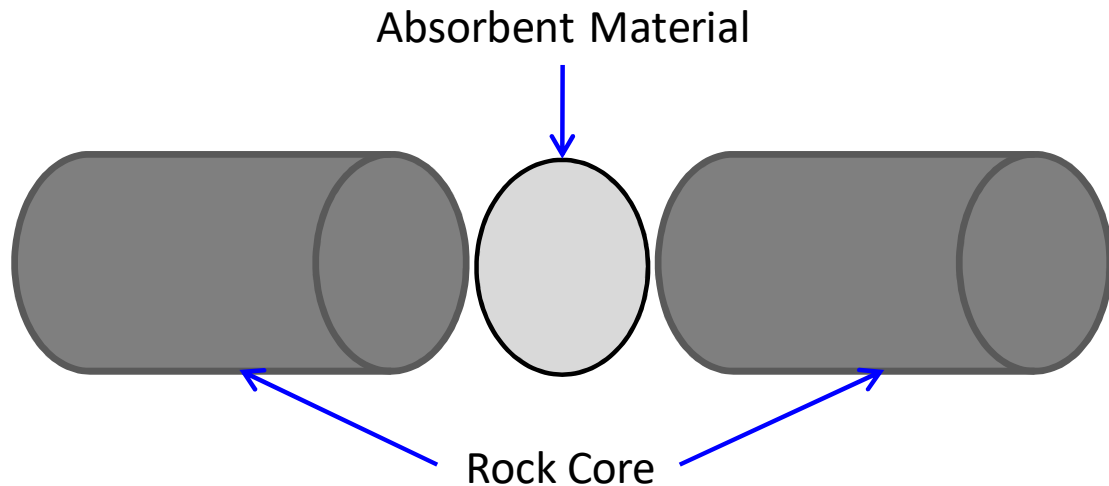


Figure 2.1. Schematic of the absorption method: an absorbent material is sandwiched between rock core segments, allowing for porewater and solute extraction by capillary action and diffusion.

2.2.1. Preliminary trial

A preliminary trial was conducted to determine the feasibility of porewater extraction by an absorbent material in direct contact with low-permeability rocks, whether quantitative analyses of solutes absorbed by the paper could be achieved, and whether solute concentrations in the porewater could be quantified. Preserved drill cores from the eastern margin of the Michigan Basin were obtained from DGR-5, one of the boreholes drilled for site characterization at the location of a proposed DGR for low- and intermediate-level nuclear waste in Kincardine, Ontario (NWMO, 2011). The sampling and preservation techniques are described by Sterling et al. (2011). Core samples were

selected from the Upper Ordovician Georgian Bay Formation shale and porewater geochemical data for Cl^- and Br^- from this interval presented by Clark et al. (2013) indicate that concentrations are uniform versus depth. The samples were cleaved parallel to bedding with a chisel, rock dust and fragments were removed with a carpenter's tack cloth (fabric treated with an organic resin designed to remove sawdust), and pre-weighed Rigaku (Tokyo, Japan) Microcarry™ X-ray fluorescence (XRF) aqueous sample holders were sandwiched between the core segments. The samples were wrapped in plastic wrap, secured with electrical tape, and refrigerated. After six weeks, the Microcarrys™ were removed and weighed to determine the mass of absorbed brine, then dried and sent to the XRF Applications Scientists at Rigaku Americas Corporation, Texas for analysis. The optimal time for porewater extraction will be dependent on the type of rock being examined. In general, samples with lower permeability and porosity will require longer equilibrium times. The six week time period was chosen with the expectation that it should be sufficient to allow for porewater equilibration with the papers, but an optimal time was not investigated experimentally. Solute analysis was done on a Rigaku ZSX Primus II XRF instrument using a method developed by specialists at Rigaku.

A mass increase was observed upon removal of the papers from cores indicating brine mass transfer from the core to the paper. However, gravimetric measurements of absorbed porewater were influenced by evaporation and transfer of rock particulates to the papers, preventing accurate gravimetric water-content measurements. Individual solute masses absorbed by each Microcarry™ were compared to absorbed Cl^- mass (Figure 2.2). The mass of solute absorbed is highly variable among individual samples because the mass of brine absorbed is different for each sample. However, consistent

solute ratios were observed indicating that the porewater concentrations for Na^+ , Mg^{2+} , Cl^- , K^+ , Ca^{2+} , Br^- and Sr^{2+} are essentially the same in all samples.

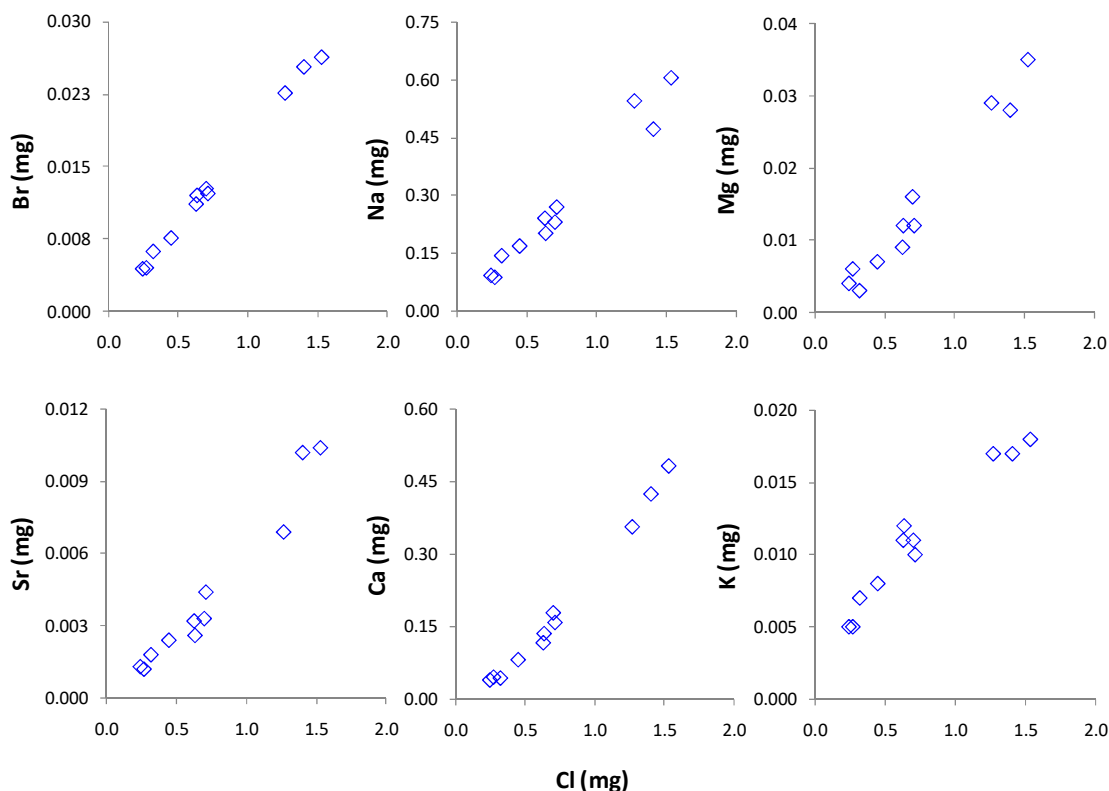


Figure 2.2. Solute mass ratios for porewater absorbed from Georgian Bay Formation shale cores. Extracted solute masses were measured by XRF.

The preliminary trial was successful in demonstrating that porewater can be absorbed by the cellulosic paper (Microcarry™) when it is placed in contact with a rock for an extended period of time. This trial provided the motivation for a comprehensive effort to develop the method and allowed for identification of issues requiring additional work; specifically, the refinement of techniques for sample preparation and the quantification of both solute and water mass in order to achieve the goal of measuring

solute concentrations in the porewater. It was recognized that this should include consideration of alternate analytical techniques and absorptive materials.

2.3. Approach

The preliminary trial quantified solutes directly on the Microcarry™ by XRF but the precision and detection limits for some elements (e.g. Mg^{2+} , K^{+} and Sr^{2+}) were not ideal. The porewater in the Georgian Bay Formation shale is highly saline (Clark et al., 2013) and it was recognized that improvements in precision and detection limits would be necessary in situations with relatively dilute porewater. Inductively-Coupled-Plasma Mass Spectrometry (ICP-MS) was chosen as an alternate analytical technique. This required an additional leaching step to bring the solutes into solution and it also allowed for consideration of alternative types of absorptive materials other than the Microcarry™.

Material selection was conducted by examining manufacturer specifications for cellulosic and synthetic materials. Cellulosic materials exhibit strong capillarity due to hydrophilic properties of the material and the small diameter of individual fibres. Whatman® 1 CHR chromatography paper was selected. It is a cellulosic paper with a low chemical background, a smooth surface and 0.18 mm thickness. It would not be possible to obtain data that are representative of the *in situ* porewater if specific solutes are preferentially adsorbed to the paper. Therefore, the Whatman® 1 CHR paper required testing for adsorption properties as a function of material surface properties, pH and solute concentration.

In addition to the determination of solute mass, representative concentration measurements for solutes in extracted porewater are also dependent on accurate and precise quantification of the absorbed water mass. Gravimetric methods used in the

preliminary trial were not accurate due to evaporation and particulate matter transfer from the core to the paper. Near infrared (NIR) spectrometry is a quick and non-destructive alternative for water mass quantification. Water content quantification is based on absorbance from three characteristic vibrations of the H O bonds in the water molecule in the NIR region (1200 nm, 1450 nm, and 1950 nm) (Siesler et al. 2002). Using this approach, rock particulate transfer to the paper, or fibre particulate transfer to the core surface, will not influence water mass measurements.

In summary, the chosen approach involves:

1. clamping sheets of cellulosic paper between rock surfaces to allow porewater absorption,
2. the clamped rock samples are wrapped to isolate from the atmosphere and stored 5 °C for a period of weeks to months,
3. the papers are removed from the enclosing rocks and the absorbed water-content is determined by NIR spectrometry,
4. the papers are leached to dissolve all contained porewater solutes, which are then quantified by ICP-MS,
5. porewater concentrations are reconstructed by normalizing the solute mass to the absorbed water mass.

2.4. Methods and Materials

2.4.1. Solute mass quantification

The ability to quantitatively leach solutes from the Whatman[®] 1 CHR paper was tested by adding a known mass of salt (Na^+ , Mg^{2+} , Cl^- , K^+ , Ca^{2+} , Br^- , Sr^{2+} and SO_4) to papers (in triplicate) by dispersing, drop by drop, 200 μL of one of eight different dilutions (Table 2.1) of a synthetic porewater (SPW, Table 2.2; Cavé et al. 2009) across the surface of each Whatman[®] 1 CHR paper (45 mm diameter). Mass measurements were conducted using a Scientech electronic balance (SA 120). The papers were air dried in a

dust free environment for 24 hours and then leached in 10 mL of Type I water for 24 hours.

Table 2.1. Total salt mass applied to papers for various experiments. The SPW dilutions were selected to contain a range of solute mass that spans the range extracted from cores in the preliminary trial.

SPW dilution factor	Total salt mass added (mg)	Experiment			
		Solute Mass Quantification	NIR calibration		
			Evaporation	Re- hydration	Verification
⁺	0	√	√	√	√
31.9	1.4			√	
17.1	2.6			√	
8.7	5.1	√	√	√	√
4.4	10.2	√	√	√	√
3.0	15.7	√	√		√
2.3	21.8	√	√		√
1.9	27.4	√	√		√
1.6	32.6	√	√		√
1.4	35.8	√	√		√
1.2	40.8	√	√		√
1.1	47.8		√		
0	52.4		√		

⁺ Blank with Type I water added to paper

Table 2.2. SPW composition

Solute	Concentration (g/kgw)
Na ⁺	37.59
Mg ²⁺	2.99
Cl ⁻	125.86
K ⁺	1.60
Ca ²⁺	32.75
Br ⁻	1.60
Sr ²⁺	0.70
I ⁻	0.03
SO ₄ ²⁻	0.08

Leachates and the initial spike solutions were prepared for ICP MS analysis in a 2 % HNO₃ matrix (trace metal grade, SCP Science). Internal standards (1500 µg In/L and 50 µg Y/L, SCP Science) were added to monitor and correct for instrumental drift. Calibration curves were generated from calibration standards, prepared from certified standards (SCP Science) and tailored to match the sample matrix.

Solutions were analyzed using an Agilent™ 7700x quadrupole ICP MS with a helium collision cell. Samples were introduced using an autosampler with a nebulizer pump flow rate of 0.1 mL/min and gas flow rate of 2 mL/min. The helium collision cell was used for Cl⁻ and Br⁻ quantification.

2.4.2. Adsorption

The Whatman® 1 CHR paper was cut into 1 cm² pieces and placed into glass vials with 10 mL of SPW, diluted by factors of 10, 100 and 250, each with the pH adjusted to 5, 6 or 7, with 0.01 M NaOH and 0.01 M HCl (Fisher Scientific) and monitored with an Oakton pH 11 Series pH meter with Oakton pH probe (WD 35801 00). This resulted in nine experimental solutions, and each was tested in triplicate. Experimental controls were prepared without paper using SPW diluted by a factor of 100, and method blanks were prepared with Type I water (18 MΩ cm) and paper. Controls and blanks were prepared at pH 5, 6 and 7 in triplicate. The papers were submersed in the solutions for 24 hours, after which the papers were discarded and the aqueous samples were prepared for ICP MS analysis.

2.4.3. Water mass quantification

Quantification of the water-content of papers was conducted using a Process Sensors Co. (Milford, MA, USA) MCT660 Bench Top NIR spectrometer. Calibration of

the instrument was conducted as water evaporated from the papers, or as the dry papers re hydrated in a humid environment, producing evaporation and re hydration curves. Evaporation curves were generated by first, evenly distributing 200 μ L of SPW dilutions (Table 2.1) on each paper and then recording both gravimetric and NIR absorbance measurements periodically during evaporation. Re hydration curves were generated by distributing 200 μ L of SPW dilutions (Table 2.1) on each paper, then drying the papers in a dust free environment for 24 hours. Once dry, the papers were placed in 100 % relative humidity chambers. Papers were removed from the chambers periodically over a period of 72 hours to record the gravimetric and NIR absorbance measurements. Data collection for each evaporation and re hydration curve was terminated when both gravimetric and NIR measurements remained constant. All data were collected in triplicate and all measurements were made in an optically clear, low volume Permanox dish (Nalge Nunc International, USA) to prevent water vapour gains or losses from the paper. Three dimensional surface equations (salt mass, water content and NIR absorption) were fitted to the evaporation and re hydration data sets using an online curve fitting program (www.zunzn.com). Water content is reported as the wet mass of the paper normalized to the dry mass. A 95 % confidence interval was calculated from the variance of the data for each equation, generating an error envelope for each surface.

2.4.4. Method verification

Two experiments were conducted to verify that the method is capable of providing precise and accurate determinations of porewater chemistry. One experiment involved spiking papers with SPW and a second experiment was conducted with rock cores that had been infiltrated with SPW.

2.4.4.1. Spiked papers

Initial mass and NIR absorbance were measured for dry 45 mm diameter Whatman[®] 1 CHR papers. A known mass of solutes was applied to each paper by distributing 200 μ L of one of eight SPW dilutions or Type I water (Table 2.1) across the surface. A uniform solution distribution could not be achieved during the addition of solutions to the paper and NIR spectrometric measurements conducted immediately after additions were imprecise. In order to obtain a uniform distribution, papers with added solutions were air dried for 24 hours, then placed in individual 85 % relative humidity chambers for 72 hours, allowing them to re hydrate evenly. Humidity chambers were constructed by placing a saturated KCl (Fisher Scientific) solution into an air-tight container. Following re hydration, mass and NIR spectrometric measurements were conducted for each paper prior to leaching the solutes into 10 mL of Type I water and then preparing the solutions for ICP MS analysis.

2.4.4.2. Core experiment

Red mudstone drill core segments (7 cm diameter, Mabou Group from the Carboniferous Maritimes Basin near Sussex, New Brunswick, Canada) were segmented into nine 10 - 15 cm long pieces. The mudstones of the Mabou Group may contain dolomite, gypsum and clay minerals including illite, chlorite, kaolinite and smectite and the porosity is on the order of 6 % (Bibby and Shimeld, 2000; Crawford, 1995).

Dry cores were obtained and then re-saturated for 33 days in three different dilutions (1, 10, 100x) of SPW solution (Table 2.2). The composition of the natural porewater that had dried in the cores is not known leading to some uncertainty, but it was assumed that the cores equilibrated with the SPW solutions during the 33 day immersion

and re-saturation period. At the end of the 33 day period, samples of the modified SPW solutions were collected for ICP-MS analysis.

The cores were removed from the jars, wrapped tightly in multiple layers of plastic wrap and secured with electrical tape to prevent evaporation. Cores were dry cut into 2 cm segments using an 18 cm diameter tile saw. The blade was cooled by directing a stream of compressed CO₂ directly at the blade during cutting using a CO₂ gun (Applied Surface Technologies, CO₂ Snow Jet Sample Cleaner, K1-10). The CO₂ gun was also used to remove powdered rock particulate from the core surface after cutting. Whatman[®] 1 CHR papers (45 mm) were prepared by pre-weighing and pre-measuring by NIR spectrometry to determine the initial water-content. These were placed between the core segments and the cores were immediately wrapped and stored at 5 °C for 14 days.

After porewater absorption, the papers were removed from the cores. The water-content was measured by NIR and the mass was recorded for each paper immediately after removal. Papers were dried for 24 hours in a dust free environment and then leached with 10 mL of Type I water. The leachates and modified SPW solutions were filtered (0.45 µm) and prepared for ICP-MS analysis.

2.5. Results and Discussion

2.5.1. Solute mass quantification

A comparison of solute masses leached from the papers to those applied to each paper (Figure 2.3) demonstrates that the leaching method achieves complete removal of solutes from the paper as the data fall on the one to one line within $\pm 2\sigma$ (error bars). These data demonstrate that leaching solutes into 10 mL of Type I water over a 24 hour period provides quantitative removal of absorbed solutes for analysis by ICP-MS.

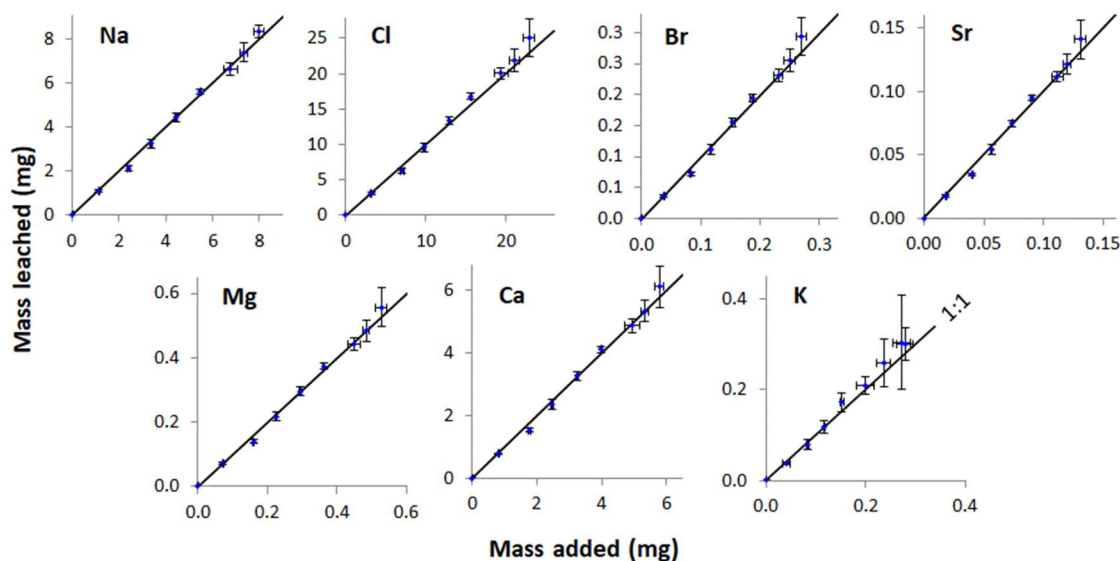


Figure 2.3. Solute mass added to the papers compared to solute mass removed from the papers. Error bars represent $\pm 2\sigma$ on replicate analyses (Appendix A).

Matrix effects that hinder accurate solute quantification by ICP-MS analysis occur in highly saline samples (total dissolved solids $> 20,000 \mu\text{g/L}$) which require dilution prior to analysis (Tan and Horlick, 1987). The increase in the size of error bars with increasing salt mass results from the large dilution factors required for sample preparation. The consistent pattern toward a slight divergence from the 1:1 line at high salinity suggests that there is a small systematic error caused by dilution during sample preparation. The poor analytical precision for K^+ is a result of intermolecular inference from Ar gas (May and Wiedmeyer, 1998).

2.5.2. Adsorption

The extent of solute adsorption to the papers is assessed by plotting sorption isotherms (Figure 2.4) that present the mass of sorbed solute per mass of paper (C^*)

versus the initial solute concentration in the experimental solutions (C_i). Values for C^* are calculated as:

$$C^* = \frac{C_i - C_f}{m_s} \quad (2.1)$$

Where C_f is the final solute concentration and m_s is the mass of the paper. Values for C^* that fall above or below zero represent adsorbed and desorbed solutes respectively, and values equal to zero indicate neither adsorption nor desorption.

Example sorption isotherms for Na^+ , and Ca^{2+} at pH 5, 6 and 7 are shown in Figure 2.4. Most of the data plot on or within error of the zero line, indicating no preferential adsorption or desorption of solutes to or from the papers. Two-tailed student's-t tests indicate that there is no significant adsorption ($p = 0.05$) for all solutes (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Cl^- and Br^-). At high solution concentrations there are data that plot slightly below and above the zero line, but most are equivalent to zero when taking analytical error into account. The absolute magnitude of these deviations from the zero line is very small compared to the mass of Na^+ and Ca^{2+} extracted during the preliminary trial and would not be distinguishable from the porewater solutes. For example, in the preliminary trial the average mass of Na^+ and Ca^{2+} extracted in the papers was 3000 mg/kg paper and 1800 mg/kg paper respectively - four orders of magnitude larger than the C^* values reported in Figure 2.4.

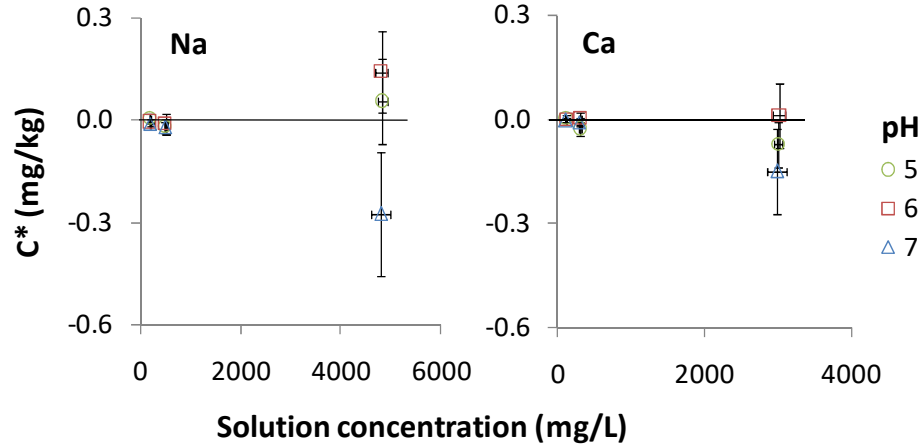


Figure 2.4. Sorption isotherms for Na^+ and Ca^{2+} at pH 5, 6 and 7. Error bars represent the $\pm 2\sigma$ on replicate analyses (Appendix A).

2.5.3. Water mass quantification

The NIR absorption by water has been shown to be salinity dependent because salts affect the vibrational properties of the H-O bonds of the water molecule (Pegau et al. 1997). Therefore, calibration of the NIR spectrometer was conducted for Whatman[®] 1 CHR papers at a range of water and solute masses (Figure 2.5) that correspond to the expected range of absorbed porewater based on data from the preliminary trial. The NIR spectrometer is most sensitive to water at the surface of the paper and, even though the paper is 0.18 mm thick, this sensitivity is evident in the measurements for the calibration particularly at low water-content (< 0.5). In the low end of the water-content range the surface of the paper dries at a faster rate than the middle of the paper during evaporation, while re-hydration leaves the surface of the paper wetter than the middle. Therefore, at low water-content, the evaporation curves are expected to under-predict the mass of water, while the re-hydration curves should over-predict the water mass. In practice, when papers are removed from rock cores the porewater distribution in the paper is expected to be uniform.

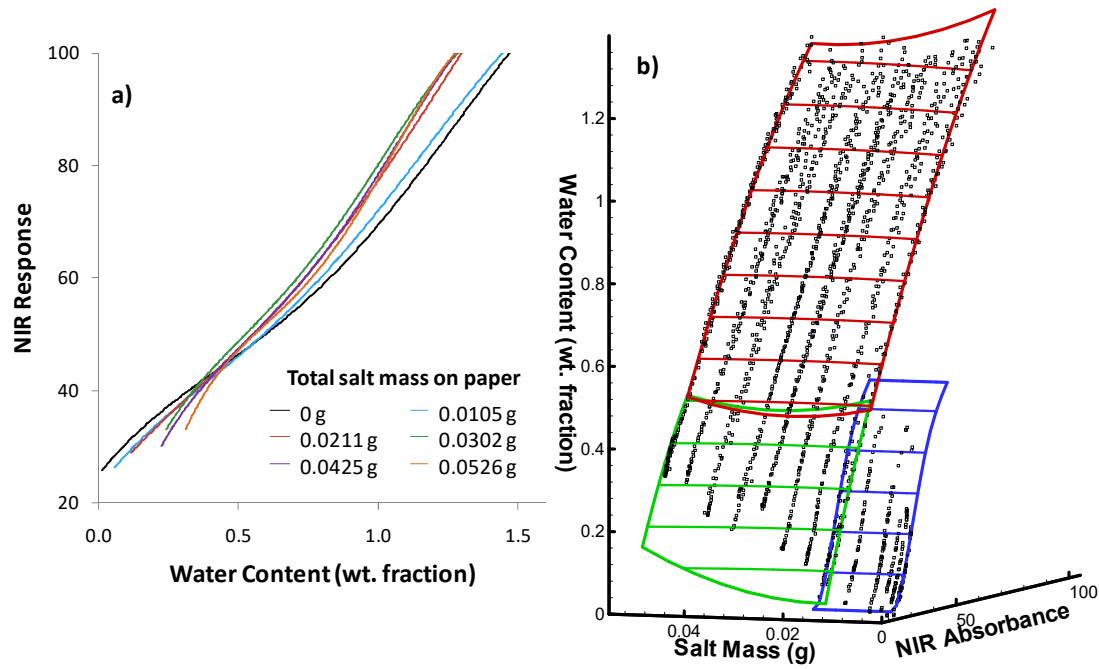


Figure 2.5. The NIR spectrometer calibration. a) Evaporation curves for a range of solute masses. b) The 3D calibration surface generated from both evaporation (total salt mass > 0.016 g) and re-hydration (total salt mass < 0.016 g) curves (Appendix A). The data points are depicted with black dots, the three surfaces are depicted by different colours.

An inflection point is observed for each evaporation curve at a NIR absorbance of $45 \% \pm 2.5 \%$ (Figure 2.5a). In order to account for this inflection and the sensitivity to salt mass, the evaporation curve data were divided into three subsets listed in Table 2.3. A surface was generated from each of the data subsets and the re-hydration curves to obtain the best possible fit to the data (Table 2.3).

The accuracy of NIR spectrometry for the quantification of absorbed water mass was assessed by comparing results to those obtained from gravimetric measurements (Figure 2.6). During porewater extraction from cores, particulate matter transfer between the core and the paper prevents the use of gravimetric measurements for water mass

quantification. In this experiment solutions were added to the papers and particulate matter transfer was not a concern so it was possible to make simultaneous NIR and gravimetric measurements of water mass for comparison. Good correlation ($R^2 = 0.988$, two tailed P test = 98%) was observed between the two methods. The difference in error observed between the low and high water-contents is attributed to the different NIR calibration surfaces used (Table 2.3).

Table 2.3. Equations for NIR spectrometer calibration.

Data subset	Evaporation			Re-hydration
NIR (%)	> 40	< 45	< 45	< 45
Salt mass (g)	> 0.016	> 0.016	< 0.016	< 0.016
z =	$a + bx + cy + dx^2 + fy^2 + gxy$	$a + bx + cy + dx^2 + fy^2 + gxy$	$a + by + cy^2 + dx + fxy + gxy^2$	$a + by + cy^2 + dy^3 + fy^4$
a	-6.13×10^{-1}	-8.69×10^{-1}	-2.10×10^{-1}	4.85
b	-2.19	1.64	1.09×10^{-4}	-6.15×10^{-1}
c	2.85×10^{-2}	4.06×10^{-2}	3.29×10^{-4}	2.75×10^{-2}
d	8.68×10^1	8.87×10^1	-2.99×10	-5.05×10^{-4}
f	-7.72×10^{-5}	-2.05×10^{-4}	1.98	3.36×10^{-6}
g	-5.52×10^{-2}	-1.68×10^{-1}	-2.19×10^{-2}	
RMSE ^a	3.04×10^{-5}	4.31×10^{-6}	1.93×10^{-2}	$.18 \times 10^{-2}$
95 % absolute	4.02×10^{-2}	1.23×10^{-2}	1.18×10^{-2}	9.83×10^{-3}
CI ^b relative	7.97 %	2.44 %	2.34 %	1.96 %

x = total salt mass, y = NIR response, z = water mass (weight fraction)

^aRoot mean square error

^b95 % CI = 95 % confidence interval

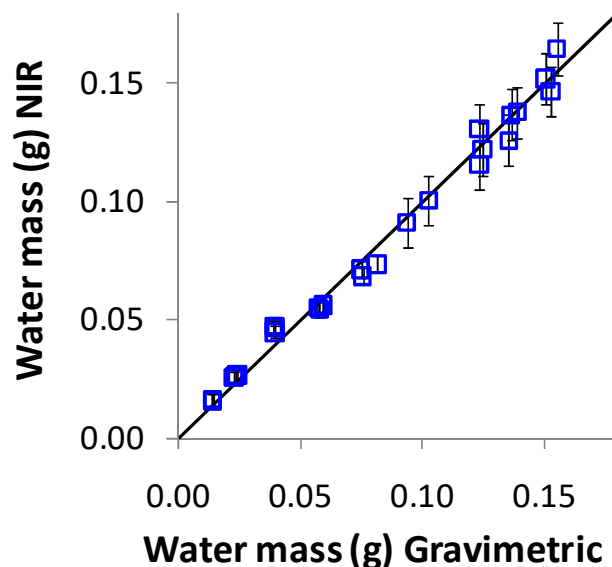


Figure 2.6. Comparison of water mass determined gravimetrically and by NIR. Error bars represent the propagated error from NIR spectrometric and gravimetric measurements although the error in gravimetric measurements is generally smaller than the symbols.

2.5.4. Method verification

2.5.4.1. Spiked papers

The extent of paper re-hydration is dependent on the total salt mass on each paper, the absorbent properties of the paper, as well as the relative humidity of the humidity chamber – the latter two being constant for all samples. Salt precipitates formed during evaporation of the SPW have hygroscopic properties, so papers with a range of added salt mass will re-hydrate with a corresponding range of water mass. Re-hydration of the papers in 85 % relative humidity resulted in final solute concentrations that are similar to SPW.

A direct comparison of Na^+ and Ca^{2+} concentrations calculated from water-contents determined both by NIR spectrometry and gravimetric measurements is depicted in Figure 2.7. For concentrations determined with NIR spectrometry the error bars

correspond to propagated error from ICP-MS and NIR spectrometry, and for concentrations determined with gravimetric measurements the error bars correspond to propagated error from ICP-MS and the electronic balance. For concentrations determined with NIR spectrometric data the relative errors range from 6 to 12 % when using the calibration from combined evaporation and re-hydration data, and from 6 to 22 % when using the calibration from evaporation data only. Relative errors range from 1 to 5 % for concentrations determined with gravimetric data.

Three distinct sets of concentration data can be discerned in Figure 2.7. The majority of the data scatter around the one-to-one line and these points correspond to samples with relatively high salt content and NIR absorbance (NIR absorbance > 40 %, salt mass > 0.016 g). Concentrations calculated using the evaporation calibration generated from low NIR absorbance (< 45 %) and low salt masses (< 0.016 g) are over-predicted. In contrast, concentrations calculated using the re-hydration calibration are under-predicted. The re-hydration NIR calibration provides the best estimation of solute concentrations but efforts will continue to improve the calibration procedure and eliminate the under-prediction of concentrations in this low range of water-content.

In order to assess the quality of the porewater concentration measurements obtained by this new method, the analytical precision obtained from the verification experiments was compared to the margin of error considered acceptable for analysis of saline water samples using US Environmental Protection Agency (US EPA) method 6020a (US EPA, 2007). These error margins range from 6 % for Ca^{2+} to 24 % for Na^+ , and are depicted by the dashed lines in Figures 2.7 and 2.8. For Ca^{2+} , the dashed lines depict ± 6 % from the one to one line, and most of the concentration measurements

calculated from both gravimetric and NIR water mass measurements fall within the EPA-recommended margin of error. The margin of error accepted for Na^+ ($\pm 24\%$), encompasses all concentration measurements. This comparison to the EPA-recommended margin of error places the results from this new absorption method in a useful perspective.

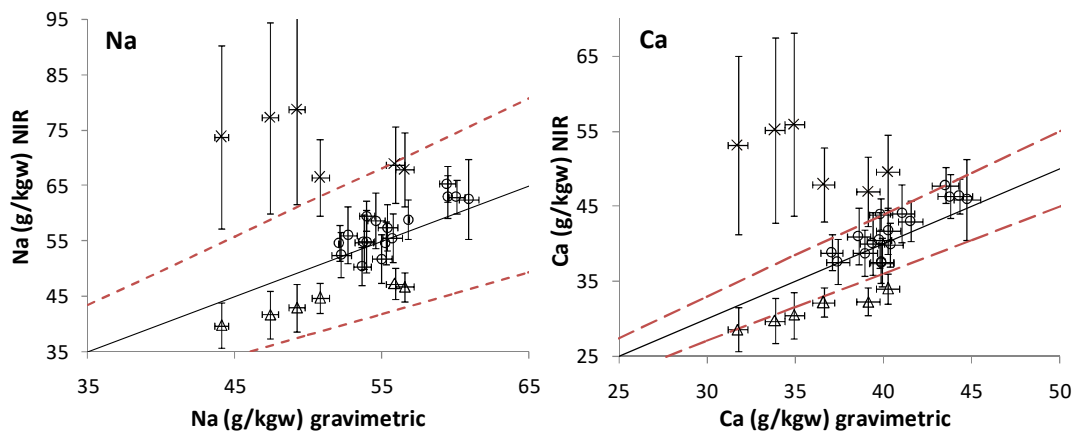


Figure 2.7. Examples of Na^+ and Ca^{2+} concentrations (g/kgw) calculated from water masses measured gravimetrically and by NIR spectrometry. Data points (○) correspond to concentrations calculated from water-contents determined by the evaporation calibration (NIR absorbance $> 40\%$ and salt mass $> 0.016\text{ g}$), data points (x) correspond to concentrations calculated from water-contents determined by the evaporation calibration (NIR absorbance $< 45\%$ and salt mass $< 0.016\text{ g}$), data points (Δ) correspond to concentrations calculated from water-contents determined by the re-hydration calibration (NIR absorbance $< 45\%$ and salt mass $< 0.016\text{ g}$). The dashed lines correspond to a relative error margin accepted by US EPA method 6020a. Error bars depict the propagated instrumental error from NIR spectrometric and gravimetric water measurements and ICP-MS solute analysis (Appendix A).

2.5.4.2. Core experiment

Re-saturation of the Mabou Group cores in SPW solutions forces the porewater chemistry toward a uniform composition. As the system equilibrates, the composition of the SPW in which the cores are immersed is expected to be modified until equilibrium is

established, at which point the porewater in the connected pore spaces should have a composition similar to the modified SPW. A direct comparison of extracted porewater and the modified SPW composition (Figure 2.8) is used to assess the ability of the method to quantitatively extract porewater and associated solutes.

All of the data are subject to some uncertainty that is hard to quantify but results from lack of knowledge of the natural porewater composition and from the possibility that the SPW did not fully equilibrate with the rocks over the 33 day time period. However, the data for Cl^- , Sr^{2+} , Na^+ and Ca^{2+} are near the one-to-one line, indicating that the extracted porewater is representative of the modified SPW solution. There is more variability observed for extracted Mg^{2+} and K^+ concentrations. This could be explained by ion exchange processes operative during re-saturation and would then indicate that the cores had not fully equilibrated with the SPW. This is a problem for short-term experiments of this nature using SPW but would not be a concern for extractions of natural porewater.

Again, as an aid to assess the quality of the porewater concentration measurements obtained by this method, the porewater concentrations measured from the core experiments were compared to the margin of error considered acceptable for analysis of saline water samples using US EPA method 6020a (US EPA, 2007). The relative error margins accepted by US EPA method 6020a are plotted for Na^+ , K^+ , Ca^{2+} and Mg^{2+} on Figure 2.8. EPA Method 6020a does not provide acceptable relative error values for Cl^- , Br^- and Sr^{2+} , but for ease of comparison we have added bounding lines representing $\pm 10\%$ relative error. As for the spiked-paper experiment, the Na^+ concentrations determined from the extractions are all within the accepted error margin

($\pm 24\%$). Similarly, most of the Ca data are within the limits defined by EPA Method 6020a. The concentration data for other elements drift outside the limits, with data for K^+ and Mg^{2+} displaying the greatest deviation.

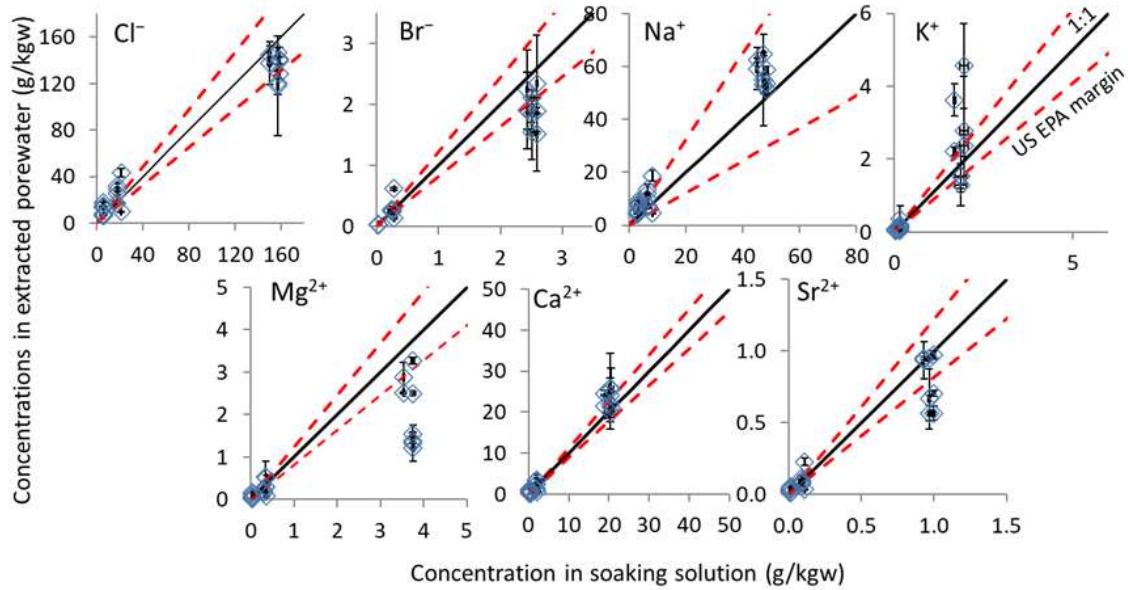


Figure 2.8. Comparison of solute concentrations (g/kgw) in the modified SPW with those in the extracted porewater. The dashed lines correspond to relative error margins considered acceptable for US EPA method 6020a for Na^+ ($\pm 24\%$), Mg^{2+} ($\pm 10\%$), Ca^{2+} ($\pm 6\%$) and K^+ ($\pm 10\%$). The dashed lines on the Cl^- , Br^- and Sr^{2+} graphs represent $\pm 10\%$ and are presented for ease of comparison. Error bars depict $\pm 2\sigma$ on replicate sample measurements (Appendix A).

2.6. Conclusions

Extraction of porewater from low-permeability rocks has been achieved using a new method that absorbs porewater into cellulosic paper placed in contact with core samples. The porewater extracted is limited to the mobile porewater from what are often termed macropores, while maintaining equilibrium with water in interlayers and the diffuse double layer, as well as soluble minerals. This leads to the potential for evaluating

anion-accessible porosity and allows for extraction of representative porewater concentrations in the presence of soluble minerals such as halite, gypsum and anhydrite. The solute concentrations in the porewater are determined from separate measurements of solute mass and water-content in the paper. Solute mass is determined by leaching the papers in Type I water followed by ICP-MS analysis. The mass of water absorbed by the paper is determined by NIR spectrometry. The method is advantageous as chemical artefacts from mineral dissolution and ion exchange are avoided, independent porosity measurements are not required, and sample preparation procedures are not complicated and could be conducted at the drill site. The absorption method holds promise in extracting very saline porewaters that are in equilibrium with soluble minerals, which is a limitation of many of the pre-existing methods.

Preliminary trials with rock core demonstrated that the method is capable of extracting sufficient porewater from low-permeability shale (Georgian Bay Formation, Michigan Basin, southwest Ontario, Canada) and that the mass ratios for solutes extracted with the porewater are consistent for all samples and solutes. The method for NIR spectrometric determination of absorbed water mass was developed and demonstrated to be effective for combining with solute mass measurements to obtain porewater chemistry. Concentration measurements obtained for Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Cl^- and Br^- in a method verification experiment using spiked papers display analytical precision within the margins of error recommended by EPA Method 6020a for analysis of saline water samples. In a method verification experiment with rock cores, Na^+ and Ca^{2+} are within the margins of error recommended by the US EPA. Concentrations of Cl^- , Br^- and Sr^{2+} deviate slightly outside a 10 % margin, while K^+ and Mg^{2+} show a great deal of

variability and are mostly outside the EPA limits. The inaccuracy for K^+ and Mg^{2+} is thought to result from incomplete equilibration of the cores with the SPW. This is not a concern when applying the method to rock samples containing natural porewater. Given that the absorption method has been demonstrated to work for extracting very small amounts of porewater, and that the concentration data are dependent on separate measurements of solute mass and water mass, the precision of the calculated concentrations in these initial trials is considered favourable.

2.7. Acknowledgements

This work was supported by funding from the Nuclear Waste Management Organization (NWMO).

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3.0. Measurement of Cl^- : Br^- Ratios in the Porewater of Clay-Rich Rocks—A Comparison of the Crush-and-Leach and the Paper-Absorption Methods

This chapter was originally published in Geofluids (open access):

Celejewski, M., Barton, D., Al, T. 2018, Measurement of Cl^- : Br^- Ratios in the Porewater of Clay-Rich Rocks-A comparison of the Crush-and-Leach and the Paper-Absorption methods. Geofluids, 2018. doi: [10.1155/2018/9682042](https://doi.org/10.1155/2018/9682042)

3.1. Abstract

Characterization of porewater chemistry in low-permeability, clay-rich rocks provides insights into solute transport mechanisms and the origin and residence time of porewater. Extraction of porewater for chemical quantification is challenging, and several methods have been applied including squeezing, advective displacement, crush and leach, and a relatively new technique that extracts porewater by absorption into a cellulosic paper by capillary action. Here we compare porewater Cl^- and Br^- mass ratios from samples using the paper-absorption and crush-and-leach techniques. Samples were obtained from Upper Ordovician shales in the Michigan Basin in Ontario, the Opalinus Clay at the Mont Terri Rock Laboratory in Switzerland, and the Upper Ordovician Lorraine Group shale in southern Quebec. The data display consistent and reproducible differences among methods for Cl^- and Br^- mass ratios, with the paper-absorption method producing systematically lower $\text{Cl}^- : \text{Br}^-$ ratios. The observed differences in $\text{Cl}^- : \text{Br}^-$ ratios are attributed primarily to anion exclusion effects which are stronger for Br^- than for Cl^- , resulting in higher Br^- concentrations in the largest pores that are preferentially sampled by the paper-absorption technique. In addition, calculations suggest that Cl^- is more effective than Br^- in forming ion pairs and clusters with neutral or positive charge which can enter the diffuse double layer. This causes a further decrease in the $\text{Cl}^- : \text{Br}^-$ ratios for the mobile water. One important message from this work is that different extraction methods should not be expected to converge on a unique porewater $\text{Cl}^- : \text{Br}^-$ ratio because each method reflects different proportions of the interlayer, diffuse double layer, and mobile fractions of porewater

3.2. Introduction

The requirement for long-term geological sequestration of CO₂ (Benson and Cole, 2008; Lackner, 2003) and nuclear waste management (Cherry et al., 2014; Hendry et al., 2015; Russell and Gale, 1982) has prompted increased interest in low-permeability, clay rich sedimentary rocks (Al et al., 2015; Bensenouci et al., 2013; Clark et al., 2013; Mäder et al., 2017, Mazurek et al., 2011; Nakata et al., 2015; Van Loon et al., 2004). These rocks are characterized by low hydraulic conductivity ($<10^{-11}$ m/s) and, as a consequence, solute transport is dominated by diffusion (Birkholzer et al., 2012; Hendry et al., 2009; Hendry and Wassenaar, 2000, 2004; Neuzil, 1986; Russell and Gale, 1982). Characterization of natural tracers, such as Cl⁻ and Br⁻ in the porewaters of low-permeability rocks is critical in establishing the provenance of salinity, whether marine or otherwise, as well as solute transport mechanisms and residence times (Clark et al., 2013; Desaulniers et al., 1981; Gimmi et al., 2007; Harrington et al., 2013; Hendry et al., 2000; Hendry and Harrington, 2014; Mazurek et al., 2011; Rübel et al., 2002). Mazurek et al. (2011) compiled measurements of natural conservative tracers (Cl⁻ and stable water isotopes) in the Opalinus Clay at Mont Terri, Switzerland, the Boom Clay at Essen, Belgium, and the Couche Silteuse at Marcoule, France, by plotting spatial profiles of tracers across these formations. The data allowed for determination of transport processes and porewater residence times.

Sampling porewater from low-permeability, clay-rich formations for chemical quantification is a challenging endeavor. This is in part due to the small volumes available for extraction and because of the complexity of water clay interactions (Appelo et al., 2010). Negatively charged clay surfaces are balanced by cation-rich water in direct

contact with the surface (Sposito and Prost, 1982; van Olphen, 1965). This cation-rich water is “bound water” and occupies the interlayer positions in clay minerals or the diffuse double layer (DDL) that surrounds mineral surfaces, extending outward into the pore spaces (Edwards, 1965; Wersin et al., 2004). “Mobile water” containing a balance of cations and anions occurs outside of the DDL in larger pore spaces. Together the bound water and mobile water constitute porewater. Figure 3.1 presents a pore-scale conceptual model for porewater in clay-rich rocks, illustrating the three principal water types: interlayer water, DDL water, and mobile water. Considering this conceptual model, it is evident that it is not appropriate to speak of a single porewater composition, and methods developed to measure the composition of porewater should be expected to provide different results if they do not sample equal fractions of these three water types.

Porewater chemistry and solute transport are generally considered in conjunction with porosity and pore geometry, because common methods for determining aqueous solute concentrations require independent measures of solute mass and pore volume. Pearson (1999) defines the porosity of a “mudrock” in terms of total physical volume (physical porosity), transport-accessible volume (transport porosity), and the volume available for geochemical reactions (geochemical porosity). Transport porosity may be further divided into porosity that is accessible to either advection or diffusion; advection porosity being limited to relatively large, interconnected spaces through which porewater can flow, while diffusion porosity includes connected and dead-end pores as well as interlayer volumes. Transport and geochemical porosities define the pore space accessible to specific solutes (solute-accessible porosity) and can be dependent on measurement techniques (Anovitz and Cole, 2015). The geometry of the pores can

influence the movement of solutes due to variations in the constrictivity, connectivity, and tortuosity of the pore channels (Keller et al., 2011). In materials with narrow pore throats, DDLs can overlap, impeding the movement of anions to cause anion exclusion effects (Lavoie et al., 2014). Size-specific anion exclusion is also possible whereby DDLs are close to overlapping resulting in channels that are passable only for the relatively small anionic species.

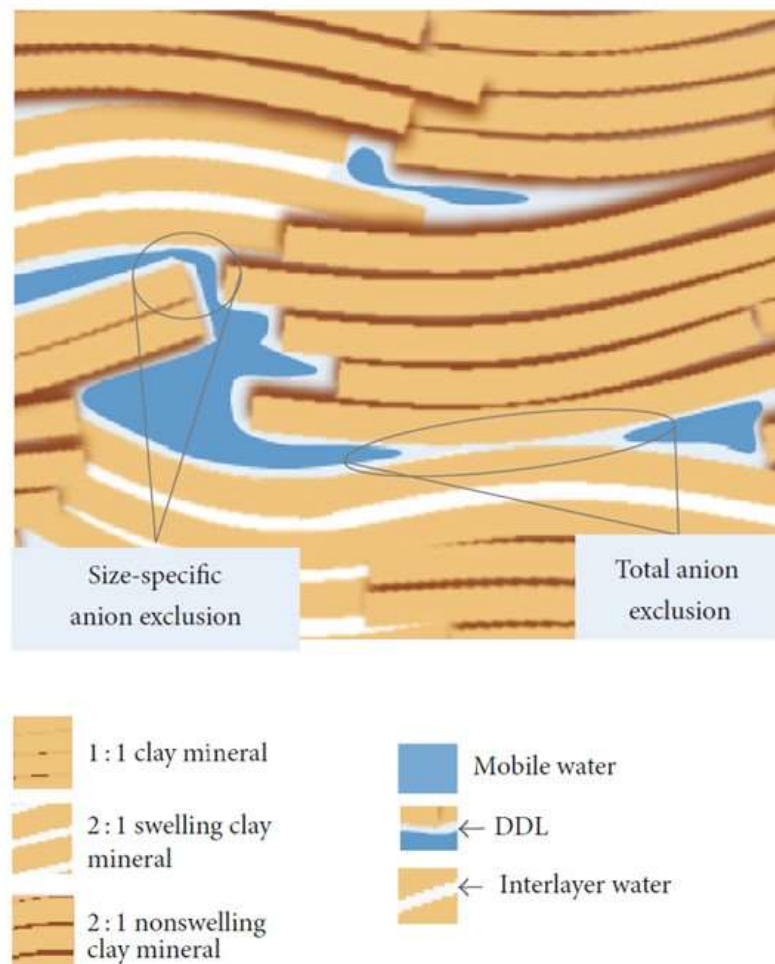


Figure 3.1. Pore-scale conceptual model for clay-rich sedimentary rock. A variety of clay minerals are depicted, including 1 : 1 clay minerals, such as kaolinite, 2 : 1 nonswelling clay minerals, such as illite, and 2 : 1 swelling clay minerals such as smectite. The negatively charged surfaces of these minerals are balanced with cation-rich water in the DDL and in the interlayer positions of the swelling clay minerals. Mobile water is found in the larger pore spaces.

There are several established methods to extract porewater from low-permeability rocks for chemical characterization. In some cases it is possible to directly sample porewater by collecting seepage, and this is thought to yield samples that are most representative of the mobile water fraction (Gascoyne, 2004; Pearson et al., 2003), but the sampling durations are very long, on the order of months to years (Waber and Smellie, 2008). Indirect methods are also available, including out-diffusion (Bensenouci et al., 2014; Savoye et al., 2006; Wittebroodt et al., 2007), ultracentrifugation (Yang et al., 2003), high-pressure squeezing (Fernández et al., 2003, 2014; Mazurek et al., 2015), crushing and leaching (Devine et al., 1973; Mazurek et al., 2015; Motellier et al., 2003; Murthy, 1973), advective displacement (Mäder et al., 2017), and absorption by paper (Celejewski et al., 2014). These methods are susceptible to artefacts from disturbance of the equilibrium between minerals, bound water, and mobile water (Sacchi et al., 2001) that result in mineral dissolution (Fernández et al., 2003), cation exchange (Appelo and Postma, 2005), and changes in DDL thickness (Wersin et al., 2016). These artefacts may cause inconsistency among methods, particularly for the reactive cation species (Azcue and Rosa, 1996; Sacchi et al., 2001). In addition, effects of anion exclusion (Nakata et al., 2015) are manifested to varying degrees for the different extraction methods. It is common to apply corrections to account for anion exclusion artefacts in order to obtain concentrations reflective of the in situ mobile water (Appelo and Wersin, 2007; Mazurek et al., 2011, 2015).

The objectives of this work are as follows: (1) to emphasize the point that the indirect methods should not be expected to provide identical results because they do not sample equal fractions of the interlayer, DDL, and mobile waters and (2) to present

evidence that demonstrates differences in ion-specific porosity for the nonreactive species Cl^- and Br^- . A comparison approach is required to address objective 1, but a comparison among methods that provide compositional data reflecting unknown fractions of the interlayer, DDL, and mobile waters is not valuable. With this in mind, we chose to compare Cl^- and Br^- mass ratios obtained from core samples using the paper-absorption method and the crush-and-leach method. Crush and leach is used as a benchmark for comparison because it is expected to provide the closest possible approximation to the entire Cl^- and Br^- budget in all porewater (Devine et al., 1973; Mazurek et al., 2015; Motellier et al., 2003; Murthy, 1973). The paper-absorption method is included in the comparison because it targets only the mobile water fraction.

3.3. Materials and methods

3.3.1. Sample collection

Clay-rich rock cores were obtained from three locations: Upper Ordovician shale from the Michigan Basin near Tiverton Ontario, Canada; Upper Ordovician Lorraine Group shale from the Appalachian Basin at St. Edouard Quebec, Canada; and the Opalinus Clay from the Mont Terri Rock Laboratory, Switzerland. The Michigan Basin borehole (DGR8) was drilled with salt water to a depth of 724 meters below ground surface (mBGS) (Geofirma Engineering Ltd., 2012). Rock core samples (76 mm in diameter and 150–200 mm in length) were collected for porewater geochemical analysis from 463 to 635 mBGS. The Opalinus Clay borehole (BDB1) was drilled, using air as a flushing medium, from a tunnel in the Mont Terri Rock Laboratory in two parts to a total depth of 247 m, with 101 mm diameter core recovered from 0 to 97 m (Hauptrogenstein and Passwang formations) and 85 mm diameter core recovered from 97 to 247 m through

the Opalinus Clay and the Staffelegg Formation. Porewater geochemistry was measured on cores between 115 and 221 m depth. A continuous slice with a maximum thickness of 10 mm was removed from the periphery of the core over the length of the borehole for petrophysical, geochemical, rock mechanical, and stratigraphic studies (Reisdorf et al., 2016). Lorraine Group shale samples were recovered from four boreholes (F-7, F-8, F-20, and F-21) drilled with freshwater, to total depths of 50 to 150 mBGS. Samples of 63.5 mm diameter and 300 mm in length were obtained from depths of 42 to 135 mBGS. All boreholes were drilled perpendicular to bedding.

Michigan Basin cores were preserved by wrapping in plastic film, then vacuum sealing, first in a nitrogen-flushed plastic bag, and then in an aluminum-lined plastic bag. Some Opalinus Clay cores were preserved by wrapping in plastic film, then vacuum sealing in an aluminum-lined plastic bag, others by vacuum sealing, first in a plastic bag, and then in an aluminum-lined plastic bag. Sample collection and preservation were completed within 30 minutes of core retrieval from the boreholes. Preserved cores were shipped in coolers with ice packs to the laboratory, where they were stored in a refrigerator at 4°C. Core from St. Edouard had been archived by enclosing in plastic wrap and zip-lock plastic bags and then freezing. They were stored at room temperature for 6 months prior to porewater extraction.

A total of seven core samples spanning the Queenston, Georgian Bay, and Blue Mountain formations were collected from the Michigan Basin. Porewater extraction was performed by paper absorption and crush and leach on the same core samples. For the Opalinus Clay, identical samples were not used for both paper absorption and crush and leach. The paper-absorption method was applied to six core samples located between 115

and 221 m along the borehole depth and 16 different core samples were collected from the same depth for crush-and-leach extraction. For the Lorraine Group, four adjacent sample pairs were collected for extraction by paper absorption and crush and leach. In all cases the cores were subsampled to provide between one and five individual extracts. Key mineralogical and physical properties of the core samples are listed in Table 3.1.

Table 3.1. Physical properties

Michigan Basin				Opalinus Clay			Lorraine Group
Queenston	Georgian Bay	Blue Mountain	Sandy facies	Carbonate sandy facies	Shaly facies		
Mineral composition (wt. %) ^{a, b, c}							
Calcite	8 – 57	3 – 31	4 – 11	4 – 22	21 – 59	12 – 36	8
Dolomite	9 – 3	2 – 41	2 – 8	0 – 6	0 – 1	0 – 1	7
Quartz	4 – 17	12 – 46	30 – 47	13 – 45	5 – 29	13 – 26	27
Clay	17 – 60	23 – 70	27 – 31	25 – 66	8 – 48	36 – 60	46
Feldspar	–	2 – 6	–	2 – 5	3	1 – 2	10
Number of core samples							
Paper absorption	3	1	2	4	–	2	4
Crush and leach	3	1	2	7	1	8	4
Hydraulic conductivity (m/s) ^{d, e}							
1.1 x 10 ⁻¹³ – 1.0 x 10 ⁻¹⁴				2.0 x 10 ⁻¹⁴ – 6.0 x 10 ⁻¹³			N/A
Porosity (water loss %) ^{f, c}							
6 – 7				12 – 15			N/A
Ionic strength (mol/L) ^{g, h}							
8.2				0.4			N/A

^a (Lavoie et al., 2014); ^b (Koroleva et al., 2008; Skowron and Hoffman, 2009); ^c Clark, Matray, and Waber: BDB-1 borehole investigation, unpublished; ^d (Raven et al., 2011); ^e (Yu et al., 2017); ^f (Sterling et al., 2011); ^g (Xiang et al., 2016); ^h (Mazurek et al., 2015; Van Loon et al., 2005), N/A = not available

3.3.2. Paper absorption

This method is based on that described by Celejewski et al. (2014). Cores were cleaved with a hammer and chisel into pucks with a minimum thickness of 20 mm to

expose fresh surfaces for porewater extraction. The surfaces were quickly dabbed with a carpenter tack cloth to remove fine particulates and then a 45 mm diameter Whatman[®] 1 CHR paper was placed between the core segments. The cores were pressed tight over the papers and then enclosed in plastic wrap and secured with vinyl tape to compress the paper between the core segments. The wrapped samples were further isolated from the environment in individual zip-lock plastic bags and refrigerated at 4°C for 55 days. We assume that all solutes are transferred to the paper at the same rate (no fractionation over time), so the only consideration for deciding the length of the extraction period is that it must be long enough to accumulate sufficient solute mass in the paper for a high-quality analysis. Therefore, although capillary-pressure gradients are responsible for extracting the water from the rock pores into the paper, hydrostatic equilibrium is not required.

Borhan and Rungta (1993) and Wang et al. (2013) conducted experiments with Whatman[®] Number 1 filter paper to measure the rate of water imbibition and spreading from a point source (capillary pressure at the source is the same as atmospheric pressure). An empirical model developed by Borhan and Rungta (1993) indicates that complete wetting of a 45 mm diameter paper occurs in 4 minutes. The much higher capillary pressure of porewater in the rock would increase the wetting time but it is likely that hydrostatic equilibrium was reached before 55 days.

Michigan Basin core samples were cleaved in a room with no humidity control, whereas Opalinus Clay and Lorraine Group shale core samples were cleaved in a humidity chamber with the relative humidity (RH) being adjusted to 95 %, in equilibrium with the anticipated porewater salinity. The equilibrium vapour pressure was determined with the equilibrium geochemical code, PHREEQC (Parkhurst and Appelo, 1999).

Evaporation rates were quantified by monitoring the mass change of 200 μL of a synthetic porewater solution with an ionic strength of 8.2 mol/L on a 45 mm diameter Whatman[®] 1 CHR paper at 12 % and 82 % RH (VWR model 61161-382 humidity and temperature meter).

After 55 days, the papers were removed from between the core segments and porewater solutes were leached from the papers for 24 hrs in 15 mL of Type-I deionized water ($>18.2 \text{ M}\Omega\cdot\text{cm}$). Leachates were acidified to 1 % HNO_3 (trace metal grade, 70 % HNO_3 , SCP Science). Concentrations of Cl^- and Br^- in the leachates were determined by ICP-MS (Agilent[™] 8800). Instrumental precision was determined from replicate analyses of matrix matched standards (SCP Science) and relative standard deviations (RSD) were less than 3 %. Instrumental accuracy was monitored by inclusion of a certified seawater standard (High Purity Standards) and all results were within 4 % of accepted values.

3.3.3. Crush and leach

The outer 10 to 20 mm of each core sample was removed with a hammer and chisel and discarded. For the Opalinus Clay and Michigan Basin samples, rock material was crushed and sieved to a 2 to 4 mm size range. Lorraine Group shale samples were crushed to a powder ($<100 \mu\text{m}$ diameter) with a ball mill. Approximately 10 g (Michigan Basin and Opalinus Clay) and 5 g (Lorraine Group) of the crushed rock material were leached for 24 hours, in 40 mL (Michigan Basin and Opalinus Clay) and 20 mL (Lorraine Group) of Type-I deionized water for a solid/liquid mass ratio of 0.25. Phase separation was conducted by centrifugation followed by filtration ($0.45 \mu\text{m}$). The concentration of Cl^- and Br^- in the leachates were analyzed by ICP-MS.

The grain-size range used for samples from the Michigan Basin and the Opalinus Clay was not consistent with that used for the Lorraine Group shale, so a separate experiment to determine the effect of grain size was conducted. Two Opalinus Clay samples from the BDB-1 borehole were selected, one from a clay-rich zone and a second from a carbonate-rich zone. Core samples, 200 mm long, from borehole depths of 166 m and 189 m, with 58 % and 8 % total clay content, respectively, were sawed along the length of the core into three segments, providing triplicate samples with consistent mineralogy. Each segment was coarsely crushed (<30 mm), homogenized, and divided into nine subsamples. Each subsample was crushed with a mortar and pestle and sieved to obtain one of nine grain-size fractions (<37, 37–75, 75–125, 125–250, 250–500, 500–1000, 1000–2000, 2000–4000, and 4000–10000 μm). Approximately 10 g of each size fraction was leached in 40 mL of Type-I deionized water for a solid/liquid mass ratio of 0.25 for 24 hours. Phase separation was conducted by centrifugation followed by filtration (0.45 μm). Concentration of Cl^- and Br^- in the leachates was quantified by ICP-MS.

3.4. Results and discussion

The paper-absorption method removes only a few tens of milligrams of porewater from the interconnected pore spaces in direct contact with the absorbing paper. The crush-and-leach method, as applied in this study, “samples” hundreds of milligrams of porewater from 5 to 10 g (approximately 2000 to 4000 mm^3) of rock. Consequently, the masses of Cl^- and Br^- extracted by the paper-absorption method are much smaller than those extracted by crush and leach (Table 3.2). To facilitate comparison of the data, scaling factors were applied to the masses extracted by crush and leach in order to fit data

from both methods on a single set of axes (Figure 3.2). The solute masses obtained by crush and leach were divided by a factor of 10 for the Michigan Basin, 20 for the Opalinus Clay, and 3.5 for the Lorraine Group shales.

The mass ratios demonstrate consistent linear trends (Figure 3.2), but compared to crush and leach, the $\text{Cl}^- : \text{Br}^-$ ratios from the paper-absorption method are consistently lower by factors of 50 % for the Lorraine Group shale, 48 % for the Michigan Basin, and 25 % for the Opalinus Clay.

For the crush-and-leach method, the grain size of samples from the Michigan Basin and the Opalinus Clay was larger than for the Lorraine Group shales. Experiments conducted to investigate the effect of particle grain size for two samples of differing clay content (58 % and 8 %) demonstrate that the $\text{Cl}^- : \text{Br}^-$ ratios are consistent regardless of clay content and grain-size fraction for a single solid/liquid ratio (0.25) and extraction duration (24 hours, Figure 3.3).

Table 3.2. Masses (μg) of Cl^- and Br^- extracted by the crush-and-leach and paper-absorption methods.

Michigan Basin						Opalinus Clay (continued)					
crush and leach			paper absorption			crush and leach			paper absorption		
sample	Cl^-	Br^-	sample	Cl^-	Br^-	sample	Cl^-	Br^-	sample	Cl^-	Br^-
463a	53928	630	463a	641	15	132.2	1454	4.74	144a	73	0.30
463b	63586	744	463b	1109	26	132.2	1554	4.90	144b	70	0.35
495a	45262	562	495a	5355	129	132.3	1576	5.00			
495b	49897	584	495b	4434	112	132.4	1467	4.47			
522	49783	615	522	4224	107	161.1	2899	9.39			
531	20635	261	531	4057	93	161.2	2832	9.00			
571a	70851	884	571a	5739	117	161.3	3049	9.70			
571b	80998	874	571b	4119	87	161.4	2539	8.02			
571c	79415	875	571c	3667	76	166.2	3418	10.84			
626a	53887	620	626a	5077	125	166.3	3367	10.73			
626b	54301	659	626b	5718	131	166.4	2886	9.21			
634a	53411	615	634a	1474	35	172.1	2469	7.86			
634b	55397	635	634b	1420	33	172.2	2581	8.36			
634c	54416	612	634c	1761	40	172.3	2517	8.11			
634d	59462	678	634d	4242	95	172.4	2519	7.94			
634e	55150	637	634e	3290	82	174.1	2702	8.42			
Lorraine Group Shales						174.2	2857	8.97			
crush and leach			paper absorption			174.3	2555	7.82			
sample	Cl^-	Br^-	sample	Cl^-	Br^-	174.4	2587	8.22			
F7-1	289	2.71	F7-3	109	1.59	179.1	1684	5.15	178a	185	0.74
F7-2	295	2.75	F7-4	91	1.32	179.2	1715	5.37	178b	177	0.75
F8-1	80	0.38	F8-3	91	0.20	179.3	1613	5.04			
F8-2	78	0.39	F8-4	24	0.16	179.4	1601	4.96			
F20-1	1162	9.87	F20-3	148	2.50	190.2	1473	4.81			
F20-2	1209	10.4	F20-4	287	5.13	190.3	1467	4.78			
444-1	121	1.66	444-2	55	1.08	190.4	1462	4.79			
Opalinus Clay						192.1	3318	10.62			
crush and leach			paper absorption			192.2	3228	10.42			
sample	Cl^-	Br^-	sample	Cl^-	Br^-	192.3	3065	10.05			
115.1	542	1.63	115	77	0.28	192.4	3222	10.28			
115.2	550	1.73				203.1	3767	11.98	204a	179	0.77
115.3	493	1.51				203.2	3712	11.78	204b	170	0.70
115.4	625	1.92				203.3	3768	12.01	204c	165	0.71
119.1	1061	3.54				203.4	3698	11.96	204d	163	0.81
119.2	984	3.32				209.1	4002	12.82			
119.3	948	3.12				209.2	3608	11.59			
119.4	996	3.37				209.3	3351	10.87			
121.1	1163	3.85	128.1	85	0.33	209.4	3365	10.73			
121.2	1185	3.85	128.2	83	0.34	220.2	2880	9.05			
121.3	1239	4.14				220.3	2752	8.54			
121.4	1131	3.72				220.4	2751	8.59			

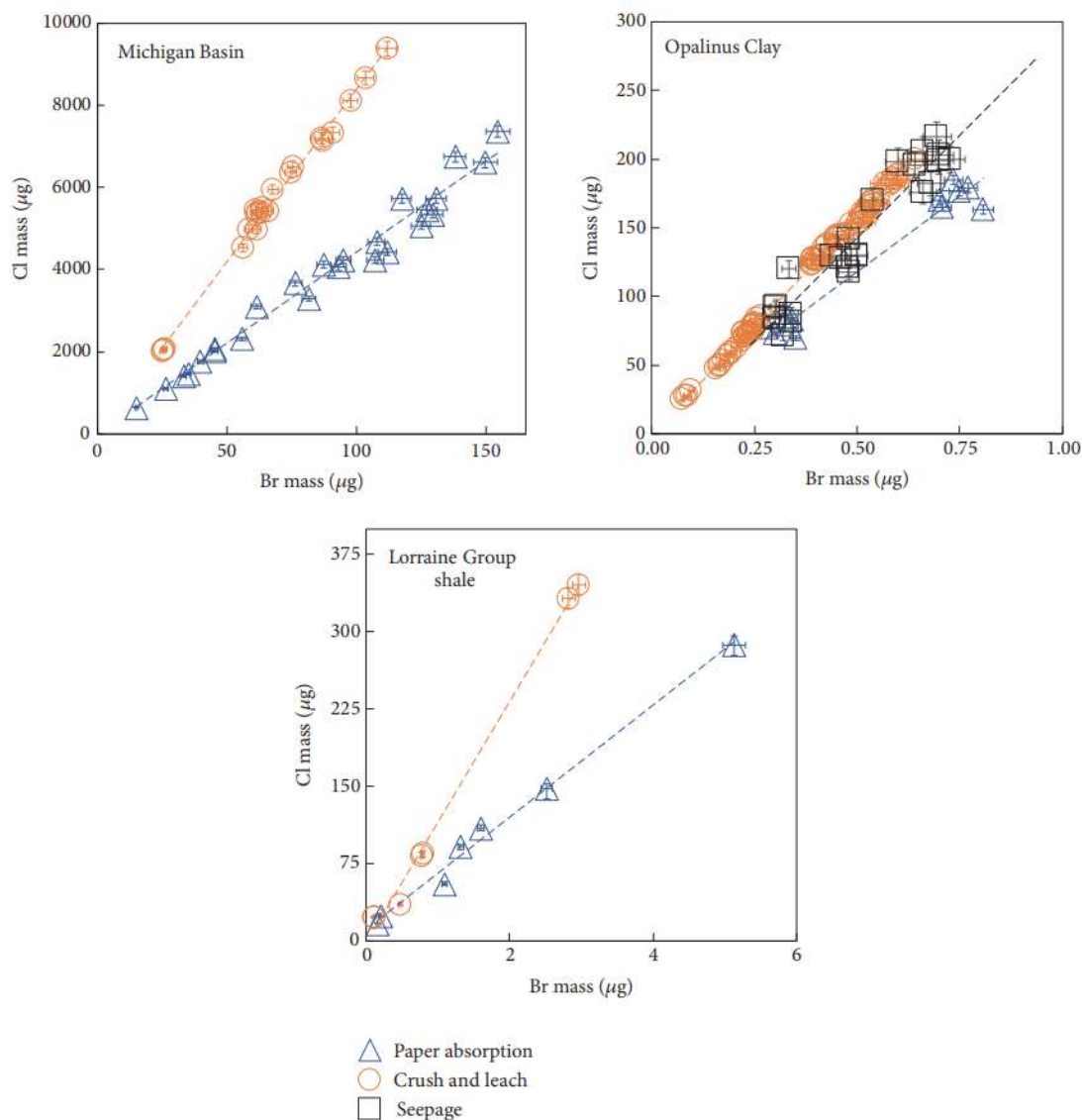


Figure 3.2. Cl^- versus Br^- mass extracted using the paper-absorption and crush-and-leach methods for rock cores from the Michigan Basin, Opalinus Clay, and the Lorraine Group. Scaling factors of 10, 20, and 3.5, respectively, were applied to the masses extracted by crush and leach to allow for direct comparison between methods (Appendix A). A scaling factor of 50 was applied to the solute masses (L-1) in the seepage water collected from boreholes in Opalinus Clay by Pearson et al. (2003). Error bars represent the instrumental error on solute analysis.

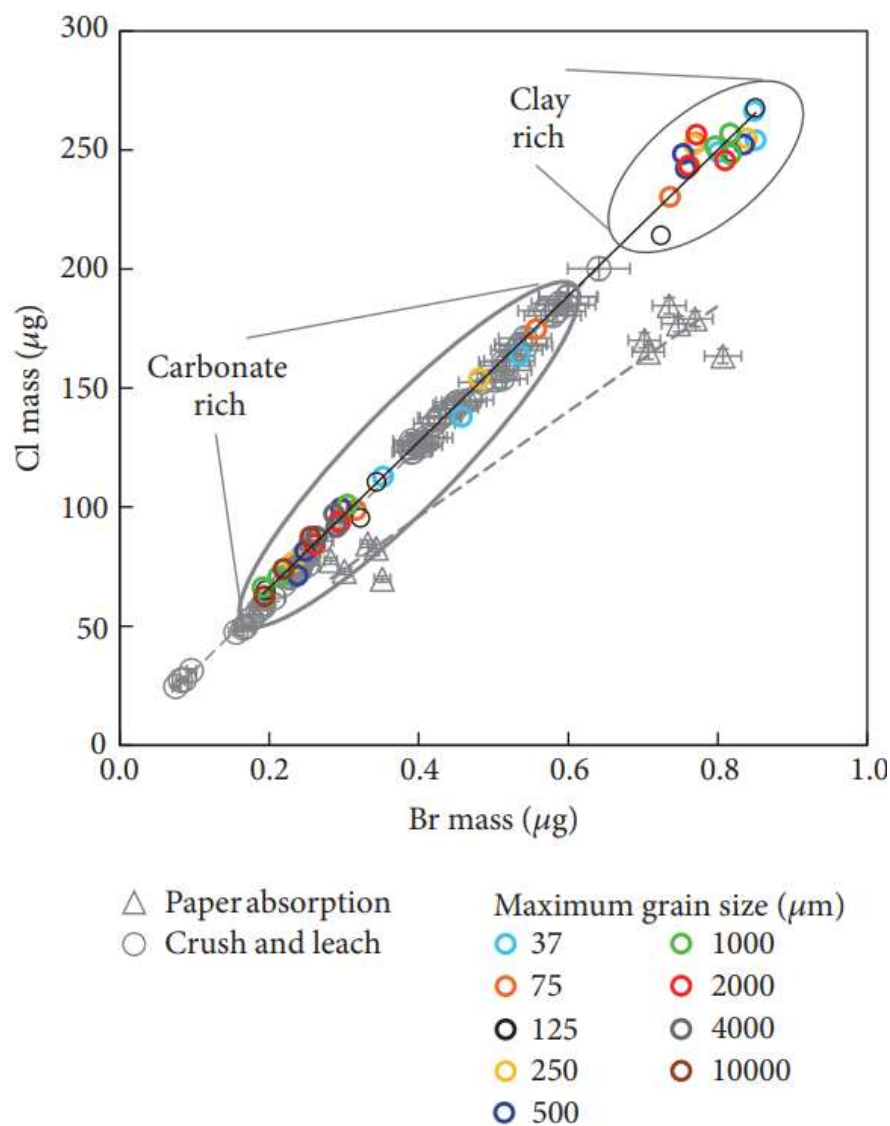


Figure 3.3. Anion masses extracted by crush and leach from Opalinus Clay samples crushed to a range of grain sizes (<37, 37–75, 75–125, 125–250, 250–500, 500–1000, 1000–2000, 2000–4000, and 4000–10000 μm).

The possibility was considered that the differences in $\text{Cl}^- : \text{Br}^-$ ratios are artefacts from mineral precipitation and/or dissolution. Halite is present in the Michigan Basin core samples (Al et al., 2015), and, as a consequence, the Cl^- ion is not entirely conservative in this system. Dissolution of pre-existing halite during the leaching step

would be expected to cause an increase in the $\text{Cl}^- : \text{Br}^-$ ratio relative to that in the mobile water. However, it is unlikely that the influence of halite dissolution would be equal for all samples and, given that there is very little scatter in the $\text{Cl}^- : \text{Br}^-$ ratios for crush-and-leach extracts from the Michigan Basin, the influence of halite dissolution is believed to be negligible (i.e., the mass balance is dominated by Cl^- in the mobile water). In processing the Michigan Basin samples for the paper-absorption method, the porewater is known to have been affected to some degree by evaporation, and this would be expected to cause precipitation of halite. The Br^- ion does not easily substitute for Cl^- in the halite structure (Herrmann, 1980), so evaporation, and subsequent halite precipitation, could cause fractionation of Cl^- and Br^- in the residual porewater, decreasing the $\text{Cl}^- : \text{Br}^-$ ratio. There is little scatter in the data so, if evaporation is responsible for the observed difference in the ratios, the degree of evaporation must have been uniform for all samples, which seems unlikely. In addition, samples from the Opalinus Clay and the Lorraine Group shale were prepared in a humidity-controlled chamber (95 % RH) and evaporation effects were eliminated (Figure 3.4) yet the differences in the $\text{Cl}^- : \text{Br}^-$ ratios are also present in those datasets. For these reasons, dissolution and precipitation of halite are not considered plausible explanations for the observed differences in $\text{Cl}^- : \text{Br}^-$ ratios.

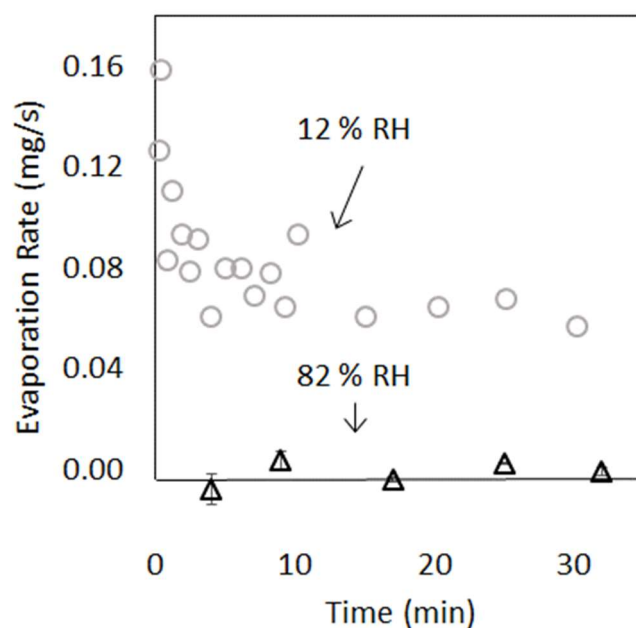


Figure 3.4. Evaporation rates of synthetic porewater (Xiang et al., 2016) under open lab conditions (12 % RH) and in a humidity chamber (82 % RH).

Additional disturbances caused during preparation of the core for porewater extraction have been considered. Oxidation of pyrite during sample preparation in aerobic conditions does not affect $\text{Cl}^- : \text{Br}^-$ ratios in porewater. A damage zone created at the surface of freshly cleaved core can promote crack formation. However, cracks should have no effect on the paper-absorption method for extracted Cl^- and Br^- masses, except perhaps a slight decrease in water yield.

The $\text{Cl}^- : \text{Br}^-$ ratios for samples of seepage collected over the span of three years from approximately 6 m long segments of boreholes in the Mont Terri Rock Laboratory and reported by Pearson et al. (2003) are presented in Figure 3.2. These samples represent water that has equilibrated with the formation as it seeps into the boreholes. The $\text{Cl}^- : \text{Br}^-$ ratios of seepage waters plot between the ratios measured in porewater extracted by the crush-and-leach and paper-absorption methods. This intermediate behavior might

be expected if the inflowing water is derived from mobile water but undergoes diffusive mixing with porewater in the rock matrix adjacent to flow paths. This form of fracture-matrix diffusive interaction was first reported by Foster (1975).

3.4.1. Porewater model

A commonly used conceptual model for porewater occurrence in low-permeability clay-rich sedimentary rock is depicted in Figure 3.5(a). This model consists of three types of water: mobile water, DDL water, and interlayer water. All types of water and the minerals are considered to be in chemical equilibrium. Both interlayer and DDL waters are in direct contact with negatively charged clay mineral surfaces and consequently are cation-rich. The thickness of the DDL is commonly equated to the Debye length (κ^{-1} , nm) [see (3.1); (Appelo and Postma, 2005; Sparks, 2003)]:

$$\kappa^{-1} = \frac{0.304}{\sqrt{I}} \quad (3.1)$$

where I is the ionic strength of the porewater (mol/L). Dissolved anionic species are considered to be limited, predominantly, to the mobile fraction of porewater, with lower concentrations in the DDL and absent from interlayer water.

Each porewater extraction method relies on different extraction mechanisms and, consequently, they do not sample equal portions of the different porewater fractions. For this reason, it is expected that the two methods should provide different results. The crush-and-leach method is assumed to extract all conservative anions from the porewater (Devine et al., 1973; Mazurek et al., 2015; Motellier et al., 2003; Murthy, 1973; Yang et al., 2003), while the paper-absorption method relies on capillary-pressure gradients to draw water from the mobile water fraction. Hodgson and Berg (2007) measured wetting

angles (θ) for individual cellulose fibres and they report angles ranging from 0° for receding measurements to $>14^\circ$ for advancing measurements. Pore-size measurements for cellulose fibres are available from Park et al. (2006) and they report pore radii on the order of 9 to 10 nm. Using a θ of 14° , a pore radius (r) of 10 nm and a surface tension (γ) for water of 0.0715 N/m (Hodgson and Berg, 2007) to calculate the capillary pressure (P_c) of water in the fibres with the Young-Laplace relationship,

$$P_c = \frac{2\gamma\cos\theta}{r} \quad (3.2)$$

yield a value of 14 MPa. Intera (Raven et al., 2011) reports air-entry pressures for the shales in the Michigan Basin ranging from 9 to 29 MPa, and Marschall et al. (2005) report air-entry pressures between 0.4 and 10 MPa for the Opalinus Clay. These values indicate that the capillary pressure in the paper exceeds that for the biggest pores in the rocks and the paper is capable of pulling water from the largest interconnected pores (Figure 3.5(b)).

The distance over which capillary-pressure gradients are operating can be roughly estimated. For the Opalinus Clay, the paper-absorption method removed up to 26 mg of porewater. With the following simplifying assumptions: (1) the mobile water porosity is equal to the anion-accessible porosity, (2) the anion-accessible porosity represents 50 % of the total porosity (Mazurek et al., 2015), (3) 50 % of the anion-accessible porewater is drained from pores adjacent to the paper, and (4) a total porosity of 12 % (Table 1); then the depth of porewater extraction is on the order of 300 μm :

$$Depth = \frac{V_{H_2O}/(n \cdot 0.5)}{2SA} \quad (3.3)$$

Where V_{H_2O} is the volume of porewater extracted, n is the anion-accessible porosity, and SA is the area of the absorbing paper.

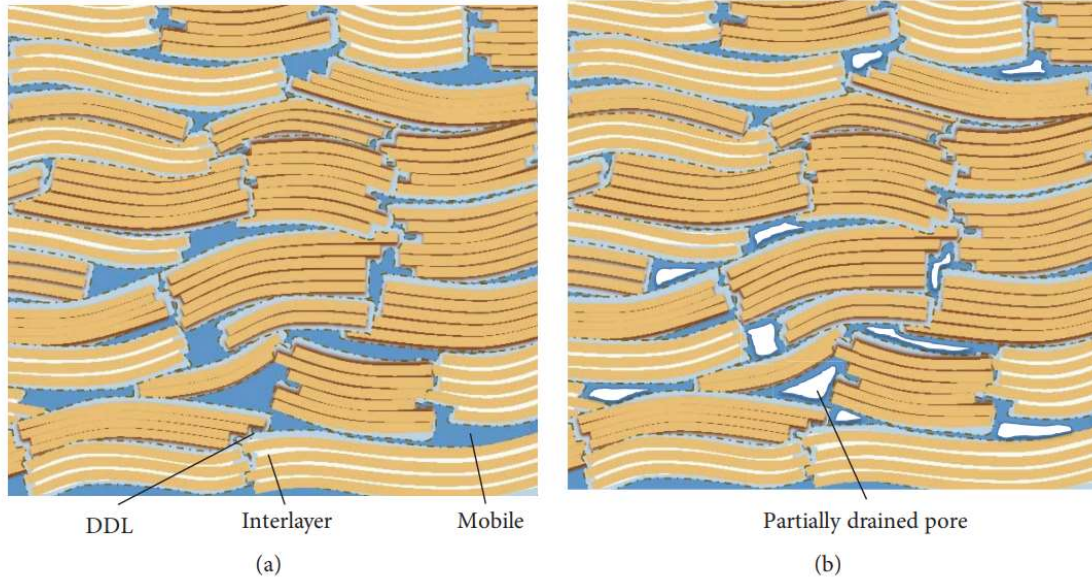


Figure 3.5. (a) A pore-scale conceptual model of the different porewater fractions found in a low-permeability clay-rich sedimentary rock. (b) The paper-absorption method extracts porewater from the largest interconnected pores. In this example, partially drained pore spaces are assumed to be connected in the third dimension.

The distribution of dissolved anions is limited, predominantly, to the mobile fraction (Appelo, 1977; Barone et al., 1990; Pearson, 1999; Tournassat et al., 2016; Tournassat and Appelo, 2011), but very little is known about the distribution of specific anions in the pore space. It is understood that anionic species are affected by anion exclusion in clay-rich media (Appelo et al., 2008; Jougnot et al., 2009; Van Loon et al., 2007) and that not all anions are affected equally (Appelo et al., 2010; Descostes et al., 2008; Tachi and Yotsuji, 2014; Van Loon et al., 2004). Appelo et al. (2010) conducted diffusion experiments using a suite of tracers, including $^{36}\text{Cl}^-$ and Br^- on a single sample

of Opalinus Clay. They describe differences in diffusive behavior of Cl^- and Br^- in terms of a geometric factor, G_f [see (3.4); (Grathwohl, 1998)]:

$$G_f = \frac{\tau^2}{\delta} \quad (3.4)$$

where τ is tortuosity and δ is constrictivity. Appelo et al. (2010) report a geometric factor of 9.24 for Cl^- and 9.54 for Br^- , indicating a lower mobility for Br^- than for Cl^- in the Opalinus Clay. They discuss the differences in anion mobility in terms of ion pairing and the orientation and number of water molecules in the first hydration shell of the ions. They suggest that differences in Na-Cl, Na-Br, and Na-I association constants reported by Fuoss (1980) could explain the variations they observe in geometric factors, but they note that the occurrence of alkali-halide ion pairing is generally not recognized in aqueous speciation modelling (e.g., PHREEQC). The issue of orientation and number of water molecules in the first hydration shell of the ions is closely related to the effect of ion size and hydration on anion exclusion which is discussed further below. Nakata et al. (2016) examined the effects of pressures and smectite content on Cl^- and Br^- concentrations in porewater squeezed from two mudstones: (1) the Wakkanai Formation at the Horonobe underground research laboratory, Japan with 40 % smectite, and (2) the Wallumbilla Formation at Marree, South Australia, containing 11 % smectite. The rocks were equilibrated with solutions of known Cl^- and Br^- concentrations and then squeezed to retrieve porewater for comparison to the known solutions. Concentrations of Cl^- and Br^- in the squeezed porewater were normalized to the equilibration solution, and at all pressure increments the concentration of Cl^- was higher than Br^- . The authors attributed this to extraction from closed pore spaces that were not accessible to equilibration with the external saturating solution. However, the consistent difference between Cl^- and Br^-

concentrations at all squeezing pressures suggests that the accessible porosities for these anions differ.

The consistent and strongly contrasting results obtained from the crush-and-leach versus the paper-absorption technique provide additional evidence that Cl^- and Br^- behave differently in the confined pore spaces of clay-rich rocks. Physical and chemical mechanisms that can explain these observations are explored below.

3.4.2. Ion pairing and clustering.

Ion pairing refers to a short-lived association between oppositely charged ions in aqueous solutions (Fuoss, 1958; Kraus, 1956; Marcus, 2006). Ion clusters that include greater than two ions are also possible and can form neutral, positively, or negatively charged species. The extent of ion pairing and clustering between alkali metals and halides has been quantified experimentally and by molecular dynamics simulations for many combinations of atoms and molecules (Chen and Pappu, 2007; Fennell et al., 2009; Fuoss, 1980; Nagy and Takács-Novák, 2000; Soniat et al., 2016; Wachter et al., 2005). These studies show that several parameters are important for ion pairing and clustering, including solute concentrations (ionic strength), solute ratios, relative sizes of ions in the pairs, and temperature. The change in speciation and ion charge caused by ion pairing between alkali metals and halides can affect transport of anions through clay matrices. Soniat et al. (2015) found that cations preferentially cluster, indicating that positively charged species form more readily than negatively charged species. These positively charged species will exhibit higher effective diffusion coefficients than negatively charged species because of their ability to diffuse through the DDL (Altmann et al., 2012; Gimmi et al., 2014).

Chen and Pappu (2007) conducted molecular dynamics simulations to estimate the importance of ion association in alkali-halide solutions and to determine ion-association coefficients (K_{assoc}) for ion pairs and clusters containing combinations of Na^+ , K^+ , Cl^- , and Br^- . The K_{assoc} values from Chen and Pappu (2007) should be considered stoichiometric equilibrium coefficients because they apply to mass-action expressions involving aqueous concentrations rather than activities. They correspond well to K_{assoc} values measured previously by Fuoss (1980) and were used to calculate the concentrations of free ions, neutral, positively, and negatively charged ion pairs, and clusters. These calculations were conducted by an iterative process in a spreadsheet using concentrations for various degrees of evaporated seawater with ionic strengths ranging from 0.7 to 11.3 mol/L (McCaffrey et al., 1987). This is a reasonable proxy because porewaters in the Michigan Basin (Al et al., 2011; Wilson and Long, 1993) and the Opalinus Clay (Pearson et al., 2003) are considered to be derived from seawater. The fractions of Cl^- and Br^- occurring in the form of positively charged and neutral species are compared in Figure 3.6. The fraction of Cl^- in positively charged and neutral species is 2 % to 7 % higher than for Br^- , and, consistent with electrolyte theory (Nordstrom and Munoz, 1994), the extent of ion pairing and clustering increases with ionic strength. In the pore space of clay-rich sedimentary rocks, this would mean that Cl^- would have a greater tendency to enter the DDL, and perhaps even the interlayer pore spaces, thereby decreasing the $\text{Cl}^- : \text{Br}^-$ ratio in the mobile water. This is consistent with the observed difference in $\text{Cl}^- : \text{Br}^-$ ratios obtained from the crush-and-leach versus the paper-absorption techniques and suggests that ion pairing behavior could be a contributing factor.

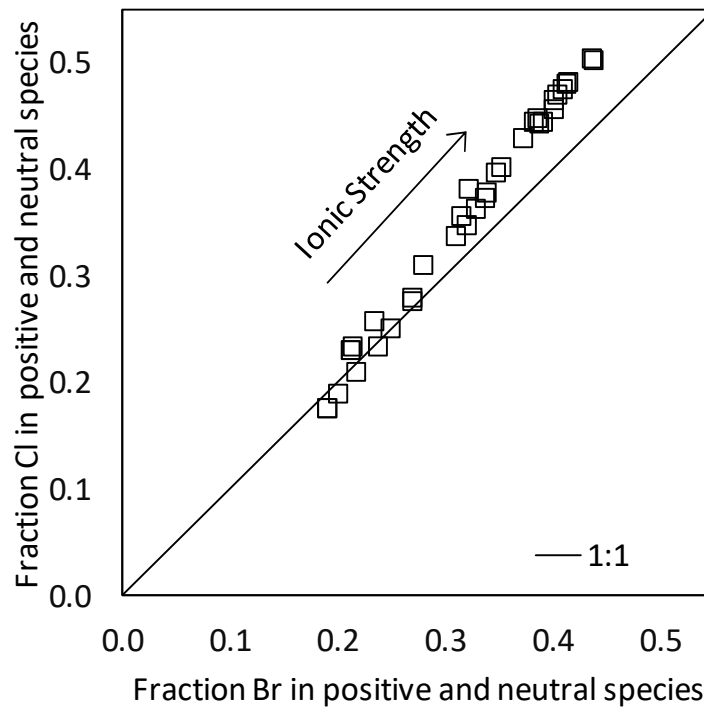


Figure 3.6. Fraction of Cl^- and Br^- occurring in the form of positively charged and neutral ion pairs and clusters. Calculations are for seawater, evaporated to variable degrees (McCaffrey et al., 1987), using K_{assoc} values from Chen and Pappu (2007, Appendix B).

3.4.3. Anion specific porosity

Solute extraction methods such as out-diffusion and crush-and-leach depend on measures of the diffusion-accessible porosity to report solute concentrations, and ion-specific diffusion-accessible porosities are required for cations and anions. The diffusion-accessible porosity for anions in the Opalinus Clay is thought to be approximately 50 % of the total diffusion-accessible porosity (Appelo et al., 2010; Fernández et al., 2014; Gimmi et al., 2007; Mazurek et al., 2011). There is an excess of cations over anions in interlayer water and the DDL in clay-rich rocks, and, as a consequence, cation-accessible porosity is greater than anion-accessible porosity (Appelo et al., 2010; Pearson, 1999).

Based on physical principles it can be expected that size-specific anion exclusion (Figure 3.1) will occur in highly compacted, clay-rich rocks (Wittebroodt et al., 2012). Size-specific anion exclusion should result in fractionation of anions of differing size/charge and a non-uniform anionic distribution in the pore spaces. Hydrated anion radii are compared in Figure 3.7, demonstrating that there is a systematic increase in radii with increasing atomic number among the halides. Based on Equation 3.1 and synthetic porewater compositions (Table 1), an estimated DDL thickness in the Michigan Basin rocks and Opalinus Clay should be on the order of 0.1 and 0.5 nm, respectively. It follows that the 5.6 % difference in hydrated-ion radii for Br^- versus Cl^- could lead to fractionation of these anions in pore spaces with connecting pore throat dimensions on the order of 1 to 2 nm. In effect, this would result in a system within which the accessible porosity for Cl^- is greater than for Br^- . There is no information available for pore throat diameters in the Lorraine Group shale, but mercury intrusion porosimetry (MIP) data are available from the Michigan Basin rocks and the Opalinus Clay (Figure 3.8). It is recognized that clay-rich rocks have pores that are inaccessible to MIP measurement, but here we assume that differences among samples will be proportional at the smallest, inaccessible pore sizes. Median pore throat diameters for the Opalinus Clay range from 20–30 nm (Houben et al., 2013) and values on the order of 9 nm are reported for shales from the Michigan Basin (Jackson and Wigston, 2010). The ionic strength effect on the respective DDL thicknesses is small in comparison, varying from 0.1 nm for the Michigan Basin, to 0.5 nm for the Opalinus Clay [see (1)]. Size-specific anion exclusion should, therefore, be more effective in the Michigan Basin rocks. This inference is consistent with the greater fractionation of Br^- from Cl^- observed for the Michigan Basin

rocks compared to the Opalinus Clay. The Lorraine Group shales are also highly indurated rocks, even more so than the shales from the Michigan Basin, so it is expected that the median pore throat diameter would be similar to the rocks from the Michigan Basin. A conceptual model for the effect of pore throat diameter on $\text{Cl}^- : \text{Br}^-$ ratios extracted using the crush-and-leach and the paper-absorption methods is presented in Figure 3.9.

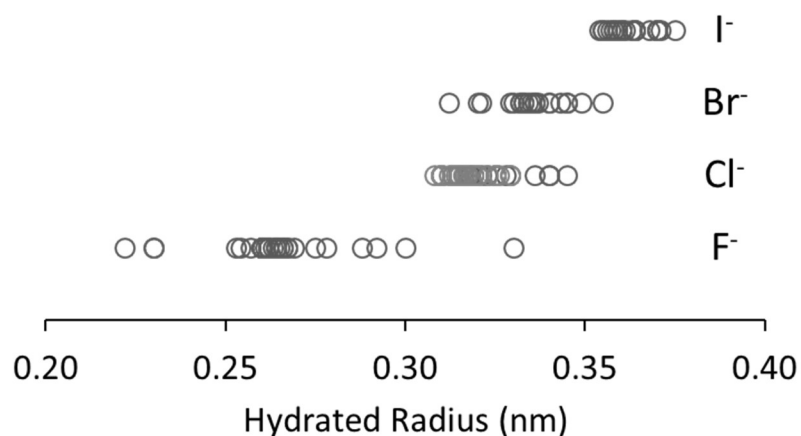


Figure 3.7. Compilation of hydrated anion radii reported in the literature (Ohtaki and Radnai, 1993; Smirnov, 2013, Appendix B).

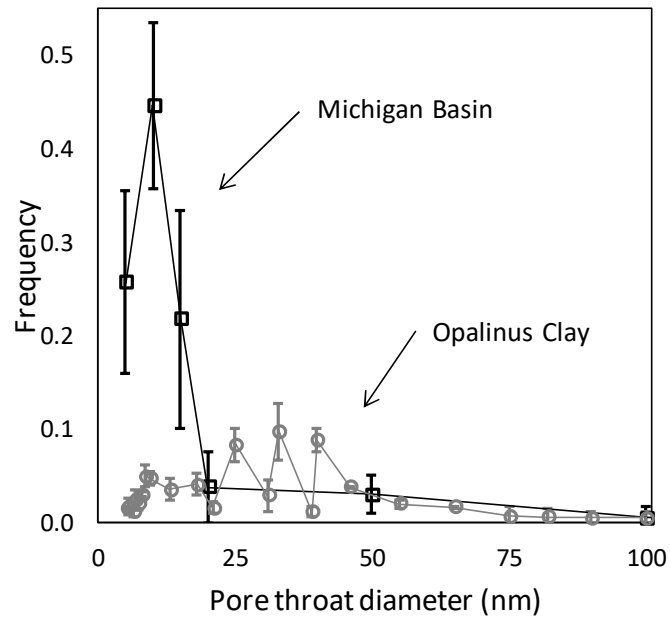


Figure 3.8. Pore throat diameters quantified by MIP. Opalinus clay data (adapted from [Houben et al., 2013](#), Appendix B) from a pair of samples from the Mont Terri Rock Laboratory (borehole BCS-2, gallery 98). Data for the Michigan Basin (adapted from [Jackson and Wigston, 2010](#), Appendix B) are from the Queenston, Georgian Bay, and Blue Mountain formation shales. The error bars represent standard deviation.

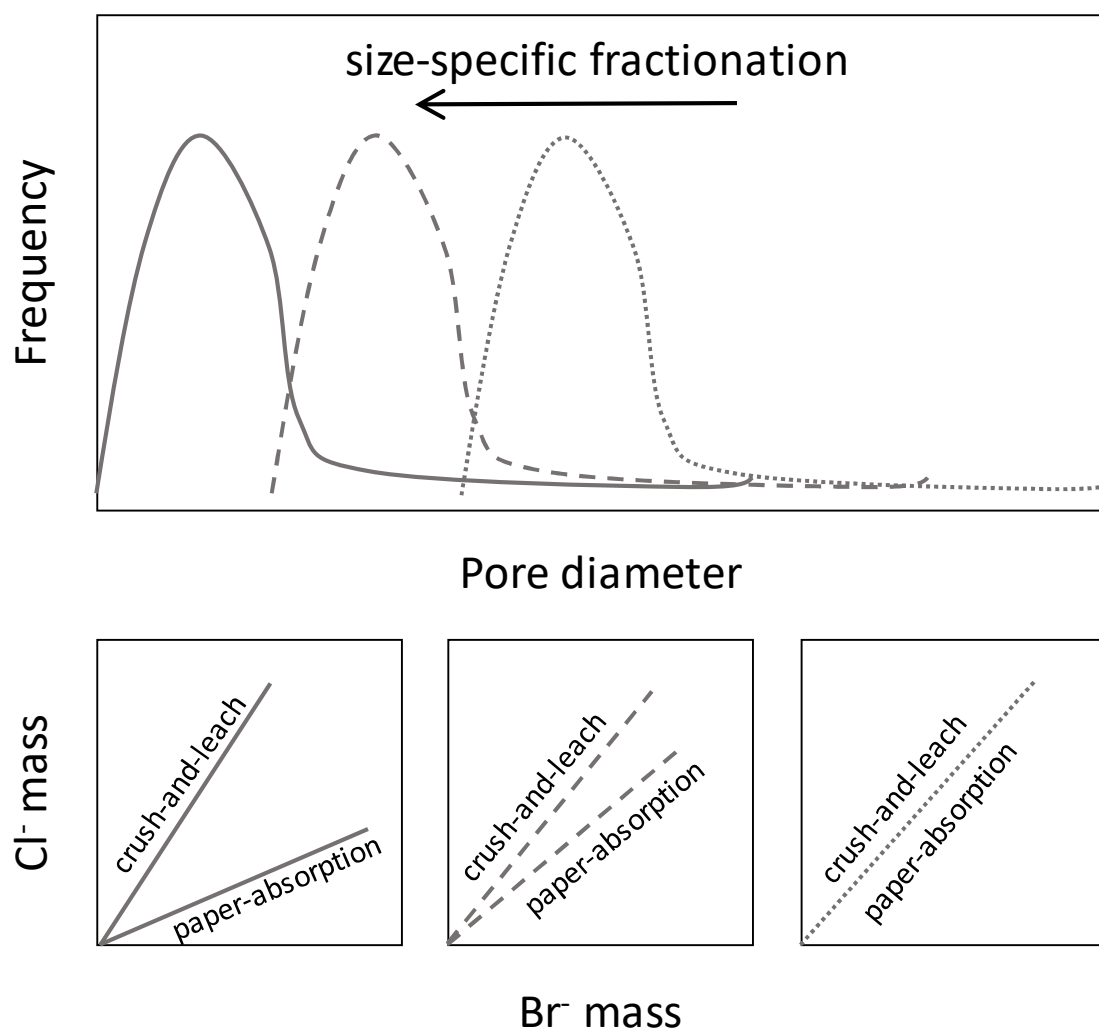


Figure 3.9. Conceptual model depicting the fractionation of Br^- from Cl^- due to size-specific anion exclusion and the relationship to pore throat diameter.

Given that capillary pressure is inversely proportional to pore diameter, the paper-absorption method will selectively extract porewater from the largest pores where $\text{Cl}^- : \text{Br}^-$ ratios are lowest due to size-specific anion exclusion. This inference is consistent with the experimental data. Crush-and-leach extraction, on the other hand, is not selective on the basis of pore size and connectivity, and it extracts virtually all porewater solutes, resulting in higher $\text{Cl}^- : \text{Br}^-$ ratios.

This study used Whatman[®] 1 CHR paper, but there will be some variability in the physical properties of different paper products. It is possible that anion ratios measured with the paper-absorption method may be somewhat specific to the choice of paper, but this remains to be tested.

If the model presented in Figure 3.9 is correct, then the air-entry pressures for the rocks should correlate to the difference in $\text{Cl}^- : \text{Br}^-$ ratios measured by the two methods. Expressed as a percent, the differences ($\Delta \text{Cl}^- : \text{Br}^-$) are 48 % for the Michigan Basin, 50 % for the Lorraine Group, and 25 % for the Opalinus Clay. There are no air-entry data available for the Lorraine Group, but the air-entry data from the Michigan Basin and the Opalinus Clay have been plotted versus $\Delta \text{Cl}^- : \text{Br}^-$ in Figure 3.10. There are only two points so it remains for future work to determine the strength and nature of such a relationship.

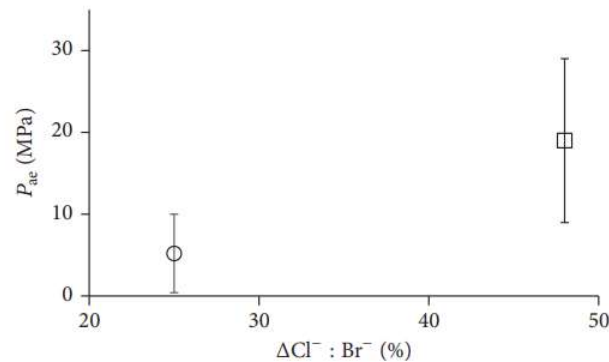


Figure 3.10. Relationship between air-entry pressure (P_{ae}) and the difference in $\text{Cl}^- : \text{Br}^-$ ratios ($\Delta \text{Cl}^- : \text{Br}^-$) measured by the crush-and-leach versus the paper-absorption method for the Opalinus Clay (circles) and the Michigan Basin (2011) (squares). The error bars represent the range of air-entry pressures reported by Intera (Raven et al., 2011) for Ordovician shales in the Michigan Basin and by Marschall et al. (2005) for the Opalinus Clay.

3.5. Conclusions

The mass ratios for Cl^- and Br^- extracted from low permeability shales differ according to the method of extraction employed. It is generally accepted that the crush-and-leach technique extracts the entire budget of conservative anions from a rock sample, so the $\text{Cl}^- : \text{Br}^-$ ratio obtained by this method can be considered a benchmark representing the overall mass ratio. The $\text{Cl}^- : \text{Br}^-$ ratio was found to be independent of the grain size used (between 37 and 10000 μm) for crush-and-leach extraction. The paper-absorption technique relies on capillary-pressure gradients and therefore extracts water from the largest, connected pores. Results from this method should reflect the mobile water with minimal influence from water contained in the DDL and in clay interlayers. The $\text{Cl}^- : \text{Br}^-$ ratios obtained from the paper-absorption method (mobile water) are consistently lower than those from crush-and-leach method, indicating that Cl^- and Br^- are not uniformly distributed in the mobile water, nor are they uniformly excluded from the interlayer and DDL water. The data indicate that Br^- is fractionated preferentially into the largest pores that are accessible by the paper absorption method. This fractionation can be explained by two mechanisms. First, size-specific anion exclusion causes the slightly larger Br^- ion to be confined in the largest pore spaces, whereas a larger fraction of the porosity is accessible to Cl^- . Second, calculations suggest that Cl^- has a greater tendency than Br^- to form ion pairs and clusters with overall neutral or positive charge that can enter the DDL and possibly even the clay interlayers. Preferential migration of Cl^- into the DDL and interlayer water, in the form of ion pairs and clusters, would decrease the $\text{Cl}^- : \text{Br}^-$ ratio in the mobile water.

There is one very broad, but important conclusion that can be drawn from this work. A variety of techniques have been developed by research groups to measure the chemical and isotopic composition of porewater in low permeability, clay-rich rocks, and there is a tendency to think that these methods should converge on a unique chemical composition. If we accept common conceptual models that suggest porewater in the clay interlayers and in the DDL are cation-rich, and the anions are mostly confined to the mobile water, then it follows that different extraction methods cannot converge on a unique porewater chemical composition unless they happen to extract identical fractions of the interlayer, DDL, and mobile fractions of the porewater. This work demonstrates that the use of multiple extraction methods can lead to an improved understanding of the porewater system.

3.6. Conflicts of interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

3.7. Acknowledgments

This research was supported by the Canadian Natural Sciences and Engineering Research Council (NSERC) and the Nuclear Waste Management Organization (NWMO) under Collaborative Research and Development Grant no. CRDPJ 477852 – 14.

3.8. References

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4.0. Porewater composition and exchangeable cation chemistry of the Champlain Sea mud near Ottawa

4.1. Abstract

The Champlain Sea mud is a sensitive marine sediment that can exhibit landslide potential when connate marine porewater is displaced by freshwater. This study presents a detailed investigation of porewater and exchangeable-cation chemistry through the depth of a continuously sampled borehole drilled in the Champlain Sea mud near the edge of a ravine carved by Billberry Creek in Orleans, Ontario. Extraction of representative porewater samples is challenging because results from different sampling techniques can reflect different fractions of mobile, clay-interlayer, and bound waters and may be subject to method specific artifacts. Here we compare results from three different porewater extraction techniques: centrifugation, paper absorption, and crush and leach together with exchangeable cation chemistry extracted using a nickel-ethylenediamine solution. Porewater compositions obtained by the three methods display similarities in ion concentrations and trends through the depth of the borehole, with maximum concentrations of major ions approaching a composition representative of 15 % seawater near the base of the deposit. Evidence of diffusion-controlled porewater freshening is observed toward the surface and in the underlying glacial till and is associated with increased alkaline-earth metal (Ca^{2+} , Mg^{2+} , Sr^{2+} , Ba^{2+}) concentrations in both the porewater and on ion exchange sites. The mud stability is thought to be influenced by repulsive forces between mineral grains due to mineral surface-charge and variations in the thickness of the associated diffuse-double layer (DDL). The net repulsion (or attraction) is likely a balance between decreasing porewater ionic strength (freshening) which expands the DDL thickness and increases repulsion (increased sensitivity), and weathering-related increases in alkaline-earth metal populations that shrink the DDL thickness leading to decreased repulsion (decreased sensitivity). Detailed measurements

of porewater and exchangeable-cation chemistry indicate spatial variations in porewater freshening and weathering-related accumulations of alkaline-earth cations that influence sensitivity, thereby contributing to an improved understanding of geotechnical stability.

4.2. Introduction

In eastern Canada, parts of the St. Lawrence lowlands are covered with marine mud, 10 to 170 m thick, that was deposited in the Champlain Sea (Russell et al., 2009). The Champlain Sea was formed by a marine incursion from the Gulf of St. Lawrence, occupying a crustal depression of glacial origin extending from Petawawa, Ontario to Quebec City, Quebec (Figure 4.1a) between 12,500 to 10,000 years B.P (Denny, 1974; Elson, 1969; Gadd, 1971; Terasmae, 1965). The sea is thought to have been a mixture of glacial melt water, local precipitation, and seawater from the Gulf of St. Lawrence (Cronin, 1977; Hillaire-Marcel, 1988). Glacial meltwater from the Laurentide ice sheet transported fine rock flour produced by erosion of Paleozoic-sedimentary and Precambrian-crystalline geologic environments into the Champlain Sea. The resulting deposits form the Champlain Sea mud and consist of clay- to silt-size particles dominated by detrital minerals including quartz, feldspar, amphiboles and carbonates (60 to 91 %), with the remainder consisting of clays and amorphous materials (Bentley and Smalley, 1979; Gillott, 1970; Jacques Locat, Lefebvre, et al., 1984). The clay-mineral fraction (3 to 9 %) consists primarily of illite and chlorite with some vermiculite and smectite (Bentley and Smalley, 1979; Gillott, 1970; Quigley, 1980; Quigley et al., 1984, 1985; Torrance, 1979).

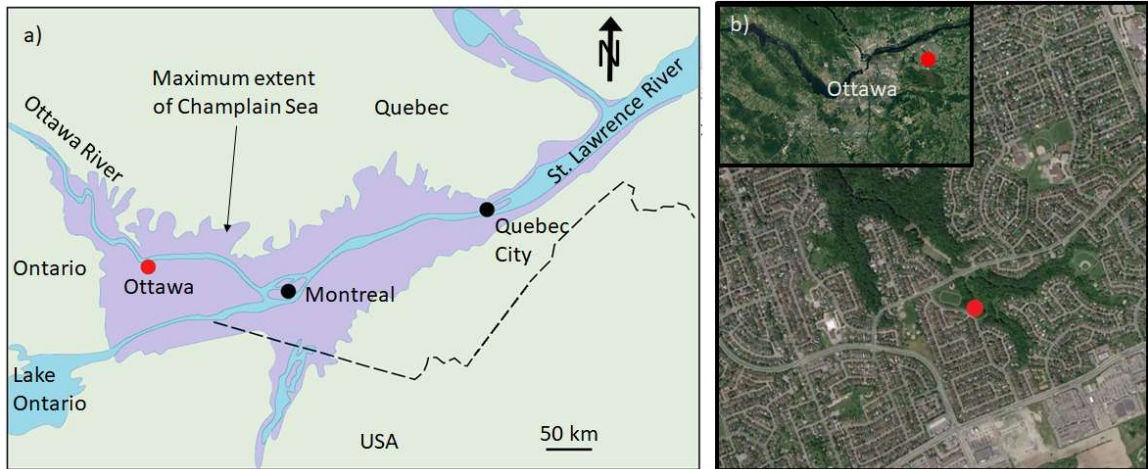


Figure 4.1. a) Map depicting the extent of the Champlain Sea where the glaciomarine sediments forming the Champlain Sea mud were deposited (adapted from Crow et al., 2020). b) The location of the borehole (BC16) drilled near a ravine formed by the Billberry Creek with an inset showing the location of the borehole relative to Ottawa (© Google Earth, 2020).

The fine-grained nature of the Champlain Sea mud and its marine depositional environment make it prone to instability leading to landslides. It is therefore considered to be a sensitive sediment. Landslides in sensitive marine muds can be triggered by excessive rainfall, earthquakes, and human activity (Evans, 2001, 2003) and have been reported in eastern Canada (Duhaime et al., 2013; Quigley, 1980; Quinn et al., 2011; Torrance, 1979, 1999), Scandinavia (Andersson-Sköld et al., 2005; T. E. Helle et al., 2016; Rosenqvist, 1984), and Japan (Ohtsubo et al., 2007; Ohtsubo et al., 1996; Tanaka et al., 2012). Landslides in these muds are responsible for 17% of Canadian landslide-related deaths (Evans, 2001), with events near the South Nation River, Ontario (1971, Eden et al., 1971), Lemieux, Ontario (1993, Brooks et al., 1994; Evans and Brooks, 1994), Mulgrave-Derry, Quebec (2010, Perret et al., 2017), and Notre-Dame-de-la-Salette, Quebec (1908, Locat et al., 2017).

Development of sensitivity in mud deposits has been linked to increased repulsion between individual mineral grains and can result from changes in porewater composition (Quigley, 1980; Torrance, 1999). Negatively charged surfaces of mineral grains result in the formation of an exchangeable, diffuse, cation-rich, charge-balancing layer in contact with the grain surface, known as the diffuse double layer (DDL). The total mineral surface charge dictates the number of cations in the DDL and may be represented by the cation exchange capacity (CEC). Values for CEC between 6 and 22 meq/100 g dry mud have been reported for the Champlain Sea mud (Helle et al., 2019; Helle et al., 2017; Laventure, 1964; Locat et al., 1984; Locat and St-Gelais, 2014). Cation rich waters of the DDL and in the interlayer spaces of swelling clay minerals are defined as “bound” water (Wersin et al., 2004) while the remaining porewater is mobile. The thickness of the DDL is inversely related to porewater salinity and directly related to the ratio of monovalent to multivalent cations (Appelo and Postma, 2004). The bound and mobile water fractions are in equilibrium; the chemistry of cation exchange sites and DDL thickness therefore depend upon composition of the mobile porewater (Sparks, 2003). This is relevant to sediment sensitivity because increases in the thickness of the DDL cause increased repulsion between particles and greater sensitivity (Quigley, 1980).

The Champlain Sea mud has low hydraulic conductivity, between 7.5×10^{-11} and 1.2×10^{-9} m/s (Desaulniers and Cherry, 1988; Lapierre et al., 1990; Locat and St-Gelais, 2014b; O’Shaughnessy and Garga, 1994) so loss of salinity, and consequent increase in sensitivity, is dominated by diffusive transport of solutes toward freshwater at the surface and in the underlying till (Andersson-Sköld et al., 2005; Bogaard et al., 2007; Chapuis and Saucier, 2013). The low hydraulic conductivity also limits weathering to shallow

depths by inhibiting infiltration of freshwater and atmospheric gases. Near-surface weathering alters mineralogy and the porewater composition, and causes development of fracture networks (Torrance, 1979; Wilson, 2004). Weathering reactions and accumulation of weathering products may lead to a decrease in mud sensitivity due to formation of the secondary clay minerals smectite and vermiculite, formation of cementing iron oxyhydroxides, and a decrease in ratios of monovalent to multivalent cations, primarily as a consequence of carbonate-mineral dissolution (Brydon and Patry, 1961; Lessard and Mitchell, 1985; Moum and Torrance, 1971; Quigley et al., 1985; Torrance, 1979, 1990, 1999).

To improve understanding of sensitivity development, measurements of porewater chemistry are important for gaining insight into weathering processes and the rates and mechanisms for porewater freshening. Several methods of porewater extraction from core samples have been described, including centrifugation, crush and leach, and paper absorption (Bufflap and Allen, 1995; Edmunds and Bath, 1976; Celejewski et al., 2014; Clark et al., 2014). Each method can extract different proportions of bound and mobile porewater, which result in method-dependent biases or artifacts in the estimated porewater composition (Bufflap and Allen, 1995; Celejewski et al., 2018; Mazurek et al., 2011; Pearson et al., 2003).

This study aims to investigate variations in porewater and cation-exchange chemistry versus depth in the Champlain Sea mud near Ottawa, Ontario, Canada. There are two main objectives: (1) compare results from three porewater extraction methods (centrifugation, paper absorption, and crush and leach), and (2) measure the CEC and the composition of cations on the exchange sites in the DDL. Measurement of exchange site

chemistry will allow for the assessment of the influence of ion exchange reactions on in-situ porewater composition and will contribute toward future explorations of potential relationships between exchangeable cation chemistry and sensitivity of marine muds. Such explorations are outside the scope of the present study.

4.2.1. Geologic Setting

A continuously cored borehole was drilled at the edge of a housing division, a few meters from a ravine formed by Billberry Creek in Orleans Ontario, Canada (Figure 4.b). The subdivision was built in the mid-1980's during which time the area was leveled and back filled with a mixture composed of Champlain Sea mud and building-material waste. Al-Mufti et al. (2022) studied the sedimentology and stratigraphy of cores retrieved from the borehole by interpreting variations in X-ray attenuation observed in computed tomography (CT) scans of the cores to define five lithologically distinct units (Figure 4.2). They observed segments with cm-scale rhythmites defined by variations in X-ray attenuation, representing alternating beds of silt- and clay-sized sediment, as well as segments where layering had been disrupted by bioturbation. The rhythmites were interpreted to be caused by cyclical changes in flow conditions of glaciogenic meltwater discharge. They were able to define the five units based on patterns of X-ray attenuation that provided insight into degree of sorting, bed thickness, sedimentary structures, and textures. The five units have sharply defined boundaries. Unit 1 overlies glacial till at the base of the Champlain Sea mud and is composed of mud rhythmites deposited in freshwater. Unit 2 contains bioturbated mud indicating the start of the marine phase of the Champlain Sea, with layer thicknesses indicating increased depositional rates. The

depositional rates further increased into Unit 3 and an increase in clay-sized particles was noted. The bed thickness and clay-sized fraction increase again into Unit 4a creating a diffusely stratified or structureless mud. Unit 4a is intersected by Unit 4b, an intensely deformed mud.

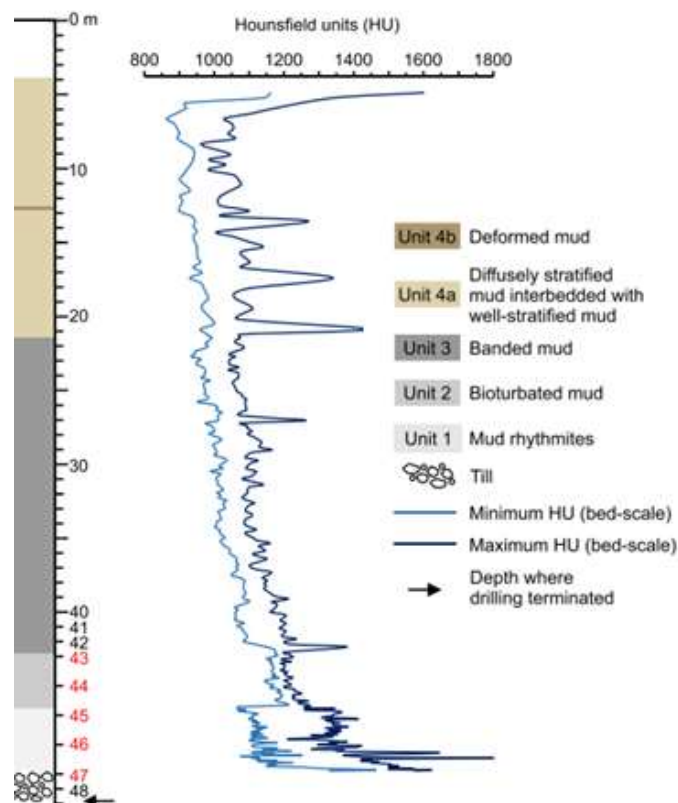


Figure 4.2. Stratigraphy of the Billberry Creek borehole as defined by Al-Mufti et al., (2022) with the corresponding X-ray attenuation profile (adapted from Al-Mufti et al., 2022).

4.3. Methods

Core samples were collected using Shelby tubes 7.3 cm in diameter and 76.2 cm long. Upon extraction, both ends of the Shelby tube were sealed according to the method

described by Alpay et al. (2020). A total of 60 Shelby tubes were collected over a depth of 67 m with an intact core recovery of 71 %.

At the base of each Shelby tube a 1 to 3 cm sub-core was collected using a fixed volume sampler for porosity and bulk-density quantification by water loss measurements. The mud was then extruded using a horizontal mechanical core extruder and a 13 cm sample was designated for porewater extraction. The extruded mud was segmented in a way that minimized effects of porewater heterogeneity through the sample by allocating the central 3 cm to the paper absorption method and bracketing 5 cm sections for the centrifuge method.

4.3.1. Porewater extraction

4.3.1.1. Centrifuge

Core samples were packed into four 50 mL Nalgene centrifuge tubes by hand. Approximately 75 g of sample material was packed into each tube, then centrifuged for 30 minutes at 18000 rpm in a Heraeus Biofuge Stratos™ centrifuge. The porewater was collected and passed through a 0.45 µm nylon filter. The remaining mud was centrifuged for another 30 min and the porewater was filtered and combined with the first porewater extract. Porewater samples allocated for ICP-MS and ICP-OES analysis in an acidic medium were acidified to 1 % HNO₃ (Optima™, Fisher Chemical) while solutions intended for anion analysis by ICP-MS in a basic medium, pH, and alkalinity measurements were left unacidified.

Alkalinity was measured by diluting a 1 mL sample tenfold with deionized (DI) water then titrating with 0.02 N or 0.1 N H₂SO₄, using bromocresol green-methyl red indicator. Duplicate measurements of pH were recorded with a probe that was calibrated

to pH 4.00, 7.00, and 10.00 prior to each measurement. Major (Ca^{2+} , K^+ , Mg^{2+} , Na^+) and minor (Li^+ , Sr^{2+} , Ba^{2+} , Rb^+) cations as well as Cl^- and Br^- were measured in a 1 % Plasma Pure Plus HNO_3 medium with an Agilent™ triple quad ICP-MS using both He (2 mL/min) and non-He modes with an Ar flow rate of 2 mL/min. Anions were also analysed by ICP-MS in a 1 % Plasma Pure Plus NH_3 medium. Major cations and S were measured using an Agilent™ 5110 ICP-OES in a 1 % Plasma Pure Plus HNO_3 medium. Analytical error is reported for each element as the percent accuracy of a certified reference material. Seawater (High Purity Standards) was used for Cl^- and Br^- , and groundwater (ES-H3, SCP Science) was used for the remaining elements.

4.3.2.2. Paper absorption method

Porewater was extracted into Whatman® 1 CHR paper according to the method described by Celejewski et al. (2014). Prior to placing the absorbent papers between core segments, the water content of the papers was quantified gravimetrically and by reflectance near infrared (NIR) spectrometry (Process Sensors, MCT660 Bench Top NIR). For each core sample, three 4.5 cm diameter absorbing papers were secured between 5 cm diameter particle transfer barriers, also composed of Whatman® 1 CHR. This assemblage was then pressed between freshly exposed core surfaces cut parallel to bedding, enclosed in food-grade plastic wrap (SealWrap) and then vacuum sealed in a polyethylene sleeve lined with nylon using an Omcan (Model VP-IT-0330) vacuum sealer. The papers and porewater were allowed to equilibrate for two weeks at 4 °C.

Papers were removed from the cores in a humidity chamber maintained at 90 % relative humidity to minimize evaporation from the paper surface. Upon removal, the papers were placed in a fluorinated ethylene propylene envelope and moisture-content

measurements using reflectance NIR spectrometry were recorded followed by gravimetric measurements. Wet papers were leached into 5 mL of DI water for 24 hours. The leachates were filtered through 0.45 μm nylon filters and a 2.5 mL aliquot was acidified to 1% HNO_3 (Plasma Pure Plus) for ICP-MS and ICP-OES analysis in an acidic medium. The remaining 2.5 mL was left unacidified for anion analysis by ICP-MS in a basic medium. Analyses were conducted as described above.

4.3.1.3. Crush and leach

A 15 g portion of mud was sampled from core segments previously used for porewater extraction by the paper absorption method. The mud subsample was mixed with a 7.5 mL aliquot of DI water and shaken by hand for 5 minutes. Samples were centrifuged at 4200 rpm for 5 to 25 minutes (longer times were required for samples with a higher clay-size fraction) to separate the leachate from the mud. Leachates were filtered through a 0.45 μm cellulose acetate filter with a glass-fibre prefilter. Half of the recovered leachate was acidified to 1% HNO_3 (Plasma Pure Plus) for ICP-MS and ICP-OES analysis in an acidic medium. The remaining 2.5 mL was left unacidified for anion analysis by ICP-MS in a basic medium. Analyses were conducted as described above.

4.3.2. Cation exchange capacity and exchangeable-cation chemistry

A solution of nickel-ethylenediamine (Ni-et), made from a mixture of $\text{NiNO}_3 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar) and ethylenediamine (Alfa Aesar), was used to extract exchangeable cations from exchange sites according to the method outlined by Baeyens and Bradbury (1991, 1994, 1998). Extractions were conducted on mud samples that had previously been used for porewater extraction by paper absorption. The extractions,

conducted in 15 mL polypropylene centrifuge tubes employed a 1:1 solid to liquid mass ratio, 15 g of mud and a 24-hour extraction time. Based on the Ni sorption isotherms from samples collected at depths of 5 and 18 mBGS (Appendix C), a solution of 0.25 M Ni-et was used for all samples below the 8 mBGS and 0.3 M Ni-et was used for all samples above 8 mBGS. After the 24-hour extraction, samples were centrifuged at 4200 rpm for 5 minutes and the leachate was filtered through a 0.45 µm nylon filter. Leachates were acidified to 1% HNO₃ (Plasma Pure Plus) and cation analyses were conducted by ICP-MS and ICP-OES, as described above. The CEC was calculated from the mass of Ni adsorbed to each sample:

$$\frac{meq\ Ni_i - meq\ Ni_f}{mass\ dry\ mud} = meq\ Ni/g\ soil \quad (4.1)$$

where $meq\ Ni_i$ is the milliequivalents of Ni in the initial solution, $meq\ Ni_f$ is the milliequivalents of Ni in the solution after extraction, and $mass\ dry\ mud$ is the mass of dry sample (mass of sample – mass of porewater) used. Cation concentrations on exchange sites were calculated by subtracting the contribution of solutes in the mobile porewater fraction, extracted by the paper absorption method, from cation concentrations in the Ni-et extracts:

$$\frac{meq\ cation_x\ in\ Ni-et\ extract - meq\ cation_x\ in\ mobile\ water}{mass\ dry\ mud} = meq\ cation_x/g\ soil \quad (4.2)$$

where $meq\ cation_x\ in\ Ni-et\ extract$ is the milliequivalents of cation “x” in the extracted solution and $meq\ cation_x\ in\ mobile\ water$ is the milliequivalents of cation “x” in the porewater of the extracted mud calculated from concentrations measured in the mobile water, extracted by the paper absorption method. Cation “x” is any measured cation.

4.3.3. Mineralogy

Samples for powder x-ray diffraction (pXRD) were taken from core segments previously used for porewater extraction by paper-absorption. Ten samples were selected with a focus near the boundaries of stratigraphic units. Samples were air dried, then pulverized using a ball mill. Diffractograms were collected using a Rigaku Ultima IV Diffractometer with CuK α radiation. Scans were conducted from 2° to 80° 2 θ with a step increment of 0.1° 2 θ and a scan speed of 0.006 degrees/s. Peak matching was done using Match! (version 3.14 Build 230) with the COD library.

4.4. Results

4.4.1. Porosity and bulk density

Both porosity and wet bulk density exhibit little variability in the Champlain Sea mud (between 5 and 45 mBGS, Figure 4.3). The average porosity is 64 % with a standard deviation of ± 5 % and the wet bulk density of the mud is 1.6 g/cm³ with a standard deviation of ± 0.2 g/cm³.

4.4.2. Porewater chemistry

Similar solute concentrations and trends were obtained by the three extraction methods through the depth of the borehole (Figure 4.3). Varying quantities of porewater were extracted from different mud masses using each method. The centrifuge, paper absorption, and crush and leach methods extracted porewater from mud sample masses of approximately 300, 185, and 15 g respectively, producing approximately 25 g, 0.2 to 0.9 g, and 6.5 g of porewater respectively.

For the purposes of the following descriptions, “surface” will be used to describe the top of the Champlain Sea mud at 5 mBGS, not the surface of the overlying fill.

Chloride concentrations increase from 22 mg/kgw at the surface to 3025 mg/kgw in Units 1 and 2 then drop to 609 mg/kgw in the till. Surface concentrations of Br^- and I^- are 0.5 and 0.18 mg/kgw respectively decreasing to 0.2 mg Br^- /kgw and 0.01 mg I^- /kgw at 9 mBGS before increasing downward to maxima in Unit 2 of 10.8 and 0.97 mg/kgw respectively. Concentrations decrease in the till to 2.1 mg Br^- /kgw and 0.02 mg I^- /kgw. Iodide concentrations are not reported for the paper absorption method. The concentrations of SO_4^{2-} extracted by the three methods are variable in the interval above 35 mBGS, ranging from below detection limit to 62 mg/kgw, but below that depth they display a smooth, coherent increasing trend increasing to 285 mg/kgw in Unit 1, below which there is an abrupt increase to 5534 mg/kgw in the till. Concentrations of SO_4^{2-} measured in crush and leach extracts are elevated compared to those obtained by paper absorption and centrifugation.

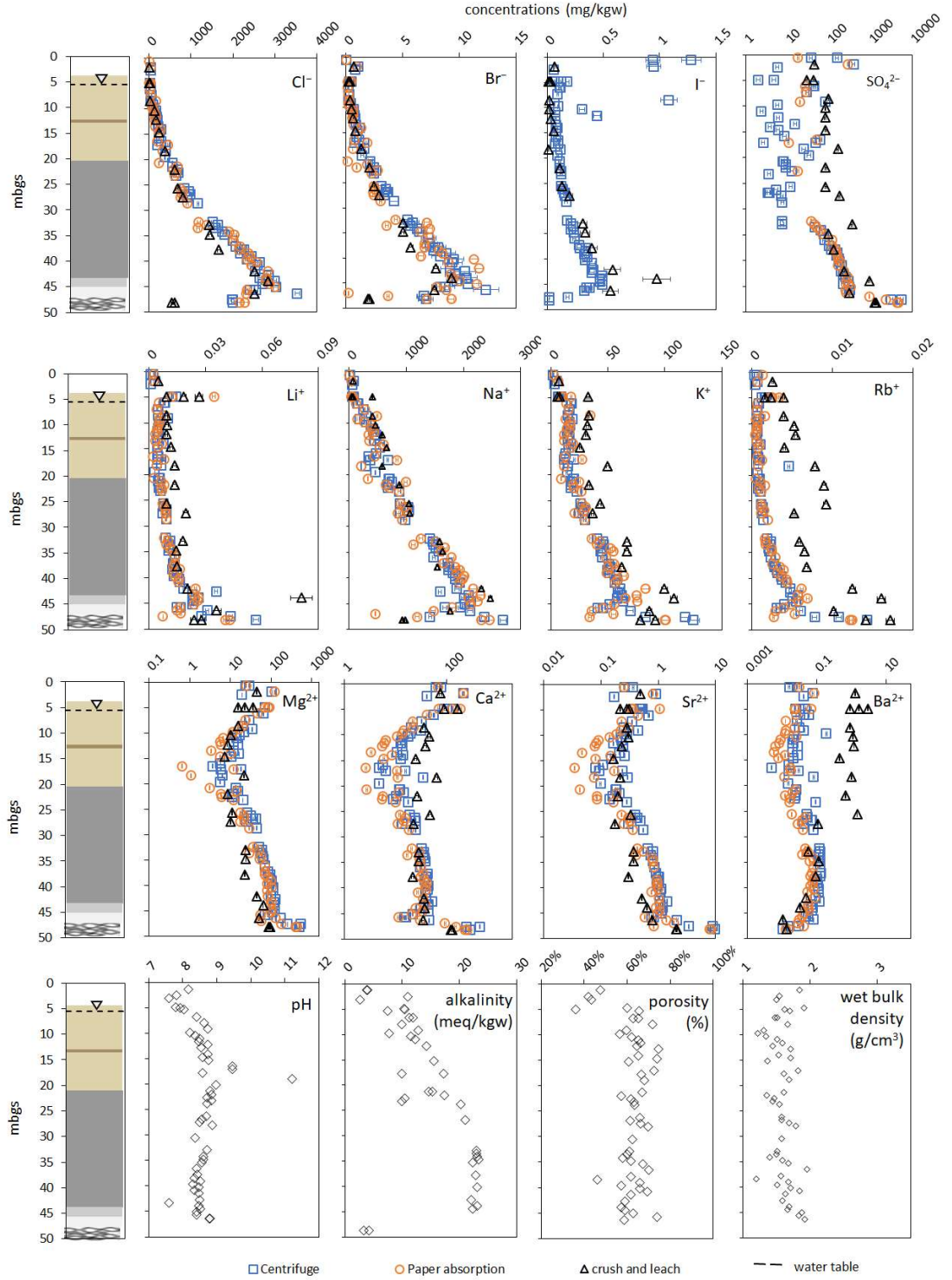


Figure 4.3. Depth profiles of solute concentrations in porewaters extracted by paper absorption (o), centrifugation ($\square$) and crush-and-leach (Δ). Porewater pH values and alkalinity quantified from centrifuge extracts and porosity, and wet bulk density depth profiles. Error bars represent 3 times the analytical accuracy (%). A logarithmic scale is used to capture the large range of concentrations for SO_4^{2-} , Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} concentrations.

The Na^+ concentrations range from 37 to 2130 mg/kgw between the surface and Unit 2, increasing relatively steadily, followed by a decrease to 825 mg/kgw in the till. Concentrations of Li^+ , K^+ , and Rb^+ are lowest at the surface (0.013, 5, and 0.002 mg/kgw respectively) remaining stable through Unit 4a then increasing gradually with depth to 0.081 mg Li^+ /kgw, 108 mg K^+ /kgw, and 0.016 mg Rb^+ /kgw in Unit 2. The Li^+ , K^+ , and Rb^+ concentrations decrease with depth through Unit 1 and into the top of the till where concentrations are 0.015 mg Li^+ /kgw, 36 mg K^+ /kgw, and 0.003 mg Rb^+ /kgw but then the concentrations rebound at the base of the till to relatively high values of 0.057 mg Li^+ /kgw, 125 mg K^+ /kgw, and 0.014 mg Rb^+ /kgw. The porewaters extracted by crush-and-leach display concentrations of Li^+ , K^+ , and Rb^+ that are elevated and somewhat erratic relative to those obtained from the centrifuge and paper-absorption methods.

Alkaline-earth metals, Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} all exhibit relatively high concentrations at the surface (91, 191, 2.9, and 0.46 mg/kgw respectively), their concentrations decrease with depth to minima in Unit 4a (1, 3, 0.1, and 0.012 mg/kgw respectively) and then gradually increase downward through Unit 3, reaching values of 122, 46, 1.2, and 0.630 mg/kgw in Unit 2. Downward through Unit 1 and into the till, the concentrations of Mg^{2+} , Ca^{2+} , and Sr^{2+} display an abrupt increase to 532, 453, and 9.7 mg/kgw respectively, while Ba^{2+} follows the opposite trend, decreasing to 0.010 mg/kgw in the till. Porewater concentrations of Ca^{2+} and Ba^{2+} are higher in crush and leach extracts than the other two methods above 35 mBGS and compare well below this depth. A good comparison between the three methods is observed for Mg^{2+} and Sr^{2+} concentrations above 35 mBGS, and below this depth the concentrations obtained by the

crush and leach method are lower than those obtained by paper-absorption and centrifugation.

The porewater pH increases from 7.8 at the surface to approximately 8.5 in Unit 4b, then remains relatively constant through the rest of the borehole. Porewater alkalinity generally follows an increasing trend from 7 meq/kgw at the surface of the mud to 23 meq/kgw in Unit 3, then decreases to 3 meq/kgw in the till.

4.4.3. Cation exchange capacity and exchangeable-cation chemistry

The CEC in the Champlain Sea mud ranges from 6.8 to 12.5 meq/100 g dry mud. An increase in CEC is observed from 6.8 meq/100 g dry mud at the water table to 11.3 meq/100 g dry mud at the base of Unit 4a. The CEC then remains relatively constant through Unit 3 then exhibits a decreasing trend downward through Units 2 and 1, dropping to below detection limit in the glacial till (Figure 4.4).

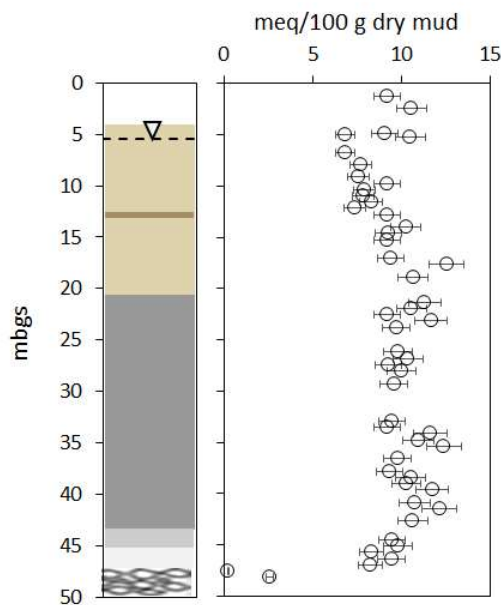


Figure 4.4. Depth profile of the CEC, measured by Ni-et extraction. Error bars represent 3 times the analytical accuracy (%).

A direct comparison of exchangeable cation chemistry to the cation concentrations in the mobile porewater is presented in Figure 4.5. Porewater solute concentrations extracted by the paper absorption method are used for comparison with the exchangeable cation chemistry because they should reflect only the mobile fraction of porewater. The abundance of cations on exchange sites generally exceeds that in the porewater so scaling factors, ranging from 1 to 100, were used to adjust the axes of each element for ease of comparison (Figure 4.5). Also, for ease of comparison, the aqueous concentrations in the porewater were transformed from units of mg/kgw to consistent units of meq/100 g dry mud using porosity and dry-bulk density data.

Exchangeable concentrations of both Li^+ and Na^+ differ by a factor of up to 8 compared to the corresponding concentrations in the porewater. This difference is much larger for the other cations. The factors representing differences between exchangeable and mobile water cation concentrations range from 10 – 74 for K^+ , 31 – 263 for Rb^+ , 2 – 473 for Mg^{2+} , 5 – 105 for Ca^{2+} , 9 – 286 for Sr^{2+} and 17 – 1166 for Ba^{2+} .

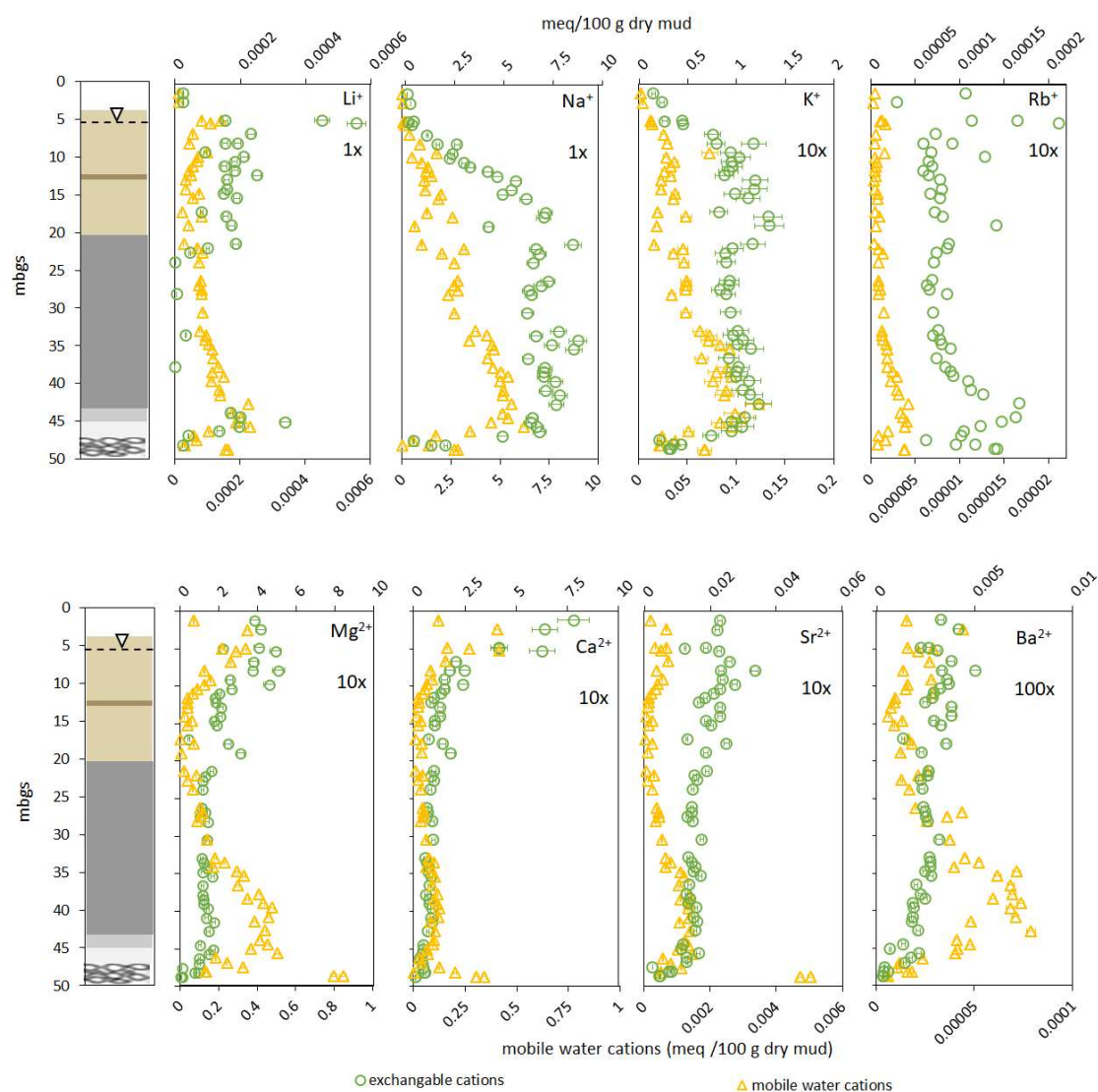


Figure 4.5. Comparison of exchangeable-cation (upper axis) and porewater (lower axis) chemistries. Two axis are used for ease of comparison because the abundance of cations on exchange sites generally exceeds that in the porewater. The difference between the axes is defined by a scaling factor (1 to 100), listed for each element. Error bars represent 3 times the analytical accuracy (%).

Concentrations of exchangeable Na^+ and K^+ display similar trends whereby the concentrations increase from 0.4 meq/100g dry mud for both elements at the surface to plateaus of approximately 8.5 and 1.2 meq/100g dry mud respectively between Unit 4a to Unit 2 followed by an abrupt decrease in the till to 0.4 meq Na^+ /100 g dry mud and 0.3 meq K^+ /100 g dry mud. Both Na^+ and K^+ concentrations on exchangeable cation sites

are relatively unchanging in Unit 3 for Na^+ and most of Unit 4a and Unit 3 for K^+ , and do not reflect the increasing porewater Na^+ and K^+ concentrations with depth.

Concentrations of exchangeable Li^+ and Rb^+ are elevated at the surface (0.00055 and 0.00021 meq/100g dry mud respectively), decreasing to below detection limit and approximately 0.00006 meq/100 g dry mud respectively at the base of Unit 4a, where the concentrations plateau between the base of Unit 4a and Unit 2 for Li^+ and between Unit 4a and the lower portion of Unit 3 for Rb^+ . An increase to 0.00034 and 0.00016 meq/100 g dry mud is observed for Li^+ and Rb^+ respectively in Unit 1 followed by an abrupt decrease in Li^+ to 0.00002 meq/100 g dry mud and variable Rb^+ concentration (0.00006 to 0.00014 meq/100 g dry mud) in the till. The concentrations of Li^+ and Rb^+ on exchange sites generally mirror the trends observed in the porewater.

Concentrations of exchangeable Mg^{2+} and Ca^{2+} follow similar trends exhibiting the highest concentrations at the surface (4.3 and 6.3 meq/100 g dry mud respectively) then decreasing, at first sharply then more gradually, to plateaus of approximately 1.3 and 0.8 meq/100g dry mud between the base of Unit 4a and Unit 2, followed by a decrease to 0.1 meq/100g dry mud into the till for both elements. Concentrations of exchangeable Sr^{2+} and Ba^{2+} are 0.012 and 0.0022 meq/100 g dry mud at the surface, increasing to peak concentrations (0.034 and 0.0050 meq/100 g dry mud respectively) just below the water table followed by a gradual decrease to approximately 0.011 meq Sr^{2+} /100 g dry mud and 0.0007 meq Ba^{2+} /100 g dry mud in Unit 2 then a sharp decrease into the till (0.004 and 0.0003 meq/100 g dry mud). The concentrations of alkaline-earth metals on exchangeable sites follow similar trends to those in the porewater above 35 mBGS, while below this

depth they decrease while porewater concentrations increase toward Unit 2 then decrease into the till.

4.4.4. Mineralogy

Samples for pXRD were selected near unit interfaces where the greatest mineralogical differences might be expected. Visual comparison of diffractograms presented in Figure 4.6 indicate little variability in mineral composition between the samples spanning the entire borehole depth. The mineralogy of the samples is dominated by quartz, feldspar, and amphiboles (81 – 91 %) with some calcite, chlorite, illite, and vermiculite.

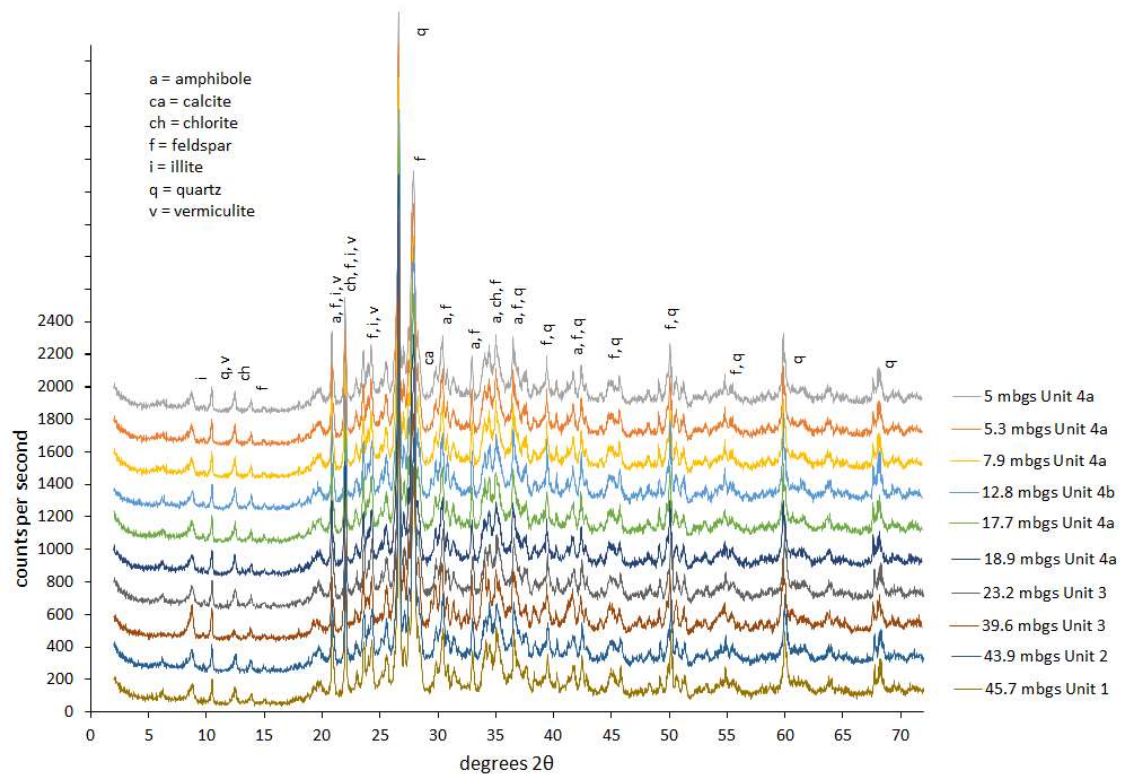


Figure 4.6. pXRD diffractograms collected for all samples. The x-axis of each diffractogram is offset by 200 counts per second along the y-axis to separate individual samples.

4.5. Discussion

4.5.1. Comparison of porewater extraction methods

4.5.1.1. Anions

The Champlain Sea mud samples have very high porosity and the pore volume should be dominated by the mobile fraction. Therefore, even if different porewater extraction methods sample variable fractions of mobile and bound waters, any effect on the resulting concentrations of conservative natural tracers Cl^- and Br^- should be negligible. The extraction results are consistent with this expectation as the porewater concentrations for Cl^- and Br^- obtained by the three different extraction methods compare well (Figure 4.3). A good comparison is also observed between I^- concentrations obtained by crush-and-leach and centrifuge extraction. Iodide concentrations are not reported for porewaters extracted by the paper absorption method because of the tendency for I^- to adsorb to organic matter (Whitehead, 1984), which makes up the cellulose based paper, making the paper absorption method a poor candidate for I^- quantification.

The three methods demonstrate good comparison where relatively high SO_4^{2-} concentrations ($> 60 \text{ mg/kgw}$) are observed below 35 mBGS, but above 35 mBGS, SO_4^{2-} concentrations obtained by all three methods are variable and scattered. Where sulphide minerals are present in the sediment, sulphide oxidation could provide a possible explanation for the scatter in the data. To minimize sulphide oxidation reactions during the extraction processes, core samples were processed immediately after core extrusion, but prior to centrifugation, core samples were broken apart to allow material to be pressed into centrifuge tubes, exposing fresh mineral surfaces to atmospheric conditions before a one-hour period of centrifugation. For the paper absorption method, the portion

of the core from which porewater is extracted is exposed to the atmosphere at the time of paper insertion, and O_2 could become trapped against the core surface by the paper allowing for continued oxidation after the papers have been inserted. Sulphate concentrations reported from crush-and-leach extracts are elevated compared to the other two methods for samples above 35 mBGS and below 45 mBGS. Core samples used for crush and leach extractions were used previously for extraction by paper absorption and between methods they had been stored in vacuum sealed polyethylene sleeves for 7 to 18 months. These samples had been exposed to the atmosphere on three separate occasions: during paper insertion, paper removal, and sampling for crush and leach extractions.

4.5.1.2. Cl : Br mass ratios

Consistent with a marine depositional environment, the average $Cl^- : Br^-$ mass ratios for extracted porewaters are comparable with that of seawater (Figure 4.7). The $Cl^- : Br^-$ mass ratio of seawater is 285, while those reported by the centrifuge, paper absorption, and crush-and-leach methods are 268 ± 12 , 274 ± 42 , and 265 ± 28 respectively.

The anions Cl^- and Br^- display conservative behaviour in most groundwater systems (Davis et al., 1998), suggesting that the mass ratio of $Cl^- : Br^-$ in porewaters extracted using different methods should yield similar values. However, Celejewski et al., (2018) found that the $Cl^- : Br^-$ mass ratio for porewaters in low-permeability shale was different for porewater extracted with the paper-absorption versus the crush-and-leach method, and they attributed the difference to variable fractions of mobile and bound waters sampled by each method and differences in mobility behaviour of the two anions.

They suggested that the small difference in hydrated ion size between Cl^- (0.302 nm diameter) and Br^- (0.332 nm diameter) affects the relative mobility of these anions as the diameter of the interconnecting pore throats decreases. They observed that the method dependent difference in $\text{Cl}^- : \text{Br}^-$ mass ratios is inversely proportional to porosity which is consistent with observations from the present study. The porosity of the Champlain Sea mud is approximately 65 % (Figure 4.3), much higher than the shales studied by Celejewski et al., (2018), and within error, there is no discernable difference in $\text{Cl}^- : \text{Br}^-$ mass ratios obtained by the three methods.

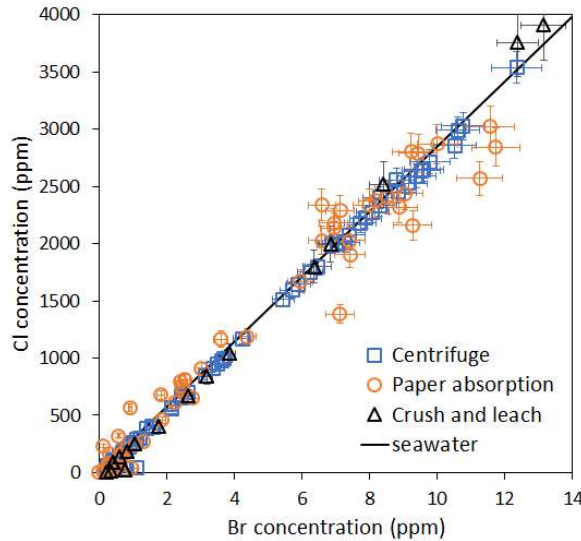


Figure 4.7. Plot of porewater Cl^- and Br^- concentrations from centrifugation ($\square$), paper absorption ($\circ$) and crush-and-leach (Δ). Error bars represent 3 times the analytical accuracy (%). The increase in error bar size with concentration is a result of using a reported percentage.

4.5.1.3. Cations

Cation concentrations in porewater extracted from the same rock, sediment, or soil sample using different methods should be expected to differ for several reasons.

First, different methods may sample different fractions of mobile and cation-rich bound

waters. Second, some methods disrupt the equilibrium between the mobile water and DDL which causes cation-exchange reactions that lead to misrepresentation of the in-situ porewater composition. The centrifuge and paper-absorption methods are thought to primarily extract the mobile water and they should not cause disruption of the equilibrium between mobile water and the DDL. Alternatively, the crush-and-leach method targets both mobile and bound water and causes disruption to the equilibrium state. Crush and leach is therefore likely to result in greater extraction-related artifacts. This expectation is consistent with observations from this dataset.

Method specific artifacts stemming from potential solute adsorption to cellulose may be expected when extracting porewater using paper absorption. The reversibility of sorption for Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Cl^- and Br^- on the Whatman[®] 1 CHR paper was investigated by Celejewski et al., (2014) and they found that desorption is completely reversible (within error of $\pm 2\sigma$ for replicate analyses). They did not examine minor and trace elements (Li^+ , Rb^+ , I^- , and Ba^{2+}), which can adsorb onto organic matter (Budd and Herrington, 1989; O'Connell et al., 2008; Reed, 1973; Whitehead, 1984).

Among the monovalent alkali-metal cations, Na^+ concentrations obtained with all three methods are similar through the depth of the borehole, but concentrations of K^+ and Rb^+ extracted by crush-and-leach are elevated compared to the paper-absorption and centrifuge methods (Figure 4.3). The Li^+ concentrations from the crush-and-leach method are also elevated above 30 mBGS, but below that depth they are consistent with the two other methods. As noted above, the anomalous concentrations obtained from the crush-and-leach method are likely related to disruption of the mobile water-DDL equilibrium during leaching with DI water. A comparison between cations in the mobile

water versus cations on ion-exchange sites demonstrates that in each case where the estimated porewater concentrations from the crush-and-leach method exceed the values from the other methods, the ratio between cation concentrations on exchange sites to those in the mobile water are also elevated (Figure 4.8). The ratios between exchangeable and mobile water cation concentrations are cation dependent and are generally higher above 25 to 30 mBGS and trend toward zero below this depth (Figure 4.8). This is evident for Li^+ ; the estimated porewater concentrations from crush and leach exceed those from the other two methods above 25 to 30 mBGS and in that same depth interval the concentration of exchangeable Li^+ is approximately three times higher than that in the mobile porewater (Figure 4.5 and 4.8). Consideration of the ratio between exchangeable and mobile water concentrations supports the inference that the anomalous porewater concentrations of Li^+ , K^+ , and Rb^+ estimated by the crush-and-leach method may be explained by excess cations released from the ion-exchange sites in the DDL.

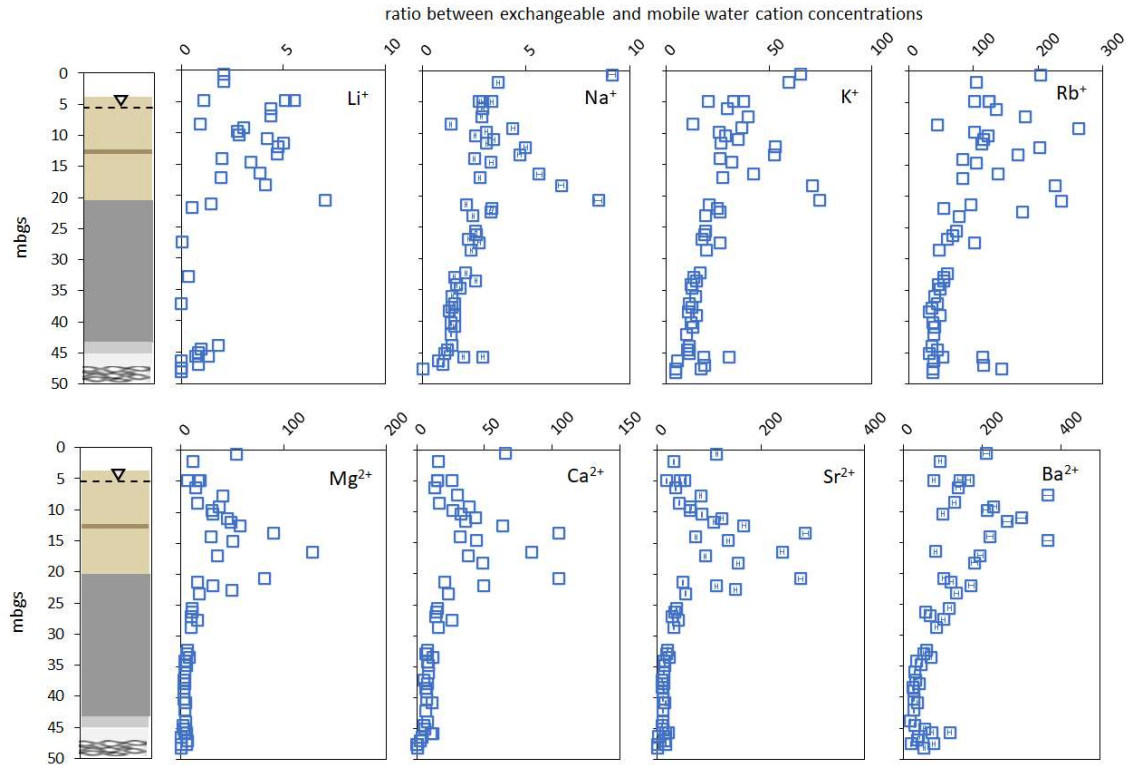


Figure 4.8. Ratio between cation concentrations on exchangeable sites and in the mobile water.

The estimated porewater concentrations from the crush-and-leach method for alkaline-earth cations (Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+}) also display significant deviation from the paper-absorption and centrifuge methods. The deviations are consistent in that the anomalous values from crush and leach are similar to, or exceed, the corresponding values from the other two methods above depths of 25 to 30 mBGS, and they are similar to, or lower, than values from the other two methods below those depths (Figure 4.3). As noted above for the alkali-metal cations, consideration of the ratios between exchangeable and mobile water cation concentrations are necessary to explain these differences. The ratio between the two cation reservoirs peaks between 10 and 25 mBGS for divalent cations (Figure 4.8) corresponding to the greatest deviation between

porewater concentrations in crush and leach extracts and the other two methods (Figure 4.3). Once again, consideration of the ratio between the two cation reservoirs demonstrates that the crush-and-leach method provides estimates for porewater concentrations that exceed the other two methods in the depth intervals where the greatest differences in cation concentrations between the exchange sites and mobile water are observed.

In general, the estimates of porewater concentrations from the paper-absorption method are equal to, or slightly lower than those from the centrifuge method. This is particularly obvious in the depths between 10 and 25 mBGS where alkaline-earth metal concentrations in the porewater are the lowest and the ratio of exchangeable to mobile water cation concentrations are the highest. The simplest explanation for these differences would be that a small fraction of the cation mass in the porewater extracted into the paper is adsorbed to the cellulose and the subsequent desorption during the paper leaching step is incomplete. In order to further evaluate the possibility that incomplete desorption can explain the observed discrepancies between the paper-absorption and centrifuge methods, data from the present study were used to construct adsorption isotherms (Figure 4.9). The isotherms were constructed by plotting the adsorbed mass, here the difference between the solute mass extracted by the two methods (C^*), versus the known concentration. The concentrations obtained by the centrifuge method were used as a benchmark. The adsorbed mass was calculated according to Equation 4.3.

$$C^* = \frac{mass_{X\ CENT} - mass_{X\ PAM}}{mass\ paper} \quad (4.3)$$

Where $mass_{X\ CENT}$ is the mass of solute “x” extracted by the centrifuge method normalized to a unit mass of porewater; $mass_{X\ PAM}$ is the mass of solute “x” extracted by

the paper absorption method, normalized to the same unit mass of porewater; and *mass paper* is the mass of paper used for the paper absorption extraction.

Concentration-dependent incomplete desorption of solutes from the paper would be characterized by a positive slope in Figure 4.9. The data for all isotherms are scattered, with R^2 values ranging from 0.0196 for Sr^{2+} to 0.407 for Ba^{2+} . No positive trend is observed for Mg^{2+} , Ca^{2+} , and Sr^{2+} , but there is a small positive slope for the Ba^{2+} isotherm suggesting that incomplete desorption of Ba^{2+} may be a factor. Celejewski et al., (2014) did not evaluate the reversibility of Ba^{2+} leaching from the Whatman[®] 1 CHR paper.

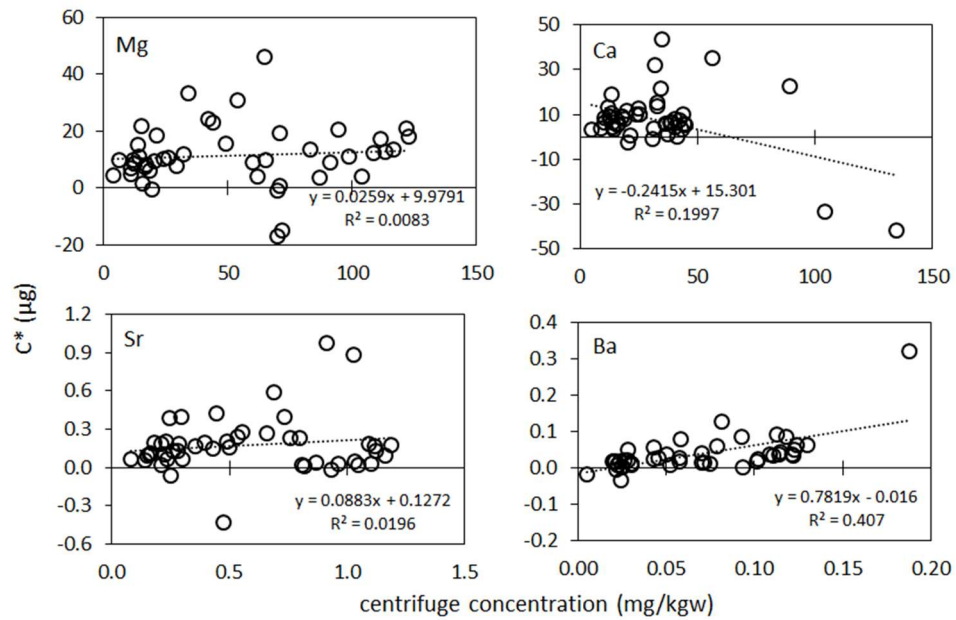


Figure 4.9. Adsorption isotherms for Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} . P values < 0.05 for all elements.

An alternative explanation for the differences among estimated porewater concentrations from the paper absorption versus centrifuge methods is provided by studies examining the fractionation of solutes during centrifugation as a function of

recovered porewater volume (Edmunds and Bath, 1976) or varying centrifuge speeds (Sheppard et al., 1992; Yokoyama et al., 2011) and extraction durations (Vidal Pérez et al., 2002). Edmunds and Bath (1976) used centrifugation to extract porewater from Cretaceous chalk and demonstrated a concentration fractionation effect whereby concentrations of Na^+ , K^+ , and Ca^{2+} decline as the fraction of the recovered porewater volume increased. However, the fractionation effect was less pronounced for Mg^{2+} and Sr^{2+} . Varying centrifuge speeds to extract porewater from a soil (Sheppard et al., 1992) and a rhyolite (Yokoyama et al., 2011) resulted in varying outcomes. Sheppard et al., (1992) reported decreasing Cl^- , Ca^{2+} , Mg^{2+} , and K^+ and increasing Na^+ concentrations with increasing speeds, while Yokoyama et al., (2011) measured increased solute concentrations for all extracted elements (Li^+ , Br^- , Na^+ , K^+ , Ca^{2+} , and Cl^-) at higher centrifuge speeds. The fractionation effect caused by centrifugation is complicated and may be related to mineralogical composition, pore geometry, and porewater and exchange site chemistry, and it is possible that the centrifuge data overestimate the in-situ concentrations.

4.5.2. Porewater composition effects on the DDL

A slight increasing trend in CEC is observed, from 6.8 to 10.7 meq/100 g dry mud, between the water table and the base of Unit 4a. Increases in CEC can be caused by increasing clay-mineral and organic matter content, decreasing grain size, and increasing pH (Ma and Eggleton, 1999; Malcolm and Kennedy, 1970; Sparks, 2003). The scope of this study did not include quantification of organic matter content, and bulk mineral analysis revealed little difference in mineral composition, including clay minerals, across the depth of the borehole (Figure 4.6). Work done by Al-Mufti et al. (2022) on the same

borehole found that grain size increased with depth, suggesting a decreasing trend in CEC might be expected. However, this is not consistent with the measured CEC values. The observed CEC increase of 3.9 meq/100 g dry mud coincides with a one unit porewater pH increase across the same depth. This trend is consistent with the literature: Jayasekera et al. (2004) found a 2 meq/100 g dry soil decrease in CEC, from 14 to 12 meq/100 g dry soil, when the pH of porewater in an Australian saline soil changed from 9 to 8, and Helling et al. (1964) quantified CEC reduction by a factor of 1.7 per pH unit decrease in soil samples collected from Wisconsin.

In previous investigations of porewater in the Champlain Sea mud, salinities of 13 and 15 g/L have been reported in Varennes, QC and in Hawkesbury, ON by Desaulniers and Cherry, (1988) and Quigley, (1980) respectively. In the Billberry Creek borehole, maximum salinity approaches 5 g/L in Unit 2 with a solute composition equivalent to approximately 15 % seawater. This suggests that freshening of the porewater has occurred throughout the thickness of the mud at this site. Above Unit 2, an upward decrease is observed in the concentrations of conservative natural tracers Cl^- and Br^- , as well as for most other solutes. Coupled with low hydraulic conductivity for the mud (Desaulniers and Cherry, 1988; Lapierre et al., 1990; Locat and St-Gelais, 2014b; O'Shaughnessy and Garga, 1994), this trend suggests that freshening occurred by diffusion-dominated transport. Freshening of porewater in marine mud has been shown to increase mud sensitivity (Andersson-Sköld et al., 2005; Bogaard et al., 2007; Helle et al., 2016; Ohtsubo et al., 2007; Torrance, 1979) which has been attributed to the relationship between porewater ionic strength and DDL thickness. The DDL thickness can be equated to the distance to which the influence from negatively charged mineral surfaces extends

outward into the porewater (Appelo and Postma, 2004). As the DDL thickens, repulsive forces between adjacent negatively charged mineral grains can overlap, creating a force that tends to push the particles apart, thereby decreasing cohesion and increasing mud sensitivity. The thickness of the DDL is often equated to the Debye length (κ^{-1} , nm, Appelo and Postman, 2005, Equation 4.4).

$$\kappa^{-1} = \frac{0.309}{\sqrt{I}} \quad (4.4)$$

where I is the ionic strength of the solution. Using Equation 4.4, the anticipated Debye length has been calculated for all samples versus depth (Figure 4.10) and the inverse relationship with ionic strength is clearly evident. The DDL thickness, as defined by the Debye length, was reported to be ~0.6 nm for Champlain Sea muds in the proposed depositional environment at Varennes, QC (Desaulniers and Cherry, 1988). In the Champlain Sea mud at Billberry Creek, the estimated DDL thickness ranges from approximately 0.9 nm at depth in Unit 2 where the ionic strength is highest, to approximately 3.0 nm near the surface.

Delage and Lefebvre (1984) and Lapierre et al. (1990) characterized pore spaces in Champlain Sea mud samples using scanning electron microscopy (SEM) and mercury-intrusion porosimetry (MIP). Images of the Champlain Sea muds were used to quantify individual pores and gain insight into pore shape and distribution through the mud, while MIP was used to measure pore-throat diameters. Based on SEM data, both studies found that the mud is composed of a small fraction (20 %) of aggregates with grain sizes between 2 and 15 μm . The pore spaces within these aggregates are filled with smaller porous aggregates and mineral grains that have diameters less than 2 μm . The MIP data collected by Lapierre et al. (1990) revealed that 10 % of the pore volume

corresponds to pore throats greater than 1 μm , 60 % between 1 and 0.1 μm , and the remaining 30 % less than 0.1 μm . Delage and Lefebvre (1984) also separated MIP results into three groups: 30 % of the pore volume between 1 and 0.25 μm , 40 % between 0.25 and 0.125 μm , and 30 % less than 0.125 μm .

Work by Jang et al., (2011) and Ren and Santamarina, (2018) demonstrates that decreasing hydraulic conductivity corresponds to decreasing pore throats and diameters, and an increase in tortuosity and constrictivity. Taking into consideration the low hydraulic conductivity of the mud samples, the pore volume fraction reported to contain pores with diameters smaller than 0.125 μm by Delage and Lefebvre (1984) and Lapierre et al. (1990) could be expected to contain a range of decreasing pore diameters including a fraction of pore throats that are small enough to accommodate DDL overlap. Based on Equation 4.4, pore throat diameters 0.006 μm or less would increase mud sensitivity caused by DDL overlap near the surface. As porewater freshening continues, the inverse relationship between Debye length and the square root of the ionic strength of porewater (Equation 4.4) will result in an exponential increase in DDL thickness, and consequently more DDL overlap.

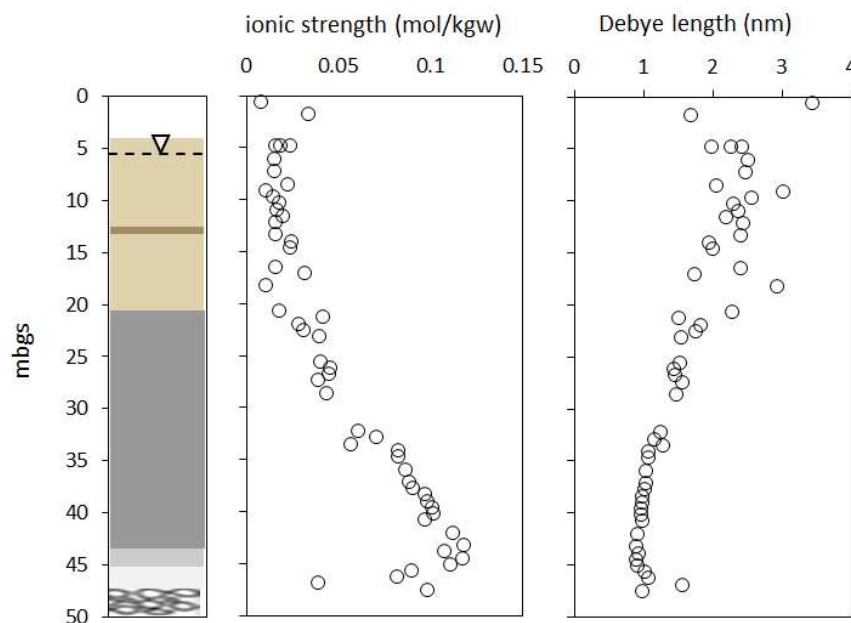


Figure 4.10. Depth profiles of ionic strength (mol/kgw) and the corresponding Debye lengths (nm) calculated from porewater ion concentrations estimated using the paper absorption method.

Equation 4.4 only considers the ionic strength of the porewater, but the thickness of the DDL is also dependent on the charge density and hydrated ion size of cation species on the exchange sites (Bhuiyan et al., 1998; McBroom and McQuarrie, 1987; Valleau and Torrie, 1982; Yu et al., 2006). Divalent cations (Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+}) have higher charge densities than monovalent cations (Li^{+} , Na^{+} , K^{+} , and Rb^{+}) and subsequently, exchanges sites with a high ratio of monovalent to divalent cations result in thicker DDLs (Egloffstein, 2001) and increased mud sensitivity.

The Champlain Sea mud porewater is of marine origin and the cation population is dominated by Na^{+} . Assuming the original connate porewater had a salinity close to 33 % seawater (Desaulniers and Cherry, 1988), porewater freshening is observed through the entire depth of the deposit at Billberry Creek. Between the base of Unit 2 and 12 mBGS the Na^{+} concentration and ionic strength decrease gradually toward the surface,

but exchange sites composition remains Na^+ dominated (Figure 4.3 and 4.5). Through this section of the deposit, it is expected that the sensitivity of the mud increases toward the surface proportionally to the decreasing ionic strength and associated expansion of the DDL (Andersson-Sköld et al., 2005; Aylsworth et al., 1997; Ohtsubo et al., 1996; Torrance, 1999).

Above 12 mBGS evidence of weathering processes resulting from carbonate mineral dissolution are observed in increased concentrations of Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} in the porewater. As Mg^{2+} and Ca^{2+} dominate the porewater composition (Figure 4.3), exchange reactions between these divalent cations and Na^+ and K^+ on exchange sites occur. This shift from monovalent to divalent cation dominated exchange sites will result in a thinning DDL and decreased mud sensitivity (Andersson-Sköld et al., 2005; Aylsworth et al., 1997; Ohtsubo et al., 1996; Torrance, 1999). The overall sensitivity of the mud above 12 mBGS becomes a balance between DDL thickening caused by decreased ionic strength and DDL thinning resulting from increased Mg^{2+} and Ca^{2+} concentrations on exchange sites.

4.6. Conclusion

Porewater from Champlain Sea mud was extracted from samples collected over the entire depth of the deposit using three different methods: centrifugation, paper-absorption, and crush-and-leach. The porewater compositions estimated from all three methods produced similar results for the conservative natural tracers Cl^- and Br^- , as well as Na^+ . For all other elements, data from the crush-and leach method display deviations from the centrifuge and paper-absorption methods. Where solute concentrations measured from crush and leach extracts are elevated above the other two

methods, the ratio between exchangeable and mobile water cation concentrations is also elevated. This indicates the differences between cation concentrations extracted by the crush-and-leach method and the paper-absorption and centrifugation methods can be explained by cation exchange reactions caused by a disruption of the mobile water-DDL equilibrium during the leaching. A good comparison was observed between the centrifuge and paper-absorption methods for Li^+ , Na^+ , K^+ , and Rb^+ concentrations as well as for SO_4^{2-} below 35 mBGS. Variability on SO_4^{2-} above 35 mGS was attributed to sulphide oxidation. Small differences were observed in Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} concentrations obtained by the centrifuge and paper-absorption methods. It is not clear whether the differences result from artifacts related to incomplete desorption of these elements from the papers during leaching or from cation fractionation during centrifugation.

Cation exchange capacity measurements range from 6.8 to 12.5 meq/100 g dry mud, consistent with values previously measured in Champlain Sea mud from different locations and depths. A slight increase in CEC values is observed between the surface and Unit 4a corresponding with an increase in pH. Overall, the cation mass balance is dominated by ions on the exchange sites. The abundance of individual cations on exchange sites is higher than in the porewater by a factor of up to 8 for Li^+ and Na^+ , 74 for K^+ , 263 for Rb^+ , 473 for Mg^{2+} , 105 for Ca^{2+} , 286 for Sr^{2+} , and 1166 for Ba^{2+} .

Porewater ionic strength decreases from a peak at the base of Unit 2 toward the freshwater at the surface and into the underlying glacial till, indicating a diffusion driven decrease in salinity. The decreasing trend in ionic strength coupled with a cation population dominated by Na^+ between Unit 2 and 12 mBGS suggests an increase in mud

sensitivity resulting from increasing DDL thickness. Above 12 mBGS weathering reactions, predominantly carbonate dissolution, result in increased concentrations of Ca^{2+} and Mg^{2+} in the porewater. Increasing Ca^{2+} and Mg^{2+} porewater concentrations lead to exchange with Na^+ and K^+ on exchangeable sites altering the system from a Na^+ to Ca^{2+} and Mg^{2+} dominated. This change in dominant cations from mono- to divalent contributes to a decrease in mud sensitivity. Mud sensitivity is a balance between DDL thickening due to decreasing ionic strength and DDL thinning caused by increased multivalent cation populations generated from weathering reactions.

Efforts to understand mud sensitivity and the potential for landslides would benefit from a complete understanding of porewater chemistry as well as ion exchange site composition. This work has presented a detailed assessment of methods that are appropriate to reaching that goal. Follow up research to link porewater and exchangeable-cation compositions to measurements of mud sensitivity could further improve the understanding of the susceptibility of these systems to slope failure.

4.7. Acknowledgment

This research is part of a larger study with the Geologic Survey of Canada (GSC), City of Ottawa, and Rideau Valley Conservation Authority aiming to examine the geotechnical stability of the Champlain Sea mud deposits. Core collection, preservation, storage, and porewater extraction by centrifugation was conducted by Sam Alpay and Marc Hinton at the GSC with help from the sedimentology laboratory team: Shauna Madore, Miriam Wygergangs, Claudia Moore, and Alain Grenier. Sampling for crush-and-leach and Ni-et extracts was done with the help of Chantal Lurette.

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5.0. Conclusion

The interest in low-permeability formations in the context of nuclear waste storage and CO₂ sequestration has presented an increased need for accurate and precise measurements of porewater chemistry and solute distribution through these rocks. Additionally, extraction and quantification of porewater from sensitive marine sediments can lead to a better understanding of mud stability and landslide potential development. Understanding the mechanisms of porewater extraction, potential method artifacts, and limits associated with different sampling methods can provide researchers, regulators, and policy makers with tools to help assess risk and evaluate potential impacts of geologic waste repositories.

The development of a method for extraction of porewater from low-permeability formations was the initial objective for this thesis. The work presented in Chapter 2 demonstrates the feasibility of the novel paper-absorption method to extract porewater solutes from low-permeability rocks. For the purpose of porewater absorption, the cellulose-based Whatman[®] 1 CHR was selected due to the high capillarity and low chemical background of the paper. This material demonstrated no major porewater solute (Na⁺, K⁺, Mg²⁺, Ca²⁺, Sr²⁺, Cl⁻, and Br⁻) adsorption during porewater extraction and complete desorption of these solutes during paper leaching. Concentrations of major solutes measured in porewater extracted by paper absorption from core samples equilibrated with a synthetic porewater of known composition established the effectiveness of combining separate measurements of extracted water by reflectance NIR spectrometry and solute masses by ICP-MS. Extracted solute concentrations displayed analytical precision within the margins of error recommended by EPA Method 6020a (for

analysis of saline water samples) for Na^+ ($\pm 24\%$) and Ca^{2+} ($\pm 6\%$). Potassium and magnesium concentrations show a great deal of variability and were mostly outside the EPA limits ($\pm 10\%$). This was attributed to an incomplete equilibration of soaking water and porewater and is not being considered a problem for rock samples containing natural porewater. The EPA Method 6020a does not provide margins of error for Cl^- , Br^- , or Sr^{2+} , but the measured concentrations fall slightly outside a 10 % limit. It is assumed that the paper-absorption method extracts porewater from the mobile water fraction, sampling only the most interconnected pore spaces. Consequently, using the paper absorption method along side other porewater extraction methods that sample bound water will provide useful information about the distribution of solutes through pore spaces.

A comparison of natural porewater tracers, Cl^- and Br^- extracted by paper absorption and crush and leach from low-permeability rocks with small pore volumes collected from three different locations benchmarked this new method against an established one (Chapter 3). This work does not provide concentrations of porewater solutes because water measurements of samples extracted by paper absorption were affected by evaporation during paper insertion and removal, and accurate porosity measurements were not available for crush-and-leach calculations. Instead, a comparison of Cl^- and Br^- ratios is presented, which contrary to expectations differed between extraction methods. The $\text{Cl}^- : \text{Br}^-$ ratios obtained in the mobile water fraction by the paper-absorption method are consistently lower than those from the total porewater extracted by crush-and-leach, indicating that Cl^- and Br^- are not uniformly distributed in the mobile water, nor are they uniformly excluded from the bound water. The difference in conservative natural tracer ratios extracted from paired samples using two different

methods demonstrates the complexity of low-permeability formations and the dependence of solute specific transport on both solute and rock properties.

The work presented in Chapter 4 directly compares solute concentrations obtained by three different porewater extraction methods, benchmarking the paper-absorption method against two established porewater extraction techniques: centrifugation and crush-and-leach. Concentrations of Cl^- and Br^- compare well between all three methods, and the data supports the hypothesis presented in Chapter 3 suggesting that pore throat diameters and pore volume influence the distribution of Cl^- and Br^- within the pore space. Cation concentrations obtained by paper-absorption and centrifugation follow similar trends but exhibit some method dependent artifacts for alkaline-earth metals, stemming either from solute adsorption to the cellulosic paper or fractionation during centrifugation. Cation concentrations measured in crush and leach extracts are elevated above the other two methods where the ratio between exchangeable and mobile water cation concentrations is also elevated indicating that cation exchange reactions caused by a disruption of the mobile water-DDL equilibrium occur during the leaching. Extraction of both the mobile porewater and the DDL separately provides a foundation for determining the effects of porewater freshening and weathering reactions on changing DDL thickness and the influence on mud stability. Combining this dataset with sensitivity measurements will improve understanding of landslide potential development in Champlain Sea muds.

One important takeaway from this work is the dependence of measured porewater concentrations on the sampling method. Understanding the mechanisms of individual porewater sampling techniques is important for estimating the fraction of mobile and

bound (DDL and clay interlayer) waters sampled and the extent of mobile water-DDL equilibrium disruption during extraction. The biases and artifacts of these extraction methods can be particularly problematic in rock samples with low-permeability and porosity, but have also been found to affect samples with larger porewater reservoirs. It is important to have a thorough grasp of the limitations and biases of each extraction method since estimates of porewater composition are used to determine the origins of porewater, mechanisms driving solute transport rates and reactions. This information then can be applied to predictive modeling of solute transport and residence times and used to make decisions about waste repositories, CO₂ sequestration, and land development policies. It should be emphasized that a whole picture approach using multiple different porewater extraction techniques targeting both mobile and bound waters separately is recommended for a better understanding of the porewater system.

5.1. Recommendations for future projects

This research presents an effort to establish the paper absorption method for extracting the mobile fraction of porewater and contributing to a more complete understanding of porewater-rock systems. During method development and the application of the paper- absorption method to rock and sediment samples, several questions have arisen as well as suggestions for method improvement.

In Chapter 4, the question of alkaline-earth metal as well as trace element adsorption to the absorbing paper was raised. An investigation of sorption isotherms of metals and trace elements to Whatman® 1 CHR during extraction of porewater and the reversibility of solute desorption during the leaching step should be conducted.

Reversibility of sorption for Na⁺, K⁺, Mg²⁺, Ca²⁺, Sr²⁺, Cl⁻ and Br⁻ on Whatman® 1 CHR

paper was presented in Chapter 2, demonstrating the complete reversibility of solute desorption from the paper within $\pm 2\sigma$ for replicate analyses. However, this work did not investigate minor and trace elements. Outlined in Appendix D is a proposal for an experiment to quantify the extent of adsorption of I^- , Br^- , Cl^- , SO_4^{2-} , F^- , Na^+ , Ca^{2+} , K^+ , Mg^{2+} , Sr^{2+} , Ba^{2+} , Al^{3+} , Fe^{2+} , Li^+ , Rb^+ , Ni^{2+} , Mn^{2+} , and B^{3+} to Whatman® 1 CHR over a range of pH values common in porewater systems.

Quantification of accurate and precise solute concentrations in porewaters extracted using the paper-absorption method from low-permeability, low-porosity rock samples has yet to be published. Solute concentrations were published as part of an international collaboration examining several porewater extraction methods conducted on Mont Terri cores obtained from the Underground Research Laboratory in Switzerland (Mazurek et al., 2017). However, solute concentrations obtained by the paper-absorption method were elevated above measurements reported by the other extraction methods (high pressure squeezing, out-diffusion, and crush-and-leach). This exercise exposed several weaknesses in the paper absorption method, many of which I have worked to remedy.

The most obvious problem was caused by evaporation of water from the core surface during paper insertion, or from the paper surface during removal. When extracting porewater masses between 5 and 30 mg, evaporation of even one microgram of water can have large effects on solute concentration measurements. For the work presented in Chapter 3, Mont Terri and Lorraine Group core samples cleaving and paper insertion was conducted inside of a humidity chamber maintained at a relative humidity at equilibrium with the anticipated salinity of the porewater. Despite this, evaporation

effects were observed, indicating evaporation during the paper removal step. To minimize evaporation during this step, paper removal was conducted in a humidity chamber when working with the Champlain Sea mud cores (Chapter 4). This approach, coupled with the relatively large amounts of water extracted from the Champlain Sea mud samples resulted in no observable evaporation effects. It is recommended that all paper insertion and removal be conducted inside a humidity chamber maintained at the appropriated relative humidity.

Another identified problem was the transfer of variable amounts of particle from the core to the paper, observed for both Michigan Basin and Mont Terri cores. This is problematic because any rock particulate on the paper will be leached form the paper with the extracted porewater solutes and will be reported as part of the porewater composition. The placement of a membrane with a small volume, high capillarity, and low chemical background between the absorbing paper and the core is required to prevent transfer. For porewater extracted from the Lorraine Group shales Kimwipes™ cut to a 5 cm diameter were used successfully as a barrier on either side of the absorbent paper. However, during this extraction it was observed that the Kimwipes™ have a significant Cl^- background that may hinder Cl^- quantification in samples with low ionic strength. A DI water leaching treatment of Kimwipes™ has been developed to remove leachable Cl^- allowing the use of this material as a particulate transfer barrier for porewater samples of all salinities.

The use of the Kimwipe™ as a particulate transfer barrier will require the measurement of adsorption properties of porewater solutes to the Kimwipe™. This can be done using the same protocol outlined for Whatman® 1 CHR in Appendix D.

Preferential adsorption of solutes to the Kimwipe™ would prevent the movement of porewater solutes into the absorbing paper which will result in method artifacts.

Quantification of water mass using reflectance NIR spectrometry is effective for 4.5 cm diameter Whatman® 1 CHR papers containing a water mass greater than 30 mg. For water samples smaller than this, reflectance NIR calibration becomes difficult because the measurements are affected by partitioning of water across the thickness of the paper. Instead, a transmission NIR spectrometer, that measures NIR absorption through the thickness of the paper, has been calibrated to both water content and total salt mass. The transmission NIR has been found to be most effective for water masses of 0 to 35 mg. The details of this spectrometer setup and calibration are provided in Appendix D.

Based on these improvements, the paper absorption method is currently being used to extract and quantify porewater chemistry from low-permeability rocks from the Michigan Basin for Geofirma and the Nuclear Waste Management Organization.

Analysis of sulphate in extracted porewater is difficult due to oxidation of sulphide upon exposure to atmospheric oxygen. To minimize the effects of oxidation, paper insertion and removal could be attempted in an anaerobic chamber maintained at the correct relative humidity. This would require a small core cleaving apparatus, which may not work with all core types.

Analysis of Sr isotopes from porewater extracted using the paper absorption method can provide additional information about the history of fluid movement. The use of radiogenic ^{87}Sr as a natural porewater tracer through groundwater is a valuable tool (Armstrong et al. 1998; Banner et al. 1994) and quantification can be performed by

thermal ionization mass spectrometry (TIMS). A Sr^{2+} mass of 0.6 μg is required for isotope quantification using the TIMS at Carleton University. The ability to analyse Sr^{2+} isotopes in porewater extracts will depend on a combination of the total porewater mass extracted and the Sr^{2+} concentration. This has been completed successfully on porewaters extracted from low-permeability rocks from the Michigan Basin, which have very high ionic strengths but yield small porewater volumes.

Stable water isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) are commonly used as conservative natural tracers and can give insight into porewater movement and origin. Isotopic composition from porewater extracted by paper absorption can be quantified using a Picarro cavity ring down spectrometer (CRDS), which requires small sample volumes for accurate isotopic analysis, and sample introduction can be achieved by volatilization directly from an introduction medium, like the absorbing paper. This work has already begun as a separate PhD project.

Porewater pH is an important variable for understanding the complete porewater system, including solute speciation, transport, and reaction processes. Measurement of pH using a conventional electrode requires volumes of water greater than those extracted by the paper absorption method. However, the absorbing paper can be saturated with a colorimetric indicator for pH prior to insertion between core segments. This would require calibration of a spectrometer in the visible light range to an indicator or indicators targeting the desired pH range.

A comparison of the porewater and exchangeable cation concentration data presented in Chapter 4 to sensitivity measurements (conducted at the GSC) of Champlain

Sea mud samples could provide a lot of insight into processes that increase sensitivity of these muds.

5.2. References

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Appendix A: Supplementary information for Chapter 2

Table A1. Average concentrations of initial and final solutions used in the solute adsorption experiment. Relative standard deviations reported on replicate samples.

				Na ⁺	Mg ²⁺		Cl ⁻		K ⁺		Ca ²⁺		Br ⁻		Sr ²⁺		
Initial solution	SPW dilution factor	pH	replicates	Average concentration (ppm)	Relative standard deviation (%)	Average concentration (ppm)	Relative standard deviation (%)	Average concentration (ppm)	Relative standard deviation (%)	Average concentration (ppm)	Relative standard deviation (%)	Average concentration (ppm)	Relative standard deviation (%)	Average concentration (ppm)	Relative standard deviation (%)	Average concentration (ppm)	Relative standard deviation (%)
i	10	5	3	4881	4%	388	4%	12924	35%	167	4%	2945	3%	199	2%	92	2%
i	100	5	3	454	12%	36	12%	1195	34%	16	12%	283	12%	19	12%	9	12%
i	250	5	3	196	6%	16	6%	530	38%	7	4%	118	7%	8	3%	4	4%
	10	5	9	4833	2%	379	2%	13757	25%	169	3%	3008	2%	203	2%	95	3%
	100	5	9	502	5%	39	6%	1525	19%	17	5%	307	4%	21	3%	10	3%
	250	5	9	193	7%	15	7%	572	18%	6	8%	117	8%	8	7%	4	7%
i	10	6	3	4932	3%	390	4%	13218	36%	171	4%	3025	4%	207	3%	95	4%
i	100	6	3	493	12%	39	12%	1091	54%	17	15%	307	12%	21	13%	10	12%
i	250	6	3	194	2%	15	2%	528	37%	7	6%	119	3%	8	2%	4	3%
	10	6	9	4812	2%	378	2%	12190	35%	163	3%	3016	3%	205	2%	96	3%
	100	6	9	502	3%	39	4%	1164	39%	17	3%	306	4%	21	4%	10	5%
	250	6	9	198	4%	15	3%	592	18%	7	17%	121	5%	8	3%	4	5%
i	10	7	3	4570	3%	360	2%	10067	45%	157	3%	2855	4%	195	3%	91	5%
i	100	7	3	469	3%	37	3%	1014	46%	17	4%	290	3%	20	3%	9	4%
i	250	7	3	186	3%	14	4%	593	5%	9	25%	114	5%	8	5%	4	6%
	10	7	9	4808	4%	378	4%	12894	30%	168	4%	2985	4%	202	5%	94	6%
	100	7	9	487	3%	38	3%	1207	34%	18	3%	299	4%	20	5%	9	5%
	250	7	9	197	4%	15	4%	484	35%	10	5%	118	5%	8	3%	4	4%

Table A2. Limit of detection and results of accuracy and precision of a calibration check standard for ICP-MS measurements.

	Na ⁺	Mg ²⁺	Cl ⁻	K ⁺	Ca ²⁺	Br ⁻	Sr ²⁺
solute adsorption experiment							
LOD (ppb)	3.30	0	11.97	2.11	0	1.75	0.01
% precision	3%	3%	2%	5%	5%	3%	4%
% accuracy	2%	2%	1%	2%	4%	2%	3%
solute leaching and spike paper experiments							
LOD (ppb)	40.7	1.5	154.0	4.0	27.4	0.6	0.6
% precision	1%	1%	3%	4%	2%	1%	2%
% accuracy	1%	9%	2%	7%	2%	7%	9%
core soaking experiments							
LOD (ppb)	1.3	4.3	83.7	1.9	772/9	4.2	0.1
% precision	6%	6%	6%	11%	8%	5%	7%
% accuracy	5%	4%	1%	6%	4%	4%	7%

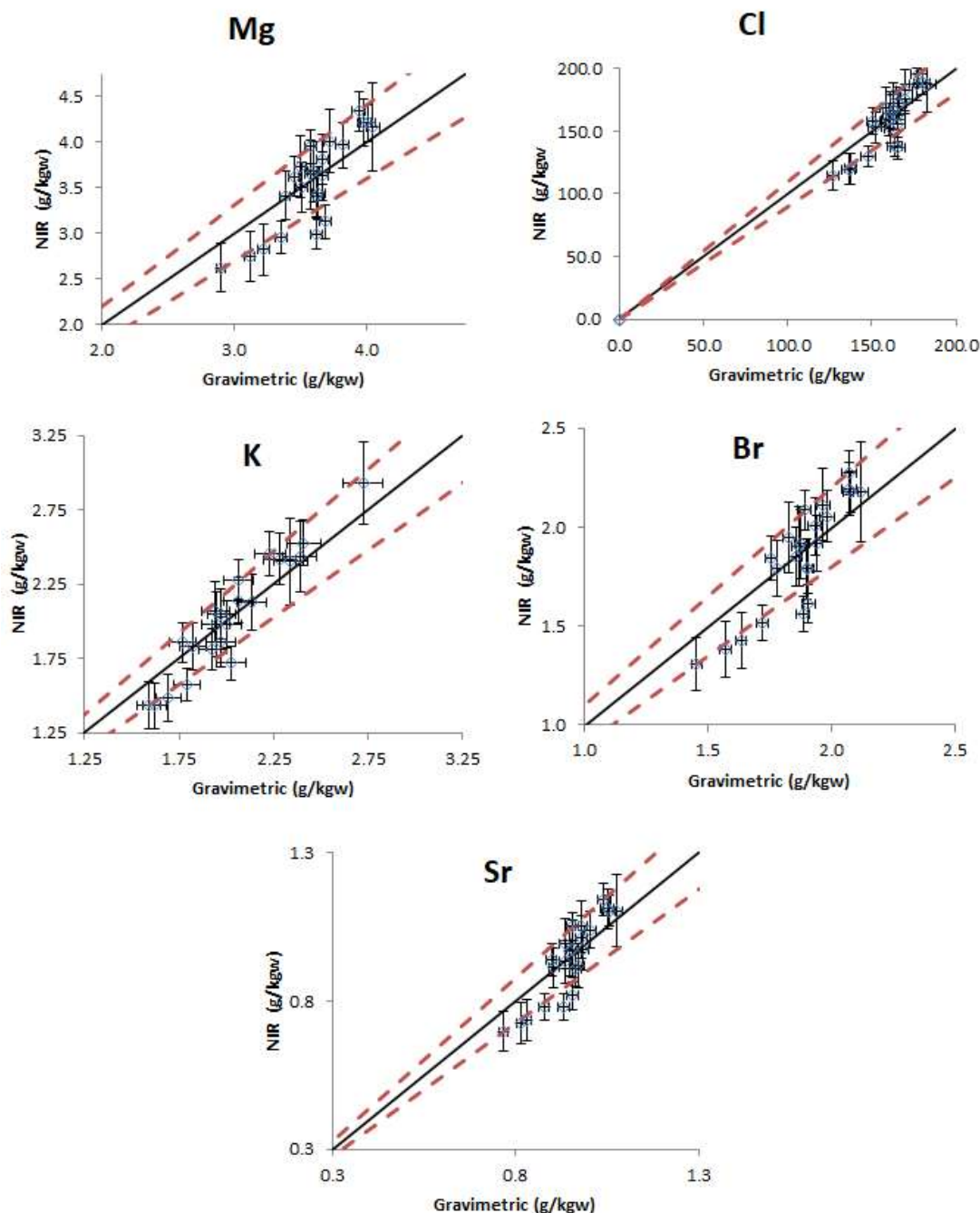


Figure A1. Concentrations of Mg^{2+} , Cl^- , K^+ , Br^- , and Sr^{2+} (g/kgw) calculated from water masses measured gravimetrically and by NIR spectrometry using the patchwork calibrations surface. The dashed lines correspond to a relative error margin accepted by US EPA method 6020a for Mg^{2+} ($\pm 10\%$) and K^+ ($\pm 10\%$). The dashed lines on the Cl^- , Br^- and Sr^{2+} graphs represent $\pm 10\%$. Error bars depict the propagated instrumental error from NIR spectrometric and gravimetric water measurements and ICP-MS solute analysis.

Table A3. Spiking solution and leached solution concentrations for spiked paper and solute leaching experiments. RSD values on triplicate measurements

Sample Name		Na ⁺	Mg ²⁺	Cl ⁻	K ⁺	Ca ²⁺	Br ⁻	Sr ²⁺
		Concentration in initial solution						
i_0	average	21	1	<0.000	5	53.8	1.5	0.6
	rsd	53%	37%	<0.000	<0.000	0.4	0.5	0.2
i_1	average	5375	355	15570	196	3943	182	89
	rsd	1%	1%	1%	18%	1%	1%	1%
i_2	average	11542	768	33832	398	8498	398	193
	rsd	1%	2%	3%	3%	1%	2%	1%
i_3	average	15855	1052	45871	547	11636	546	263
	rsd	1%	1%	1%	1%	1%	2%	1%
i_4	average	20510	1360	59498	704	15025	712	340
	rsd	1%	1%	0%	3%	0%	2%	0%
i_5	average	24689	1636	70990	904	18110	846	407
	rsd	0%	1%	1%	9%	1%	2%	1%
i_6	average	30043	1997	86086	1048	21921	1025	494
	rsd	4%	4%	4%	6%	4%	3%	4%
i_7	average	32287	2133	92896	1197	23457	1099	527
	rsd	2%	2%	3%	6%	2%	4%	3%
i_8	average	34869	2307	100109	1217	25269	1179	572
	rsd	3%	3%	3%	6%	2%	3%	4%
		Concentration in spiked paper solution						
s_0	average	105	4	0	0	0	0	0
	rsd	18%	94%	0%	0%	0%	0%	50%
s_1	average	5304	348	15087	185	3790	176	85
	rsd	4%	4%	4%	5%	4%	5%	4%
s_2	average	10593	689	30944	411	7478	357	169
	rsd	5%	3%	5%	11%	3%	4%	3%
s_3	average	15447	1018	44996	553	11067	525	254
	rsd	5%	6%	7%	11%	7%	7%	7%
s_4	average	20561	1367	61734	795	15128	716	344
	rsd	4%	4%	12%	4%	5%	4%	4%
s_5	average	25437	1690	76132	947	18616	883	428
	rsd	2%	2%	2%	9%	2%	3%	2%
s_6	average	29516	1965	89084	1152	21617	1025	495
	rsd	4%	4%	4%	20%	4%	4%	4%
s_7	average	32628	2132	96579	1339	23559	1125	536
	rsd	6%	7%	7%	34%	7%	7%	7%
s_8	average	36423	2432	109294	1312	26734	1282	616
	stdev	1301	79	3528	57	837	42	20

rsd = relative standard deviation, stdev = standard deviation

Table A4. PHREEQC output for Mabou Group core saturation duration

time step (hours)	Na ⁺	Cl ⁻	K ⁺	Ca ²⁺	Mg ²⁺
	mol/kgw				
-99	1.0810E+00	2.3490E+00	2.7000E-02	5.4000E-01	8.1000E-02
-99	1.0000E-03	0.0000E+00	2.0000E-04	0.0000E+00	0.0000E+00
-99	1.0810E+00	2.3490E+00	2.7000E-02	5.4000E-01	8.1000E-02
1	1.0810E+00	2.3490E+00	2.7000E-02	5.4000E-01	8.1000E-02
0	1.0000E-03	0.0000E+00	2.0000E-04	0.0000E+00	0.0000E+00
790	1.0418E+00	2.2637E+00	2.6027E-02	5.2040E-01	7.8060E-02
791	1.0420E+00	2.2641E+00	2.6032E-02	5.2049E-01	7.8073E-02
792	1.0422E+00	2.2645E+00	2.6036E-02	5.2058E-01	7.8086E-02

Table A5. Error and data statistics of NIR spectrometer calibration surfaces (summary of zunzun.com output)

	> 40 evaporation, > 0.016 g sale			< 45 evaporation, > 0.016 g sale			rehydration			< 45 evaporation, < 0.016 g sale		
	Error Statistics											
	Absolute Error	Relative Error		Absolute Error	Relative Error		Absolute Error	Relative Error		Absolute Error	Relative Error	
Minimum:	-0.3564	-0.2277		-5.92E-02	-3.24E-01		-0.0286	-0.2695		-2.65E-02	-7.51E-01	
Maximum:	0.1032	0.1391		6.57E-02	2.20E-01		0.0259	1.4176		4.56E-02	2.05E-01	
Mean:	0.0000	0.0014		1.14E-12	8.46E-04		0.0000	0.0197		-4.38E-16	-1.77E-02	
Std. Error of												
Mean:	0.0010	0.0010		6.33E-04	2.47E-03		0.0006	0.0101		6.32E-04	6.30E-03	
Median:	0.0004	0.0005		5.80E-04	1.87E-03		0.0007	0.0038		-6.47E-04	-2.89E-03	
Variance:	0.0016	0.0014		1.51E-04	2.30E-03		0.0001	0.0283		1.40E-04	1.39E-02	
Standard												
Deviation:	4.0181E-02	0.0379		1.23E-02	4.80E-02		9.8634E-03	0.1683		1.18E-02	1.18E-01	
Skew:	-2.6263	-0.8096		9.20E-02	-1.30E+00		-0.2420	4.7656		4.00E-01	-2.43E+00	
Kurtosis:	16.9748	3.9851		2.75E+00	1.04E+01		-0.0768	30.7778		5.78E-01	9.68E+00	
	Data Statistics											
	X	Y	Z	X	Y	Z	X	Y	Z	Y	Z	
Minimum:	0.00E+00	4.60E+01	4.46E-01	1.55E-02	2.68E+01	7.41E-02	0.0000	22.3000	0.0092	0.00E+00	2.52E+01	1.24E-02
Maximum:	5.26E-02	1.01E+02	1.56E+00	5.26E-02	4.59E+01	5.11E-01	0.0741	50.7000	0.6166	1.58E-02	4.98E+01	6.18E-01
Mean:	2.77E-02	7.22E+01	9.25E-01	3.44E-02	3.76E+01	3.21E-01	0.0306	29.1663	0.1753	6.72E-03	3.59E+01	2.51E-01
Std. Error of												
Mean:	4.28E-04	3.81E-01	6.15E-03	6.40E-04	2.30E-01	4.98E-03	0.0017	0.2834	0.0074	2.86E-04	3.90E-01	9.16E-03
Median:	3.20E-02	7.18E+01	9.31E-01	3.22E-02	3.72E+01	3.32E-01	0.0255	28.2000	0.1420	6.90E-03	3.53E+01	2.29E-01
Variance:	2.82E-04	2.24E+02	5.81E-02	1.54E-04	1.99E+01	9.35E-03	0.0008	22.0871	0.0151	2.85E-05	5.32E+01	2.93E-02
Standard												
Deviation:	1.68E-02	1.50E+01	2.41E-01	1.24E-02	4.47E+00	9.67E-02	0.0277	4.6997	0.1230	5.34E-03	7.29E+00	1.71E-01
Skew:	-1.41E-01	8.11E-02	2.60E-02	7.22E-02	4.01E-02	-4.15E-01	0.4670	1.5260	1.1709	5.37E-02	2.36E-01	2.98E-01
Kurtosis:	-1.23E+00	-1.08E+00	-8.39E-01	-1.32E+00	-7.77E-01	-5.41E-01	-1.3171	3.3913	1.0361	-1.12E+00	-1.16E+00	-1.17E+00

Table A6. Background mass of major porewater solutes on 4.5 cm diameter Whatman® 1 CHR papers collected during various porewater extraction experiments.

Experiment	Sample	Mass of paper (g)	Na ⁺	Cl ⁻	Mg ²⁺	Ca ²⁺	K ⁺	Sr ²⁺	Br ⁻
Mass of solute extracted from a 4.5 cm diameter paper (mg)									
DBA - humidity chamber, cleaved	Method blank 1	0.14 0.12	0.0242	0.0092	0.0005	0.0024	0.0024	0.0000	ND
	Method blank 2		0.0303	0.0099	0.0012	0.0123	0.0036	0.0000	0.0000
DBA/DGR - ambient, cleaved	Method blank 1		0.0257	0.0156	0.0007	0.0005	0.0012	0.0001	0.0002
	Method blank 2		0.0249	0.0135	0.0003	0.0001	0.0009	0.0000	0.0001
	Method blank 3		0.0211	0.0116	0.0002	0.0001	0.0010	0.0000	0.0001
	Paper blank 1		0.0231	0.0116	0.0004	0.0002	0.0007	0.0000	0.0002
	Paper blank 2		0.0237	0.0117	0.0004	0.0002	0.0006	0.0000	0.0002
	Paper blank 3		0.0233	0.0119	0.0003	0.0001	0.0006	0.0000	0.0002
DBA - particulate leaching	Paper blank 1		0.0189	0.0123	0.0001	0.0008	0.0007	0.0000	0.0000
	Paper blank 2		0.0192	0.0123	0.0001	0.0009	0.0006	0.0000	0.0000
	Paper blank 3		0.0198	0.0128	0.0001	0.0010	0.0010	0.0000	0.0000
DGR - sawed	Method blank 1	0.14 0.12	0.0213	0.0120	0.0003	0.0009	0.0012	0.0000	0.0000
	Method blank 2		0.0214	0.0120	0.0001	0.0004	0.0009	0.0000	0.0000
	Method blank 3		0.0210	0.0115	0.0001	0.0004	0.0009	0.0000	0.0000
core saturation experiment	Paper blank 1		0.0220	0.0146	0.0003	0.0004	0.0005	0.0000	0.0001
	Paper blank 2		0.0239	0.0131	0.0004	0.0022	0.0007	0.0000	0.0000
	Paper blank 3		0.0225	0.0170	0.0004	0.0004	0.0005	0.0000	0.0000

Table A7. Data used to generate reflectance NIR spectrometer calibration surfaces
(zunzun.com input) – Part 1.

> 40 evaporation, > 0.016 g sale				< 45 evaporation, > 0.016 g sale				rehydration			
total salt mass (g)	NIR response	Water content (% mass)	Predicted water content (% mass)	total salt mass (g)	NIR response	Water content (% mass)	Predicted water content (% mass)	total salt mass (g)	NIR response	Water content (% mass)	Predicted water content (% mass)
0.0526	101	1.27	1.27	0.0526	46.0	0.49	0.49	0.0157	46	0.54	0.54
0.0473	101	1.27	1.27	0.0473	46.0	0.48	0.48	0.0157	42	0.49	0.49
0.0420	101	1.28	1.28	0.0420	46.0	0.47	0.47	0.0157	38	0.42	0.42
0.0367	101	1.28	1.28	0.0367	46.0	0.46	0.46	0.0157	34	0.32	0.32
0.0314	101	1.30	1.30	0.0314	46.0	0.46	0.46	0.0157	30	0.20	0.20
0.0261	101	1.32	1.32	0.0261	46.0	0.47	0.47	0.0157	26	0.08	0.08
0.0208	101	1.34	1.34	0.0208	46.0	0.48	0.48	0.0157	22	0.02	0.02
0.0155	101	1.37	1.37	0.0155	46.0	0.49	0.49	0.0135	46	0.54	0.54
0.0526	96	1.22	1.22	0.0526	43.5	0.46	0.46	0.0135	42	0.49	0.49
0.0473	96	1.22	1.22	0.0473	43.5	0.44	0.44	0.0135	38	0.42	0.42
0.0420	96	1.22	1.22	0.0420	43.5	0.43	0.43	0.0135	34	0.32	0.32
0.0367	96	1.23	1.23	0.0367	43.5	0.42	0.42	0.0135	30	0.20	0.20
0.0314	96	1.24	1.24	0.0314	43.5	0.42	0.42	0.0135	26	0.08	0.08
0.0261	96	1.26	1.26	0.0261	43.5	0.42	0.42	0.0135	22	0.02	0.02
0.0208	96	1.28	1.28	0.0208	43.5	0.43	0.43	0.0112	46	0.54	0.54
0.0155	96	1.31	1.31	0.0155	43.5	0.44	0.44	0.0112	42	0.49	0.49
0.0526	91	1.16	1.16	0.0526	41.0	0.42	0.42	0.0112	38	0.42	0.42
0.0473	91	1.16	1.16	0.0473	41.0	0.40	0.40	0.0112	34	0.32	0.32
0.0420	91	1.16	1.16	0.0420	41.0	0.39	0.39	0.0112	30	0.20	0.20
0.0367	91	1.17	1.17	0.0367	41.0	0.38	0.38	0.0112	26	0.08	0.08
0.0314	91	1.18	1.18	0.0314	41.0	0.38	0.38	0.0112	22	0.02	0.02
0.0261	91	1.19	1.19	0.0261	41.0	0.38	0.38	0.0090	46	0.54	0.54
0.0208	91	1.21	1.21	0.0208	41.0	0.38	0.38	0.0090	42	0.49	0.49
0.0155	91	1.24	1.24	0.0155	41.0	0.39	0.39	0.0090	38	0.42	0.42
0.0526	86	1.11	1.11	0.0526	38.5	0.38	0.38	0.0090	34	0.32	0.32
0.0473	86	1.10	1.10	0.0473	38.5	0.36	0.36	0.0090	30	0.20	0.20
0.0420	86	1.10	1.10	0.0420	38.5	0.35	0.35	0.0090	26	0.08	0.08
0.0367	86	1.10	1.10	0.0367	38.5	0.33	0.33	0.0090	22	0.02	0.02
0.0314	86	1.11	1.11	0.0314	38.5	0.33	0.33	0.0067	46	0.54	0.54
0.0261	86	1.13	1.13	0.0261	38.5	0.33	0.33	0.0067	42	0.49	0.49
0.0208	86	1.15	1.15	0.0208	38.5	0.33	0.33	0.0067	38	0.42	0.42
0.0155	86	1.17	1.17	0.0155	38.5	0.34	0.34	0.0067	34	0.32	0.32
0.0526	81	1.04	1.04	0.0526	36.0	0.34	0.34	0.0067	30	0.20	0.20
0.0473	81	1.03	1.03	0.0473	36.0	0.32	0.32	0.0067	26	0.08	0.08
0.0420	81	1.03	1.03	0.0420	36.0	0.30	0.30	0.0067	22	0.02	0.02
0.0367	81	1.04	1.04	0.0367	36.0	0.29	0.29	0.0045	46	0.54	0.54

Table A7. cont.											
> 40 evaporation, > 0.016 g sale				< 45 evaporation, > 0.016 g sale				rehydration			
total salt mass (g)	NIR response	Water content (% mass)	Predicted water content (% mass)	total salt mass (g)	NIR response	Water content (% mass)	Predicted water content (% mass)	total salt mass (g)	NIR response	Water content (% mass)	Predicted water content (% mass)
0.0314	81	1.04	1.04	0.0314	36.0	0.28	0.28	0.0045	42	0.49	0.49
0.0261	81	1.06	1.06	0.0261	36.0	0.27	0.27	0.0045	38	0.42	0.42
0.0208	81	1.07	1.07	0.0208	36.0	0.28	0.28	0.0045	34	0.32	0.32
0.0155	81	1.10	1.10	0.0155	36.0	0.28	0.28	0.0045	30	0.20	0.20
0.0526	76	0.97	0.97	0.0526	33.5	0.30	0.30	0.0045	26	0.08	0.08
0.0473	76	0.97	0.97	0.0473	33.5	0.27	0.27	0.0045	22	0.02	0.02
0.0420	76	0.96	0.96	0.0420	33.5	0.25	0.25	0.0022	46	0.54	0.54
0.0367	76	0.96	0.96	0.0367	33.5	0.24	0.24	0.0022	42	0.49	0.49
0.0314	76	0.97	0.97	0.0314	33.5	0.22	0.22	0.0022	38	0.42	0.42
0.0261	76	0.98	0.98	0.0261	33.5	0.22	0.22	0.0022	34	0.32	0.32
0.0208	76	1.00	1.00	0.0208	33.5	0.22	0.22	0.0022	30	0.20	0.20
0.0155	76	1.02	1.02	0.0155	33.5	0.22	0.22	0.0022	26	0.08	0.08
0.0526	71	0.90	0.90	0.0526	31.0	0.25	0.25	0.0022	22	0.02	0.02
0.0473	71	0.89	0.89	0.0473	31.0	0.22	0.22	0.0000	46	0.54	0.54
0.0420	71	0.89	0.89	0.0420	31.0	0.20	0.20	0.0000	42	0.49	0.49
0.0367	71	0.89	0.89	0.0367	31.0	0.18	0.18	0.0000	38	0.42	0.42
0.0314	71	0.89	0.89	0.0314	31.0	0.17	0.17	0.0000	34	0.32	0.32
0.0261	71	0.90	0.90	0.0261	31.0	0.16	0.16	0.0000	30	0.20	0.20
0.0208	71	0.92	0.92	0.0208	31.0	0.16	0.16	0.0000	26	0.08	0.08
0.0155	71	0.94	0.94	0.0155	31.0	0.16	0.16	0.0000	22	0.02	0.02
0.0526	66	0.83	0.83	0.0526	28.5	0.20	0.20				
0.0473	66	0.82	0.82	0.0473	28.5	0.17	0.17				
0.0420	66	0.81	0.81	0.0420	28.5	0.15	0.15				
0.0367	66	0.81	0.81	0.0367	28.5	0.13	0.13				
0.0314	66	0.81	0.81	0.0314	28.5	0.11	0.11				
0.0261	66	0.82	0.82	0.0261	28.5	0.10	0.10				
0.0208	66	0.83	0.83	0.0208	28.5	0.10	0.10				
0.0155	66	0.85	0.85	0.0155	28.5	0.10	0.10				
0.0526	61	0.75	0.75	0.0526	26.0	0.15	0.15				
0.0473	61	0.74	0.74	0.0473	26.0	0.12	0.12				
0.0420	61	0.73	0.73	0.0420	26.0	0.09	0.09				
0.0367	61	0.73	0.73	0.0367	26.0	0.07	0.07				
0.0314	61	0.73	0.73	0.0314	26.0	0.05	0.05				
0.0261	61	0.73	0.73	0.0261	26.0	0.04	0.04				
0.0208	61	0.75	0.75	0.0208	26.0	0.03	0.03				
0.0155	61	0.76	0.76	0.0155	26.0	0.03	0.03				
0.0526	56	0.67	0.67								

Table A7. cont.

> 40 evaporation, > 0.016 g sale					
total salt mass (g)	NIR response	Water content (% mass)	Predicted water content (% mass)		
0.0473	56	0.65	0.65		
0.0420	56	0.64	0.64		
0.0367	56	0.64	0.64		
0.0314	56	0.64	0.64		
0.0261	56	0.64	0.64		
0.0208	56	0.65	0.65		
0.0155	56	0.67	0.67		
0.0526	51	0.58	0.58		
0.0473	51	0.56	0.56		
0.0420	51	0.55	0.55		
0.0367	51	0.55	0.55		
0.0314	51	0.55	0.55		
0.0261	51	0.55	0.55		
0.0208	51	0.56	0.56		
0.0155	51	0.57	0.57		
0.0526	46	0.49	0.49		
0.0473	46	0.47	0.47		
0.0420	46	0.46	0.46		
0.0367	46	0.45	0.45		
0.0314	46	0.45	0.45		
0.0261	46	0.45	0.45		
0.0208	46	0.46	0.46		
0.0155	46	0.47	0.47		

Table A8 Data used to generate reflectance NIR spectrometer calibration surfaces
(zunzun.com input) – Part 2.

< 45 evaporation, > 0.016 g salt											
total salt mass (g)	NIR response	Water content (% mass)	Predicted water content (% mass)	total salt mass (g)	NIR response	Water content (% mass)	Predicted water content (% mass)	total salt mass (g)	NIR response	Water content (% mass)	Predicted water content (% mass)
0.0000	25.3	0.01	0.00	0.0069	29.0	0.09	0.09	0.0105	37.6	0.32	0.30
0.0000	25.3	0.01	0.00	0.0069	29.6	0.10	0.10	0.0105	38.7	0.34	0.32
0.0000	25.8	0.02	0.01	0.0069	30.1	0.11	0.12	0.0105	39.6	0.36	0.34
0.0000	25.9	0.02	0.01	0.0069	31.3	0.13	0.14	0.0105	40.7	0.39	0.37
0.0000	25.9	0.02	0.01	0.0069	32.9	0.16	0.18	0.0105	42.1	0.42	0.40
0.0000	26.0	0.02	0.02	0.0069	33.7	0.18	0.19	0.0105	43.5	0.45	0.43
0.0000	26.0	0.02	0.02	0.0069	35.0	0.21	0.22	0.0105	44.8	0.47	0.46
0.0000	26.2	0.03	0.02	0.0069	36.1	0.23	0.25	0.0105	45.9	0.50	0.49
0.0000	26.3	0.02	0.02	0.0069	36.5	0.25	0.26	0.0105	47.2	0.52	0.52
0.0000	26.3	0.02	0.02	0.0069	37.4	0.27	0.28	0.0105	48.6	0.55	0.55
0.0000	26.3	0.02	0.02	0.0069	38.0	0.29	0.29	0.0105	26.8	0.06	0.05
0.0000	26.3	0.02	0.02	0.0069	39.2	0.32	0.32	0.0105	27.2	0.07	0.06
0.0000	26.3	0.02	0.02	0.0069	40.7	0.36	0.36	0.0105	28.0	0.08	0.08
0.0000	26.3	0.02	0.02	0.0069	42.3	0.39	0.40	0.0105	28.7	0.10	0.10
0.0000	26.4	0.03	0.02	0.0069	43.1	0.42	0.42	0.0105	30.0	0.12	0.13
0.0000	26.4	0.02	0.02	0.0069	45.6	0.47	0.48	0.0105	31.2	0.14	0.15
0.0000	26.4	0.02	0.02	0.0069	46.3	0.49	0.50	0.0105	32.5	0.17	0.18
0.0000	26.5	0.02	0.02	0.0069	47.3	0.52	0.52	0.0105	33.2	0.19	0.20
0.0000	26.6	0.03	0.03	0.0069	48.4	0.54	0.55	0.0105	33.6	0.20	0.21
0.0000	26.7	0.03	0.03	0.0069	25.5	0.04	0.02	0.0105	34.2	0.22	0.22
0.0000	26.9	0.03	0.03	0.0069	25.8	0.04	0.03	0.0105	35.2	0.24	0.24
0.0000	26.9	0.03	0.03	0.0069	26.0	0.04	0.03	0.0105	35.9	0.26	0.26
0.0000	27.1	0.04	0.03	0.0069	26.4	0.05	0.04	0.0105	36.7	0.28	0.28
0.0000	27.1	0.03	0.03	0.0069	26.9	0.06	0.05	0.0105	37.4	0.30	0.29
0.0000	27.1	0.04	0.03	0.0069	27.7	0.07	0.06	0.0105	38.4	0.32	0.32
0.0000	27.5	0.04	0.04	0.0069	28.2	0.07	0.08	0.0105	39.3	0.35	0.34
0.0000	27.7	0.05	0.05	0.0069	29.2	0.09	0.10	0.0105	40.7	0.37	0.37
0.0000	27.7	0.04	0.05	0.0069	30.6	0.12	0.13	0.0105	41.8	0.40	0.39
0.0000	27.9	0.05	0.05	0.0069	31.4	0.13	0.14	0.0105	42.7	0.41	0.41
0.0000	28.3	0.05	0.06	0.0069	32.5	0.16	0.17	0.0105	43.8	0.44	0.44
0.0000	28.5	0.06	0.06	0.0069	33.2	0.17	0.18	0.0105	45.2	0.47	0.47
0.0000	28.7	0.06	0.06	0.0069	34.6	0.20	0.21	0.0105	46.4	0.49	0.50
0.0000	29.4	0.08	0.08	0.0069	35.3	0.22	0.23	0.0105	47.4	0.52	0.52
0.0000	29.9	0.08	0.09	0.0069	36.4	0.26	0.26	0.0105	48.7	0.54	0.55
0.0000	30.1	0.09	0.09	0.0069	36.9	0.27	0.27	0.0106	28.8	0.08	0.10
0.0000	30.1	0.08	0.09	0.0069	37.9	0.30	0.29	0.0106	28.9	0.09	0.10

Table A8. cont.

< 45 evaporation, > 0.016 g salt											
total salt mass (g)	NIR response	Water content (% mass)	Predicted water content (% mass)	total salt mass (g)	NIR response	Water content (% mass)	Predicted water content (% mass)	total salt mass (g)	NIR response	Water content (% mass)	Predicted water content (% mass)
0.0000	30.9	0.09	0.11	0.0069	39.0	0.32	0.32	0.0106	29.0	0.10	0.10
0.0000	31.3	0.11	0.12	0.0069	39.4	0.34	0.33	0.0106	29.6	0.12	0.12
0.0000	31.3	0.10	0.12	0.0069	41.3	0.38	0.37	0.0106	29.6	0.12	0.12
0.0000	31.9	0.11	0.13	0.0069	42.3	0.41	0.40	0.0106	30.1	0.13	0.13
0.0000	32.1	0.12	0.13	0.0069	43.3	0.42	0.42	0.0106	30.5	0.13	0.14
0.0000	32.6	0.13	0.14	0.0069	43.9	0.44	0.44	0.0106	31.2	0.15	0.15
0.0000	32.8	0.13	0.15	0.0069	44.7	0.46	0.46	0.0106	31.3	0.14	0.16
0.0000	32.9	0.13	0.15	0.0069	45.2	0.47	0.47	0.0106	31.8	0.18	0.17
0.0000	33.0	0.14	0.15	0.0069	47.0	0.50	0.52	0.0106	32.8	0.18	0.19
0.0000	33.9	0.17	0.17	0.0069	48.9	0.54	0.56	0.0106	33.4	0.20	0.20
0.0000	34.0	0.15	0.17	0.0069	49.8	0.56	0.59	0.0106	33.5	0.21	0.20
0.0000	34.0	0.16	0.17	0.0069	25.2	0.02	0.01	0.0106	34.6	0.24	0.23
0.0000	34.7	0.17	0.19	0.0069	25.3	0.03	0.02	0.0106	35.3	0.23	0.25
0.0000	34.8	0.18	0.19	0.0069	25.3	0.02	0.02	0.0106	36.3	0.28	0.27
0.0000	34.8	0.18	0.19	0.0069	25.4	0.03	0.02	0.0106	37.4	0.31	0.29
0.0000	35.5	0.20	0.21	0.0069	25.5	0.03	0.02	0.0106	37.5	0.29	0.29
0.0000	35.8	0.20	0.22	0.0069	25.7	0.03	0.02	0.0106	38.6	0.32	0.32
0.0000	35.9	0.22	0.22	0.0069	25.9	0.03	0.03	0.0106	38.8	0.35	0.32
0.0000	36.2	0.22	0.22	0.0069	26.1	0.04	0.03	0.0106	39.3	0.34	0.34
0.0000	36.3	0.22	0.23	0.0069	26.6	0.04	0.04	0.0106	39.5	0.36	0.34
0.0000	36.3	0.22	0.23	0.0069	26.9	0.05	0.05	0.0106	39.9	0.35	0.35
0.0000	36.5	0.24	0.23	0.0069	27.1	0.05	0.05	0.0106	41.2	0.38	0.38
0.0000	37.0	0.25	0.24	0.0069	27.5	0.06	0.06	0.0106	42.0	0.42	0.40
0.0000	37.1	0.24	0.25	0.0069	28.2	0.07	0.08	0.0106	42.2	0.40	0.40
0.0000	37.2	0.25	0.25	0.0069	28.6	0.08	0.08	0.0106	43.0	0.42	0.42
0.0000	37.3	0.26	0.25	0.0069	29.4	0.09	0.10	0.0106	43.6	0.44	0.43
0.0000	37.7	0.27	0.26	0.0069	30.0	0.10	0.11	0.0106	44.0	0.46	0.44
0.0000	38.0	0.27	0.27	0.0069	30.8	0.11	0.13	0.0106	44.8	0.46	0.46
0.0000	38.4	0.29	0.28	0.0069	31.7	0.13	0.15	0.0106	45.2	0.49	0.47
0.0000	38.6	0.28	0.28	0.0069	32.4	0.14	0.17	0.0106	46.3	0.49	0.50
0.0000	38.6	0.29	0.28	0.0069	34.0	0.17	0.20	0.0106	47.2	0.54	0.52
0.0000	38.8	0.31	0.29	0.0069	35.9	0.22	0.24	0.0106	47.6	0.52	0.53
0.0000	39.3	0.31	0.30	0.0069	38.2	0.29	0.30	0.0106	48.1	0.56	0.54
0.0000	39.4	0.30	0.30	0.0069	41.3	0.36	0.37	0.0106	49.4	0.59	0.57
0.0000	39.7	0.33	0.31	0.0069	43.8	0.41	0.43	0.0106	49.4	0.56	0.57
0.0000	40.1	0.32	0.32	0.0069	45.9	0.46	0.49	0.0155	26.8	0.07	0.07
0.0000	40.1	0.34	0.32	0.0069	47.1	0.48	0.52	0.0155	27.0	0.07	0.07
0.0000	40.4	0.34	0.33	0.0069	25.3	0.02	0.02	0.0155	27.2	0.08	0.08

Table A8. cont.

< 45 evaporation, > 0.016 g salt											
total salt mass (g)	NIR response	Water content (% mass)	Predicted water content (% mass)	total salt mass (g)	NIR response	Water content (% mass)	Predicted water content (% mass)	total salt mass (g)	NIR response	Water content (% mass)	Predicted water content (% mass)
0.0000	40.6	0.35	0.34	0.0069	25.3	0.02	0.02	0.0155	27.5	0.08	0.08
0.0000	41.0	0.36	0.35	0.0069	25.4	0.03	0.02	0.0155	28.0	0.09	0.10
0.0000	41.0	0.36	0.35	0.0069	25.5	0.03	0.02	0.0155	28.8	0.11	0.11
0.0000	41.2	0.37	0.35	0.0069	25.7	0.03	0.02	0.0155	29.8	0.12	0.14
0.0000	41.4	0.38	0.36	0.0069	25.8	0.03	0.03	0.0155	30.6	0.14	0.16
0.0000	41.8	0.37	0.37	0.0069	26.1	0.04	0.03	0.0155	31.6	0.16	0.18
0.0000	41.8	0.39	0.37	0.0069	26.6	0.05	0.04	0.0155	32.0	0.17	0.19
0.0000	41.9	0.39	0.37	0.0069	27.4	0.06	0.06	0.0155	33.3	0.21	0.22
0.0000	42.3	0.41	0.38	0.0069	28.4	0.08	0.08	0.0155	34.4	0.23	0.24
0.0000	42.5	0.38	0.39	0.0069	28.9	0.08	0.09	0.0155	35.9	0.27	0.28
0.0000	42.7	0.42	0.39	0.0069	29.6	0.10	0.10	0.0155	36.7	0.29	0.30
0.0000	43.0	0.42	0.40	0.0069	30.4	0.11	0.12	0.0155	37.5	0.31	0.31
0.0000	43.6	0.41	0.42	0.0069	31.1	0.12	0.14	0.0155	38.7	0.34	0.34
0.0000	43.6	0.44	0.42	0.0069	32.0	0.14	0.16	0.0155	39.6	0.36	0.36
0.0000	43.8	0.44	0.43	0.0069	32.3	0.16	0.16	0.0155	40.3	0.37	0.37
0.0000	44.4	0.43	0.44	0.0069	33.1	0.18	0.18	0.0155	41.5	0.39	0.40
0.0000	44.5	0.46	0.45	0.0069	33.7	0.19	0.19	0.0155	42.5	0.42	0.42
0.0000	44.6	0.47	0.45	0.0069	34.7	0.21	0.22	0.0155	43.6	0.43	0.44
0.0000	44.9	0.48	0.46	0.0069	35.9	0.24	0.24	0.0155	44.5	0.46	0.46
0.0000	45.4	0.46	0.47	0.0069	36.7	0.26	0.26	0.0155	46.2	0.49	0.49
0.0000	45.6	0.49	0.48	0.0069	37.3	0.29	0.28	0.0155	47.0	0.51	0.51
0.0000	45.6	0.49	0.48	0.0069	40.2	0.35	0.35	0.0155	48.3	0.53	0.53
0.0000	46.3	0.51	0.50	0.0069	42.3	0.41	0.40	0.0157	32.4	0.19	0.20
0.0000	46.3	0.51	0.50	0.0069	43.1	0.43	0.42	0.0157	32.9	0.21	0.21
0.0000	46.7	0.52	0.51	0.0069	45.8	0.49	0.48	0.0157	33.8	0.23	0.23
0.0000	46.8	0.48	0.52	0.0069	47.3	0.51	0.52	0.0157	35.2	0.27	0.26
0.0000	46.9	0.53	0.52	0.0069	49.6	0.56	0.58	0.0157	36.5	0.30	0.29
0.0000	47.6	0.54	0.54	0.0105	26.5	0.06	0.05	0.0157	38.3	0.34	0.33
0.0000	47.9	0.52	0.55	0.0105	26.6	0.06	0.05	0.0157	40.3	0.38	0.37
0.0000	47.9	0.54	0.55	0.0105	26.9	0.06	0.06	0.0157	43.9	0.44	0.45
0.0000	48.2	0.56	0.56	0.0105	27.4	0.08	0.07	0.0157	48.7	0.53	0.54
0.0000	48.2	0.56	0.56	0.0105	27.9	0.09	0.08	0.0158	32.1	0.19	0.19
0.0000	48.7	0.58	0.57	0.0105	28.7	0.11	0.10	0.0158	32.2	0.20	0.20
0.0000	48.7	0.53	0.57	0.0105	29.6	0.12	0.12	0.0158	32.4	0.21	0.20
0.0000	48.8	0.58	0.58	0.0105	30.9	0.15	0.15	0.0158	32.9	0.21	0.21
0.0000	49.2	0.55	0.59	0.0105	31.6	0.17	0.16	0.0158	33.3	0.23	0.22
0.0000	49.6	0.60	0.60	0.0105	32.2	0.18	0.17	0.0158	35.0	0.26	0.26
0.0000	49.7	0.60	0.61	0.0105	32.8	0.20	0.19	0.0158	36.8	0.31	0.30

Table A8. cont.											
< 45 evaporation, > 0.016 g salt											
total salt mass (g)	NIR response	Water content (% mass)	Predicted water content (% mass)	total salt mass (g)	NIR response	Water content (% mass)	Predicted water content (% mass)	total salt mass (g)	NIR response	Water content (% mass)	Predicted water content (% mass)
0.0000	49.8	0.62	0.61	0.0105	33.7	0.21	0.21	0.0158	37.6	0.32	0.32
0.0069	27.8	0.06	0.07	0.0105	34.4	0.23	0.22	0.0158	38.5	0.35	0.34
0.0069	27.8	0.06	0.07	0.0105	35.2	0.26	0.24	0.0158	41.5	0.40	0.40
0.0069	28.2	0.07	0.07	0.0105	36.1	0.28	0.26	0.0158	45.6	0.47	0.48
0.0069	28.7	0.08	0.09	0.0105	36.9	0.30	0.28	0.0158	47.5	0.51	0.52

Table A9. Reflectance NIR check standards measured during calibration and data collection.

SPW dilution factor and trial run	Blank		Low response standard		High response standard	
	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation
H ₂ O – 1	25.3	0.1	26.5	0.2	41.0	0.1
H ₂ O – 2	25.4	0.0	26.6	0.1	41.0	0.1
H ₂ O – 3	25.4	0.0	26.7	0.0	41.1	0.0
6.5-SPW – 1	25.4	0.0	26.6	0.1	40.9	0.1
6.5-SPW – 2	25.4	0.0	26.6	0.1	40.9	0.1
6.5-SPW – 3	25.4	0.0	26.5	0.1	40.9	0.0
6.5-SPW – 4	25.3	0.0	26.5	0.1	40.8	0.1
6.5-SPW – 5	25.3	0.0	26.5	0.1	40.8	0.1
6.5-SPW – 6	25.3	0.0	26.5	0.0	40.9	0.0
4.3-SPW – 1	25.4	0.0	26.6	0.0	41.1	0.1
4.3-SPW – 2	25.4	0.0	26.6	0.0	41.1	0.1
4.3-SPW – 3	25.3	0.0	26.5	0.0	41.0	0.1
4.3-SPW – 4	25.3	0.1	26.5	0.1	40.8	0.2
4.3-SPW – 5	25.3	0.1	26.5	0.1	40.8	0.2
3.0-SPW – 1	25.4	0.0	26.6	0.1	41.0	0.2
3.0-SPW – 2	25.4	0.0	26.6	0.1	41.0	0.2
3.0-SPW – 3	25.3	0.0	26.4	0.1	40.8	0.0
2.2-SPW – 1	25.4	0.0	26.6	0.0	41.1	0.1
2.2-SPW – 2	25.4	0.0	26.6	0.0	41.0	0.1
2.2-SPW – 3	25.4	0.0	26.6	0.0	41.1	0.1
1.8-SPW – 1	25.4	0.0	26.6	0.0	41.1	0.0
1.8-SPW – 2	25.4	0.0	26.6	0.0	41.1	0.1
1.8-SPW – 3	25.4	0.0	26.6	0.0	41.1	0.1
1.5-SPW – 1	25.4	0.0	26.7	0.0	41.2	0.1

Table A9. cont.						
SPW dilution factor and trial run	Blank		Low response standard		High response standard	
	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation
1.5-SPW – 2	25.4	0.0	26.7	0.0	41.1	0.1
1.5-SPW – 3	25.4	0.0	26.7	0.0	41.1	0.1
1.4-SPW – 1	25.4	0.0	26.6	0.0	41.0	0.0
1.4-SPW – 2	25.4	0.0	26.5	0.1	41.1	0.1
1.4-SPW – 3	25.4	0.0	26.7	0.0	41.2	0.1
1.2-SPW – 1	25.3	0.0	26.5	0.0	41.0	0.1
1.2-SPW – 2	25.3	0.0	26.5	0.1	41.1	0.1
1.2-SPW – 3	25.4	0.0	26.6	0.0	41.0	0.0
1.1-SPW – 1	25.4	0.0	26.6	0.0	41.1	0.1
1.1-SPW – 2	25.4	0.0	26.6	0.1	41.1	0.0
1.1-SPW – 3	25.4	0.0	26.6	0.0	41.1	0.0
SPW – 1	25.4	0.0	26.6	0.1	41.1	0.1
SPW – 2	25.4	0.0	26.6	0.0	40.9	0.0
SPW – 3	25.4	0.0	26.6	0.1	41.0	0.1

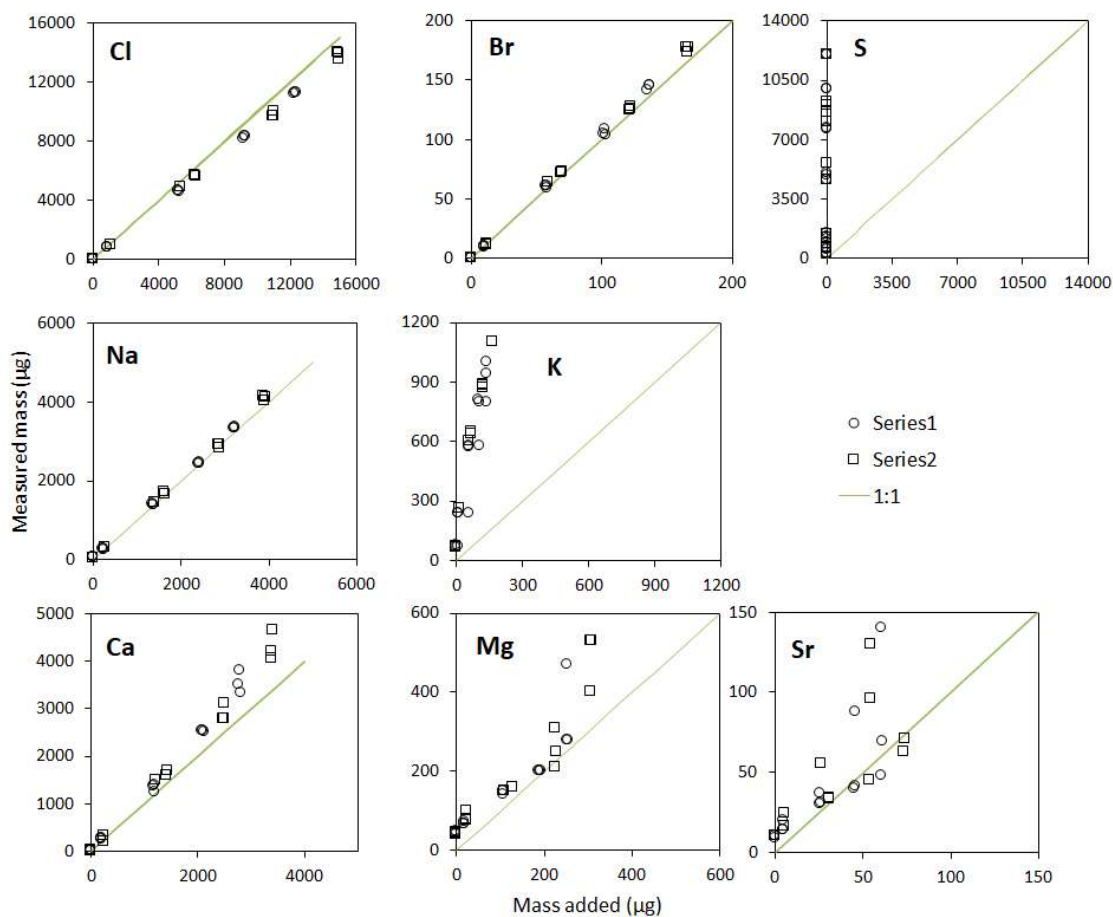


Figure D1. Results of neutron activation analysis comparing solutes added to Rigaku Microcarries (□) and Whatman® 1 CHR (o) to measured values. Neutron activation analysis did not yield satisfactory results and will not be used in future analysis.

Appendix B: Supplementary information for Chapter 3

Table B3. Solute and water masses extracted by the paper absorption method from Michigan Basin samples quantified by NIR (water) and ICP-MS (solutes).

Sample Name	mg water extracted (NIR)	Na ⁺	Mg ²⁺	Cl ⁻	K ⁺	Ca ²⁺	Br ⁻	Sr ²⁺
Mass of solute extracted (ug)								
334.1	52	2030	192	3533	45	732	17	170
334.2	50	2293	263	4129	435	1672	34	62
383.1	44	10044	787	22755	369	3307	177	56
383.2	48	10747	846	24652	396	3543	200	58
421.1	5	840	57	2313	68	694	56	12
421.2	5	6082	683	21394	475	6703	512	158
421.3	3	635	53	2068	50	543	45	11
431.1	11	1359	284	7368	127	2909	154	70
431.2	13	1314	268	6612	137	2686	149	65
431.3	8	1206	211	5449	131	2095	127	48
431.4	12	1419	276	6743	171	3230	138	64
431.5	12	1112	180	4676	99	1851	108	43
431.6	5	579	116	3089	54	1128	61	28
463.1	2	352	7	641	23	113	15	1
463.2	3	568	13	1109	36	194	26	3
496.1	7	1316	169	5355	103	2180	129	44
496.2	7	1294	112	4434	103	1494	112	29
520.1	6	1312	94	4224	84	1401	107	24
52.1	3	774	31	2027	49	469	45	8
530	3	1256	103	4057	87	1324	93	26
572.1	11	1436	141	5739	121	1878	117	53
572.2	6	1352	80	4119	92	1181	87	29
572.3	6	1073	96	3667	93	1259	76	32
626.1	7	1460	116	5077	147	1754	125	47
626.2	10	1779	134	5718	91	1925	131	52
634.1a	4	574	25	1474	37	460	35	8
634.1b	4	539	28	1420	37	447	33	8
634.1c	4	683	29	1761	38	580	40	11
634.2	4	1240	102	4242	83	1570	95	40
634.3	3	1389	49	3290	78	892	81	21
658.1a	2	479	15	971	31	256	21	4
658.1b	2	454	11	913	28	277	19	4
658.1	2	486	14	959	34	316	19	4
658.2	3	608	20	1296	49	335	28	6
658.3	2	349	10	707	28	201	14	2
662.1	1	194	6	313	10	171	6	1
662.3	1	917	39	2063	50	417	35	9
683.1	8	905	134	3273	67	965	58	30
707.2	4	752	57	2194	38	567	42	12
707.3	2	337	10	578	19	230	12	2
723.2	2	333	3	471	18	117	9	0
723.3	2	269	3	373	10	80	7	0

Table B1 cont.								
Sample Name	mg water extracted (NIR)	Na ⁺	Mg ²⁺	Cl ⁻	K ⁺	Ca ²⁺	Br ⁻	Sr ²⁺
Mass of solute extracted (ug)								
723.4	2	385	3	538	14	62	10	1

Table B4. Limit of detection and results of accuracy and precision of a calibration check standard for ICP-MS measurements.

		Na ⁺	Mg ²⁺	Cl ⁻	K ⁺	Ca ²⁺	Br ⁻	Sr ²⁺
Michigan Basin porewater samples extracted by paper absorption.								
	LOD (ppm)	0.008	0.000	0.043	0.007	0.002	0.003	0.000
calibration check	precision	1%	3%	2%	1%	2%	3%	1%
standard	accuracy	3%	3%	1%	0%	4%	0%	2%
Michigan Basin porewater samples extracted by crush and leach								
	LOD (ppm)	0.00	0.00	0.22	0.00	0.00	0.00	0.000
2000x seawater	precision	1%	1%	2%	2%	2%	6%	1%
standard	accuracy	2%	1%	2%	-2%	11%	2%	1%
750x seawater	precision	1%	2%	2%	2%	1%	2%	2%
standard	accuracy	3%	0%	4%	-7%	3%	3%	0%
Lorraine Group shale porewater samples extracted by paper absorption and crush and leach								
	LOD (ppm)			0.02			0.03	
calibration	precision			22%			2%	
check standard	accuracy			1%			1%	
Opalinus Clay porewater samples extracted by paper absorption								
	LOD (ppm)	0.006	0.001	0.583	0.006	0.002	0.000	0.000
2000x seawater	precision	2%	5%	7%	5%	9%	12%	4%
standard	accuracy	6%	2%	5%	3%	9%	1%	3%
750x seawater	precision	3%	4%	5%	3%	6%	7%	5%
standard	accuracy	0%	2%	5%	3%	1%	1%	3%
Opalinus Clay porewater samples extracted by crush and leach.								
	LOD (ppm)	0.13	0.009	0.12	0.00	0.03	BDL	0.0008
2000x seawater	precision	2%	3%	2%	5%	2%	9%	5%
standard	accuracy	2%	6%	2%	4%	1%	5%	2%
750x seawater	precision	2%	3%	3%	6%	3%	0%	4%
standard	accuracy	8%	6%	9%	4%	7%	5%	2%

Table B3. Solute and water masses extracted by the paper absorption method from Lorraine Group shales samples quantified by NIR (water) and ICP-MS (solutes).

Sample Name	mg water extracted (NIR)	Na ⁺	Mg ²⁺	Cl ⁻	K ⁺	Ca ²⁺	Br ⁻	Sr ²⁺
Mass of solute extracted (ug)								
F7-3	12.84	1461	0.38	109	BDL	2.1	1.6	0.18
F7-4	9.05	1195	0.34	91	BDL	1.8	1.3	0.09
F8-3	20.17	479	0.08	24	BDL	1.2	0.2	0.00
F8-3	16.24	495	0.07	16	BDL	0.8	0.2	0.00
F20-3	7.29	1747	0.38	148	BDL	2.2	2.5	0.00
F20-4	27.36	3192	0.55	287	BDL	3.6	5.1	0.02
444-1	8.27	958	0.40	55	BDL	2.8	1.3	0.01

Table B4 Solute masses extracted by the crush and leach method from Michigan Basin samples quantified by NIR (water) and ICP-MS (solutes).

Sample	rock	water	Na ⁺	Mg ²⁺	Cl ⁻	K ⁺	Ca ²⁺	Br ⁻	Sr ²⁺
Name	mass (g)	mass (g)	Mass of solute extracted (ug)						
334a	10.32	39.87	732	162	4067	108	942	50	697
334b	10.47	39.68	759	159	3852	86	912	32	829
334c	10.57	39.95	728	158	3252	99	813	28	795
383a	10.48	39.67	32615	4410	82397	1801	16838	715	283
383c	10.17	39.73	27642	4051	73304	1624	12718	650	261
421a	10.06	39.68	17347	3295	81025	4483	23092	976	685
421b	10.33	39.70	17746	3461	86635	4730	24539	1036	715
421c	10.54	39.72	19383	3682	93755	5013	26400	1117	771
431a	10.79	39.61	15841	2943	73221	5209	20410	905	606
431b	10.40	39.65	15825	2853	71462	5082	19111	869	580
431c	10.28	39.68	15941	2804	71901	4977	19022	863	569
463a	9.71	39.75	12408	1923	53928	3218	16294	630	382
463b	10.83	39.65	14519	2295	63586	3700	19116	744	438
496a	10.09	39.65	10918	1567	45262	3252	11911	562	305
496b	10.63	39.66	11626	1675	49897	3489	12567	584	335
522a	10.58	39.57	12320	1731	49783	3616	13277	615	345
530a	10.75	39.85	4667	903	20635	1616	6991	261	172
572a	9.99	39.63	27036	1415	70851	3624	12208	884	413
572b	10.57	39.73	33223	1444	80998	3783	12587	874	420
572c	9.82	39.62	32063	1500	79415	3871	13113	875	422
625a	9.86	39.64	14683	1434	53887	3354	12615	620	434
625b	10.37	39.81	15356	1510	54301	3516	13466	659	450
634a	9.78	39.57	15132	1442	53411	3300	12625	615	436
634b	10.28	39.63	15535	1462	55596	3315	12981	635	453
634c	10.41	39.65	14979	1399	54416	3185	12703	612	439
634d	10.71	39.71	16227	1546	59462	3440	13539	678	481
634e	10.23	39.57	15797	1461	55150	3332	13055	637	456

Table B4 cont.									
Sample	rock	water	Na ⁺	Mg ²⁺	Cl ⁻	K ⁺	Ca ²⁺	Br ⁻	Sr ²⁺
Name	mass (g)	mass (g)	Mass of solute extracted (ug)						
658a	9.96	39.48	10347	1040	32620	2938	7652	359	225
658b	10.24	39.73	10732	1079	34308	3090	8093	377	235
658c	10.53	39.66	11379	1285	37920	3276	9028	403	264
662a	10.59	39.59	657	124	4138	413	883	56	29
662b	10.52	39.66	624	129	3705	382	943	54	32
662c	10.76	39.54	671	126	4386	394	886	52	31
670a	10.60	39.60	992	202	6090	471	1486	75	46
670b	10.38	39.58	1162	247	6805	597	1762	87	56
670c	9.80	39.70	1346	255	8109	592	1711	92	56
683a	9.91	39.74	1146	194	5022	666	1137	63	39
683b	10.01	39.79	1223	204	5895	651	1122	61	40
683c	10.70	39.43	1428	231	7075	786	1256	86	43
689a	10.62	39.63	2871	381	12835	1053	2596	139	89
689b	10.64	39.52	2610	368	12639	1018	2567	137	88
689c	10.47	39.55	2414	345	11385	990	2354	128	80
695a	10.60	39.81	906	238	5562	533	1720	66	39
695b	10.17	39.65	922	237	5052	502	1596	62	37
695c	9.84	39.62	950	247	5847	527	1600	65	39
707a	10.10	39.60	2538	296	10099	1179	2021	105	53
707b	10.91	39.51	5242	380	15647	1496	2704	148	71
707c	10.15	39.58	7362	518	20318	1940	3338	188	88
723a	10.58	39.64	2548	348	11035	1060	2686	113	65
723c	10.08	39.61	1872	272	8034	824	2159	89	51

Table B5. Solute masses extracted by the crush and leach method from Lorraine Group shale samples quantified by NIR (water) and ICP-MS (solute).

Sample	Na ⁺	Mg ²⁺	Cl ⁻	K ⁺	Ca ²⁺	Br ⁻	Sr ²⁺
Name	Mass of solute extracted (ug)						
F7-1	3080	0.90	290	43	1.92	2.71	0.06
F7-2	3104	1.31	295	42	1.30	2.75	0.02
F8-1	3108	1.01	80	14	1.31	0.38	BDL
F8-2	3054	5.97	78	25	2.47	0.39	0.11
F20-1	2435	1.62	1162	54	2.47	9.88	0.20
F20-2	2417	1.65	1210	48	2.42	10.38	0.19
444-1	3777	0.59	121	53	2.77	1.66	0.22

Table B6. Solute masses extracted by the paper absorption method from Opalinus Clay samples quantified by NIR (water) and ICP-MS (solutes).

Sample Name	mg water extracted (NIR)	Na ⁺	Mg ²⁺	Cl ⁻	K ⁺	Ca ²⁺	Br ⁻	Sr ²⁺
Mass of solute extracted (ug)								
75	14.93	93	4.9	158	2.2	59	0.66	0.9
82	23.44	35	6.9	21	3.8	140	0.05	10.6
83a	25.68	31	5.9	15	3.1	159	0.01	10.8
83b	25.68	31	6.0	13	3.2	160	0.03	10.7
83c	25.68	31	6.2	12	3.2	158	0.03	10.9
100.1a	18.65	47	4.1	36	2.9	108	0.13	1.9
100.1b	18.65	47	4.2	35	2.9	110	0.11	1.9
100.1b	18.65	47	4.2	35	2.9	110	0.11	1.9
100.1c	18.65	48	4.1	36	2.9	109	0.10	1.9
100.2	18.51	54	5.1	35	3.2	94	0.15	12.7
115.1a	18.60	67	4.4	73	2.6	106	0.28	1.3
115.1b	18.60	67	4.5	82	2.7	104	0.28	1.3
115.1c	18.60	67	4.4	78	2.6	103	0.29	1.3
128.1	14.32	74	3.7	85	2.7	25	0.33	1.0
128.2	15.16	71	3.2	83	3.6	28	0.34	0.8
144.1a	7.65	61	1.5	74	1.9	16	0.30	0.3
144.1b	7.65	60	1.5	73	1.9	16	0.29	0.3
144.1c	7.65	61	1.5	72	1.9	15	0.31	0.3
144.2a	9.19	61	1.2	70	2.4	17	0.35	0.2
144.2b	9.19	61	1.2	69	2.2	17	0.34	0.2
144.2c	9.19	62	1.2	70	2.1	17	0.36	0.2
178.1	11.23	108	5.3	185	2.4	47	0.74	1.0
178.2a	14.18	108	5.7	177	2.9	87	0.75	1.1
204.1	12.64	109	4.2	179	2.2	37	0.77	0.8
204.2a	13.72	110	4.3	171	2.5	70	0.72	0.8
204.2b	13.72	110	4.3	170	2.6	70	0.72	0.8
204.2c	13.72	111	4.3	169	2.5	70	0.67	0.8
204.3	10.48	101	4.1	165	2.2	35	0.71	0.7
204.4a	12.24	106	4.1	163	2.6	34	0.81	0.7

Table B7. Solute masses extracted by the crush and leach method from Opalinus Clay samples quantified by NIR (water) and ICP-MS (solutes).

Sample	rock	water	Na ⁺	Mg ²⁺	Cl ⁻	K ⁺	Ca ²⁺	Br ⁻	Sr ²⁺
Name	mass (g)	mass (g)	Mass of solute extracted (ug)						
67.1	0.4285	43.0215	0.270	1.227	0.173	0.419	6.178	0.002	0.368
67.2	0.4375	42.3458	0.278	1.236	0.120	0.423	6.092	0.001	0.111
67.3	0.4277	43.1550	0.274	1.247	0.140	0.440	6.178	0.001	0.103
67.4	0.4553	40.1926	0.286	1.322	0.140	0.436	6.294	0.001	0.103
89.1	0.4501	43.8906	1.975	1.817	0.196	1.001	6.164	0.001	0.130
89.2	0.4423	42.6987	1.826	1.723	0.179	0.935	6.041	0.001	0.123
89.3	0.4553	41.6428	1.999	1.885	0.197	0.987	6.215	0.001	0.131
89.4	0.4428	41.1369	2.034	1.914	0.201	1.001	6.436	0.001	0.135
93.1	0.6274	41.4593	3.328	1.013	0.252	1.067	2.550	0.001	0.101
93.2	0.6296	42.5180	3.443	1.046	0.263	1.135	2.514	0.001	0.093
93.3	0.6465	40.9494	3.473	1.027	0.269	1.080	2.461	0.001	0.097
93.4	0.6287	41.5754	3.379	1.003	0.269	1.082	2.461	0.001	0.091
101.2	0.3481	41.6953	2.377	0.755	0.498	0.731	3.080	0.002	0.045
101.3	0.3524	42.2850	2.316	0.740	0.517	0.717	2.899	0.002	0.045
101.4	0.3412	41.6067	2.406	0.785	0.505	0.735	3.110	0.002	0.047
115.1	0.5329	42.7772	3.628	0.131	0.542	0.582	0.431	0.002	0.009
115.2	0.5247	42.3389	3.697	0.127	0.550	0.581	0.414	0.002	0.008
115.3	0.5238	42.1568	3.261	0.127	0.493	0.536	0.422	0.002	0.009
115.4	0.5375	42.9259	3.948	0.147	0.625	0.617	0.452	0.002	0.009
119.1	0.5327	41.4960	6.691	0.183	1.061	0.800	0.460	0.004	0.011
119.2	0.5176	41.0915	6.306	0.174	0.984	0.760	0.429	0.003	0.010
119.3	0.5241	43.2603	6.008	0.154	0.948	0.730	0.377	0.003	0.009
119.4	0.5177	42.7372	6.420	0.179	0.996	0.794	0.463	0.003	0.011
121.1	0.6268	41.7408	6.389	0.115	1.163	0.652	0.269	0.004	0.006
121.2	0.6290	42.5876	6.217	0.101	1.185	0.617	0.236	0.004	0.006
121.3	0.6271	41.5592	6.761	0.106	1.239	0.668	0.257	0.004	0.006
121.4	0.6333	41.1308	6.036	0.098	1.131	0.601	0.238	0.004	0.006
128.1	0.6138	42.1956	6.661	0.202	1.429	0.795	0.513	0.005	0.011
128.2	0.6164	42.1458	6.618	0.209	1.408	0.806	0.526	0.005	0.011
128.3	0.6134	42.4482	6.454	0.206	1.353	0.785	0.530	0.004	0.011
128.4	0.6139	42.3767		0.219	1.513	0.857	0.563	0.005	0.012
132.2	0.6382	41.2940	6.440	0.089	1.454	0.584	0.247	0.005	0.005
132.2	0.6020	40.9735	6.639	0.083	1.554	0.627	0.229	0.005	0.005
132.3	0.6081	42.2931	6.809	0.085	1.576	0.635	0.234	0.005	0.005
132.4a	0.6001	42.6663	6.154	0.075	1.467	0.589	0.219	0.004	0.004
132.4b	0.6001	42.6663	6.169	0.075	1.470	0.589	0.218	0.004	0.004
132.4c	0.6001	42.6663	6.180	0.075	1.418	0.592	0.211	0.005	0.004
172.1	0.5703	41.4575	6.496	0.052	2.469	0.420	0.151	0.008	0.002
172.2	0.5663	41.4315	6.748	0.052	2.581	0.432	0.154	0.008	0.002
172.3	0.5663	42.4106	6.636	0.052	2.517	0.434	0.152	0.008	0.002
172.4	0.5717	42.1052	6.689	0.055	2.519	0.449	0.164	0.008	0.003
174.1	0.5572	41.8182	6.946	0.086	2.702	0.531	0.230	0.008	0.004

Table B7 cont.									
Sample	rock	water	Na ⁺	Mg ²⁺	Cl ⁻	K ⁺	Ca ²⁺	Br ⁻	Sr ²⁺
Name	mass (g)	mass (g)	Mass of solute extracted (ug)						
174.2	0.5525	42.8874	7.199	0.082	2.857	0.543	0.224	0.009	0.004
174.3a	0.5555	42.8874	6.579	0.082	2.555	0.496	0.219	0.008	0.003
174.3b	0.5555	42.8874	6.483	0.081	2.530	0.491	0.216	0.008	0.003
174.3c	0.5555	42.4932	6.497	0.079	2.460	0.485	0.208	0.008	0.003
174.4	0.5551	41.4851	6.606	0.085	2.587	0.499	0.229	0.008	0.004
179.1	0.2895	42.2355	4.082	0.160	1.684	0.465	0.497	0.005	0.007
179.2	0.2887	42.1369	4.258	0.162	1.715	0.476	0.490	0.005	0.007
179.3	0.2880	41.9230	3.935	0.171	1.613	0.463	0.537	0.005	0.008
179.4	0.2896	42.2482	3.949	0.156	1.601	0.452	0.490	0.005	0.007
190.2	0.2321	41.7601	4.097	0.998	1.473	0.712	5.839	0.005	0.029
190.3	0.2337	42.3175	4.062	0.924	1.467	0.685	5.204	0.005	0.027
190.4	0.2316	42.7906	4.183	0.982	1.462	0.705	5.623	0.005	0.030
192.1	0.6427	41.4187	7.385	0.068	3.318	0.461	0.246	0.011	0.003
192.2	0.6097	41.1696		0.074	3.228	0.455	0.282	0.010	0.003
192.3	0.6057	42.5256		0.057	3.065	0.425	0.211	0.010	0.003
192.4	0.6072	42.5728		0.076	3.222	0.471	0.282	0.010	0.003
203.1	0.6695	42.9048		0.036	3.767	0.344	0.130	0.012	0.001
203.2a	0.6715	42.5710		0.035	3.712	0.340	0.122	0.012	0.001
203.2b	0.6715	42.5710		0.033	3.650	0.329	0.117	0.011	0.001
203.2c	0.6715	42.5710		0.033	3.645	0.325	0.113	0.012	0.001
203.3	0.6708	41.9285	6.634	0.035	3.768	0.347	0.128	0.012	0.001
203.4	0.6699	41.7434		0.034	3.698	0.329	0.120	0.012	0.001
209.1	0.6440	41.6246		0.048	4.002	0.410	0.174	0.013	0.002
209.2	0.6474	42.7302		0.044	3.608	0.371	0.153	0.012	0.002
209.3	0.6416	42.3402		0.041	3.351	0.351	0.140	0.011	0.002
209.4	0.6397	41.6624		0.040	3.365	0.355	0.143	0.011	0.002
220.2	0.5614	41.8655		0.026	2.880	0.311	0.081	0.009	0.001
220.3	0.5374	41.3845	6.444	0.025	2.752	0.313	0.081	0.009	0.001
220.4	0.5351	42.2922	6.519	0.025	2.751	0.318	0.075	0.009	0.001
246.1	0.5785	40.9322		0.375	3.187	0.550	1.894	0.010	0.019
246.2	0.5721	41.1020		0.366	3.149	0.536	1.886	0.010	0.018
246.3	0.5745	41.6791		0.370	3.077	0.533	1.938	0.010	0.018
246.4	0.5739	41.2956		0.376	3.140	0.538	1.865	0.010	0.018

Table B8. Example of positive and neutral ion cluster calculations

					DGR Depth 334 m		
					Species Mass Balance		
					Na ⁺	1.84	
					K ⁺	0.12	
					Cl ⁻	2.12	
					Br ⁻	0.007	
					Cl ⁻ /Br ⁻	143.8489	
					Sum of positive and neutral species		
					total	fraction	
					Cl ⁻	0.89	42%
					Br ⁻	0.00	38%
Cluster size	Clustering equations	Log K _{assoc}	K _{assoc}		Negatively charged species	Neutral species	Positively charged species
2	Na ⁺ + Cl ⁻ = NaCl	-0.119	0.76			4.145E-01	
3	NaCl + Cl ⁻ = NaCl ₂ ⁻	-0.585	0.26	9.097E-02			
4	NaCl ₂ ⁻ + Cl ⁻ = NaCl ₃ ⁻²	-0.886	0.13	9.983E-03			
3	NaCl + Na ⁺ = Na ₂ Cl ⁺	-0.538	0.29				7.759E-02
4	Na ₂ Cl ⁺ + Na ⁺ = Na ₃ Cl ⁺²	-0.959	0.11				5.509E-03
4	Na ₂ Cl ⁺ + Cl ⁻ = Na ₂ Cl ₂	0.064	1.16			7.588E-02	
4	NaCl ₂ ⁻ + Na ⁺ = Na ₂ Cl ₂	0.107	1.28			7.519E-02	
4	NaCl + NaCl = Na ₂ Cl ₂	-0.357	0.44			7.554E-02	
5	Na ₂ Cl ₂ + Cl ⁻ = Na ₂ Cl ₃ ⁻	-0.357	0.44	2.802E-02			
5	NaCl ₃ ⁻² + Na ⁺ = Na ₂ Cl ₃ ⁻	0.651	4.48	2.887E-02			
5	NaCl ₂ ⁻ + NaCl = Na ₂ Cl ₃ ⁻	-0.125	0.75	2.828E-02			
6	Na ₂ Cl ₃ ⁻ + Cl ⁻ = Na ₂ Cl ₄ ⁻²	-0.62	0.24	5.726E-03			
5	Na ₃ Cl ⁺² + Cl ⁻ = Na ₃ Cl ₂ ⁺	0.713	5.16				2.401E-02
5	Na ₂ Cl ₂ + Na ⁺ = Na ₃ Cl ₂ ⁺	-0.319	0.48				2.341E-02
5	Na ₂ Cl ⁺ + NaCl = Na ₃ Cl ₂ ⁺	-0.131	0.74				2.379E-02
6	Na ₃ Cl ₂ ⁺ + Cl ⁻ = Na ₃ Cl ₃	0.097	1.25			2.510E-02	
6	Na ₂ Cl ₃ ⁻ + Na ⁺ = Na ₃ Cl ₃	0.137	1.37			2.505E-02	
6	Na ₂ Cl ₂ + NaCl = Na ₃ Cl ₃	-0.097	0.80			2.505E-02	
7	Na ₃ Cl ₃ + Cl ⁻ = Na ₃ Cl ₄ ⁻	-0.208	0.62	1.309E-02			
7	Na ₂ Cl ₄ ⁻² + Na ⁺ = Na ₃ Cl ₄ ⁻	0.54	3.47	1.283E-02			
7	Na ₂ Cl ₃ ⁻ + NaCl = Na ₃ Cl ₄ ⁻	0.045	1.11	1.300E-02			
6	Na ₃ Cl ₂ ⁺ + Na ⁺ = Na ₄ Cl ₂ ⁺²	-0.62	0.24				3.687E-03
6	Na ₃ Cl ⁺² + NaCl = Na ₄ Cl ₂ ⁺²	0.207	1.61				1.588E-02
7	Na ₄ Cl ₂ ⁺² + Cl ⁻ = Na ₄ Cl ₃ ⁺	0.517	3.29				1.023E-02
7	Na ₃ Cl ₃ + Na ⁺ = Na ₄ Cl ₃ ⁺	-0.208	0.62				1.002E-02
7	Na ₃ Cl ₂ ⁺ + NaCl = Na ₄ Cl ₃ ⁺	0.013	1.03				1.016E-02
8	Na ₄ Cl ₃ ⁺ + Cl ⁻ = Na ₄ Cl ₄	0.114	1.30			1.115E-02	
8	Na ₃ Cl ₄ ⁻ + Na ⁺ = Na ₄ Cl ₄	0.117	1.31			1.100E-02	
8	Na ₃ Cl ₃ + NaCl = Na ₄ Cl ₄	0.029	1.07			1.110E-02	
2	K ⁺ + Cl ⁻ = KCl	-0.244	0.57			3.609E-02	

Table B8 cont.

Cluster size	Clustering equations	Log K_{assoc}	K_{assoc}	Negatively charged species	Neutral species	Positively charged species
3	$\text{KCl} + \text{Cl}^- = \text{KCl}_2^-$	-0.721	0.19	5.791E-03		
4	$\text{KCl}_2^- + \text{Cl}^- = \text{KCl}_3^{-2}$	-1.155	0.07	3.420E-04		
3	$\text{KCl} + \text{K}^+ = \text{K}_2\text{Cl}^+$	-0.658	0.22			5.949E-04
4	$\text{K}_2\text{Cl}^+ + \text{K}^+ = \text{K}_3\text{Cl}^{+2}$	-1	0.10			4.462E-06
4	$\text{K}_2\text{Cl}^+ + \text{Cl}^- = \text{K}_2\text{Cl}^2$	-0.027	0.94		4.719E-04	
4	$\text{KCl}_2^- + \text{K}^+ = \text{K}_2\text{Cl}_2$	0.021	1.05		4.558E-04	
4	$\text{KCl} + \text{KCl} = \text{K}_2\text{Cl}_2$	-0.456	0.35		4.558E-04	
5	$\text{K}_2\text{Cl}_2 + \text{Cl}^- = \text{K}_2\text{Cl}_3^-$	-0.495	0.32	1.231E-04		
5	$\text{KCl}_3^{-2} + \text{K}^+ = \text{K}_2\text{Cl}_3^-$	0.67	4.68	1.200E-04		
5	$\text{KCl}_2^- + \text{KCl} = \text{K}_2\text{Cl}_3^-$	-0.237	0.58	1.211E-04		
6	$\text{K}_2\text{Cl}_3^- + \text{Cl}^- = \text{K}_2\text{Cl}_4^{-2}$	-0.921	0.12	1.246E-05		
5	$\text{K}_3\text{Cl}^{+2} + \text{Cl}^- = \text{K}_3\text{Cl}_2^+$	0.577	3.78			1.422E-05
5	$\text{K}_2\text{Cl}_2 + \text{K}^+ = \text{K}_3\text{Cl}_2^+$	-0.409	0.39			1.333E-05
5	$\text{K}_2\text{Cl}^+ + \text{KCl} = \text{K}_3\text{Cl}_2^+$	-0.194	0.64			1.374E-05
6	$\text{K}_3\text{Cl}_2^+ + \text{Cl}^- = \text{K}_3\text{Cl}_3$	-0.036	0.92		1.067E-05	
6	$\text{K}_2\text{Cl}_3^- + \text{K}^+ = \text{K}_3\text{Cl}_3$	0.053	1.13		1.043E-05	
6	$\text{K}_2\text{Cl}_2 + \text{KCl} = \text{K}_3\text{Cl}_3$	-0.201	0.63		1.036E-05	
7	$\text{K}_3\text{Cl}_3 + \text{Cl}^- = \text{K}_3\text{Cl}_4^-$	-0.444	0.36	3.166E-06		
7	$\text{K}_2\text{Cl}_4^{-2} + \text{K}^+ = \text{K}_3\text{Cl}_4^-$	0.547	3.52	3.293E-06		
7	$\text{K}_2\text{Cl}_3^- + \text{KCl} = \text{K}_3\text{Cl}_4^-$	-0.149	0.71	3.152E-06		
6	$\text{K}_3\text{Cl}_2^+ + \text{K}^+ = \text{K}_4\text{Cl}_2^{+2}$	-0.796	0.16			1.648E-07
6	$\text{K}_3\text{Cl}^{+2} + \text{KCl} = \text{K}_4\text{Cl}_2^{+2}$	0.029	1.07			5.300E-07
7	$\text{K}_4\text{Cl}_2^{+2} + \text{Cl}^- = \text{K}_4\text{Cl}_3^+$	0.401	2.52			3.502E-07
7	$\text{K}_3\text{Cl}_3 + \text{K}^+ = \text{K}_4\text{Cl}_3^+$	-0.347	0.45			3.518E-07
7	$\text{K}_3\text{Cl}_2^+ + \text{KCl} = \text{K}_4\text{Cl}_3^+$	-0.143	0.72			3.567E-07
8	$\text{K}_4\text{Cl}_3^+ + \text{Cl}^- = \text{K}_4\text{Cl}_4$	-0.06	0.87		2.622E-07	
8	$\text{K}_3\text{Cl}_4^- + \text{K}^+ = \text{K}_4\text{Cl}_4$	0.033	1.08		2.550E-07	
8	$\text{K}_3\text{Cl}_3 + \text{KCl} = \text{K}_4\text{Cl}_4$	-0.167	0.68		2.562E-07	
9	$\text{K}_4\text{Cl}_4 + \text{Cl}^- = \text{K}_4\text{Cl}_5^-$	-0.377	0.42	9.077E-08		
9	$\text{K}_3\text{Cl}_4^- + \text{KCl} = \text{K}_4\text{Cl}_5^-$	-0.097	0.80	9.098E-08		
9	$\text{K}_4\text{Cl}_4 + \text{K}^+ = \text{K}_5\text{Cl}_4^+$	-0.292	0.51			9.810E-09
9	$\text{K}_4\text{Cl}_3^+ + \text{KCl} = \text{K}_5\text{Cl}_4^+$	-0.149	0.71			9.134E-09
2	$\text{Na}^+ + \text{Br}^- = \text{NaBr}$	-0.149	0.71		1.879E-03	
3	$\text{NaBr} + \text{Br}^- = \text{NaBr}_2^-$	-0.658	0.22	1.694E-06		
4	$\text{NaBr}_2^- + \text{Br}^- = \text{NaBr}_3^{-2}$	-0.921	0.12	8.329E-10		
3	$\text{NaBr} + \text{Na}^+ = \text{Na}_2\text{Br}^+$	-0.569	0.27			3.275E-04
4	$\text{Na}_2\text{Br}^+ + \text{Na}^+ = \text{Na}_3\text{Br}^{+2}$	-1	0.10			2.116E-05
4	$\text{Na}_2\text{Br}^+ + \text{Br}^- = \text{Na}_2\text{Br}_2$	0.013	1.03		1.384E-06	
4	$\text{NaBr}_2^- + \text{Na}^+ = \text{Na}_2\text{Br}_2$	0.09	1.23		1.346E-06	
4	$\text{NaBr} + \text{NaBr} = \text{Na}_2\text{Br}_2$	-0.42	0.38		1.343E-06	
5	$\text{Na}_2\text{Br}_2 + \text{Br}^- = \text{Na}_2\text{Br}_3^-$	-0.319	0.48	2.647E-09		
5	$\text{NaBr}_3^{-2} + \text{Na}^+ = \text{Na}_2\text{Br}_3^-$	0.686	4.85	2.611E-09		

Table B8 cont.

Cluster size	Clustering equations	Log K_{assoc}	K_{assoc}	Negatively charged species	Neutral species	Positively charged species
5	$\text{NaBr}_2^- + \text{NaBr} = \text{Na}_2\text{Br}_3^-$	-0.081	0.83	2.641E-09		
6	$\text{Na}_2\text{Br}_3^- + \text{Br}^- = \text{Na}_2\text{Br}_4^{-2}$	-0.853	0.14	1.519E-12		
5	$\text{Na}_3\text{Br}^{+2} + \text{Br}^- = \text{Na}_3\text{Br}_2^+$	0.606	4.04			3.502E-07
5	$\text{Na}_2\text{Br}_2 + \text{Na}^+ = \text{Na}_3\text{Br}_2^+$	-0.432	0.37			3.216E-07
5	$\text{Na}_2\text{Br}^+ + \text{NaBr} = \text{Na}_3\text{Br}_2^+$	-0.268	0.54			3.321E-07
6	$\text{Na}_3\text{Br}_2^+ + \text{Br}^- = \text{Na}_3\text{Br}_3$	0.185	1.53		2.085E-09	
6	$\text{Na}_2\text{Br}_3^- + \text{Na}^+ = \text{Na}_3\text{Br}_3$	0.076	1.19		2.033E-09	
6	$\text{Na}_2\text{Br}_2 + \text{NaBr} = \text{Na}_3\text{Br}_3$	-0.097	0.80		2.023E-09	
7	$\text{Na}_3\text{Br}_3 + \text{Br}^- = \text{Na}_3\text{Br}_4^-$	-0.553	0.28	2.333E-12		
7	$\text{Na}_2\text{Br}_4^{-2} + \text{Na}^+ = \text{Na}_3\text{Br}_4^-$	0.365	2.32	2.274E-12		
7	$\text{Na}_2\text{Br}_3^- + \text{NaBr} = \text{Na}_3\text{Br}_4^-$	-0.337	0.46	2.285E-12		
8	$\text{Na}_3\text{Br}_4^- + \text{Br}^- = \text{Na}_3\text{Br}_5^{-2}$	-0.268	0.54	5.054E-15		
8	$\text{Na}_2\text{Br}_4^{-2} + \text{NaBr} = \text{Na}_3\text{Br}_5^{-2}$	0.243	1.75	4.996E-15		
6	$\text{Na}_3\text{Br}_2^+ + \text{Na}^+ = \text{Na}_4\text{Br}_2^{+2}$	-0.921	0.12			2.573E-08
6	$\text{Na}_3\text{Br}^{+2} + \text{NaBr} = \text{Na}_4\text{Br}_2^{+2}$	-0.18	0.66			2.627E-08
7	$\text{Na}_4\text{Br}_2^{+2} + \text{Br}^- = \text{Na}_4\text{Br}_3^+$	0.853	7.13			7.521E-10
7	$\text{Na}_3\text{Br}_3 + \text{Na}^+ = \text{Na}_4\text{Br}_3^+$	-0.26	0.55			7.216E-10
7	$\text{Na}_3\text{Br}_2^+ + \text{NaBr} = \text{Na}_4\text{Br}_3^+$	0.068	1.17			7.299E-10
8	$\text{Na}_4\text{Br}_3^+ + \text{Br}^- = \text{Na}_4\text{Br}_4$	-0.081	0.83		2.484E-12	
8	$\text{Na}_3\text{Br}_4^- + \text{Na}^+ = \text{Na}_4\text{Br}_4$	0.215	1.64		2.421E-12	
8	$\text{Na}_3\text{Br}_3 + \text{NaBr} = \text{Na}_4\text{Br}_4$	-0.201	0.63		2.405E-12	
9	$\text{Na}_4\text{Br}_4 + \text{Br}^- = \text{Na}_4\text{Br}_5^-$	0.179	1.51	1.629E-14		
9	$\text{Na}_3\text{Br}_4^- + \text{NaBr} = \text{Na}_4\text{Br}_5^-$	0.538	3.45	2.703E-15		
2	$\text{K}^+ + \text{Br}^- = \text{KBr}$	-0.187	0.65		1.999E-04	
3	$\text{KBr} + \text{Br}^- = \text{KBr}_2^-$	-0.678	0.21	1.720E-07		
4	$\text{KBr}_2^- + \text{Br}^- = \text{KBr}_3^{-2}$	-1.398	0.04	2.821E-11		
3	$\text{KBr} + \text{K}^+ = \text{K}_2\text{Br}^+$	-0.602	0.25			3.749E-06
4	$\text{K}_2\text{Br}^+ + \text{K}^+ = \text{K}_3\text{Br}^{+2}$	-0.959	0.11			3.090E-08
4	$\text{K}_2\text{Br}^+ + \text{Br}^- = \text{K}_2\text{Br}_2$	0.009	1.02		1.569E-08	
4	$\text{KBr}_2^- + \text{K}^+ = \text{K}_2\text{Br}_2$	0.076	1.19		1.537E-08	
4	$\text{KBr} + \text{KBr} = \text{K}_2\text{Br}_2$	-0.409	0.39		1.558E-08	
5	$\text{K}_2\text{Br}_2 + \text{Br}^- = \text{K}_2\text{Br}_3^-$	-0.444	0.36	2.299E-11		
5	$\text{KBr}_3^{-2} + \text{K}^+ = \text{K}_2\text{Br}_3^-$	0.782	6.05	1.281E-11		
5	$\text{KBr}_2^- + \text{KBr} = \text{K}_2\text{Br}_3^-$	-0.187	0.65	2.236E-11		
6	$\text{K}_2\text{Br}_3^- + \text{Br}^- = \text{K}_2\text{Br}_4^{-2}$	-0.881	0.13	1.206E-14		
5	$\text{K}_3\text{Br}^{+2} + \text{Br}^- = \text{K}_3\text{Br}_2^+$	0.584	3.84			4.861E-10
5	$\text{K}_2\text{Br}_2 + \text{K}^+ = \text{K}_3\text{Br}_2^+$	-0.377	0.42			4.909E-10
5	$\text{K}_2\text{Br}^+ + \text{KBr} = \text{K}_3\text{Br}_2^+$	-0.18	0.66			4.952E-10
6	$\text{K}_3\text{Br}_2^+ + \text{Br}^- = \text{K}_3\text{Br}_3$	0.004	1.01		2.031E-12	
6	$\text{K}_2\text{Br}_3^- + \text{K}^+ = \text{K}_3\text{Br}_3$	0.079	1.20		2.012E-12	
6	$\text{K}_2\text{Br}_2 + \text{KBr} = \text{K}_3\text{Br}_3$	-0.18	0.66		2.058E-12	
7	$\text{K}_3\text{Br}_3 + \text{Br}^- = \text{K}_3\text{Br}_4^-$	-0.367	0.43	3.543E-15		

Table B8 cont.

Cluster size	Clustering equations	Log K_{assoc}	K_{assoc}	Negatively charged species	Neutral species	Positively charged species
7	$\text{K}_2\text{Br}_4^{-2} + \text{K}^+ = \text{K}_3\text{Br}_4^-$	0.607	4.05	3.659E-15		
7	$\text{K}_2\text{Br}_3^- + \text{KBr} = \text{K}_3\text{Br}_4^-$	-0.097	0.80	3.575E-15		
8	$\text{K}_3\text{Br}_4^- + \text{Br}^- = \text{K}_3\text{Br}_5^{-2}$	-0.678	0.21	3.077E-18		
8	$\text{K}_2\text{Br}_4^{-2} + \text{KBr} = \text{K}_3\text{Br}_5^{-2}$	0.121	1.32	3.185E-18		
6	$\text{K}_3\text{Br}_2^+ + \text{K}^+ = \text{K}_4\text{Br}_2^{+2}$	-0.699	0.20			7.363E-12
6	$\text{K}_3\text{Br}^{+2} + \text{KBr} = \text{K}_4\text{Br}_2^{+2}$	0.079	1.20			7.410E-12
7	$\text{K}_4\text{Br}_2^{+2} + \text{Br}^- = \text{K}_4\text{Br}_3^+$	0.455	2.85			8.607E-14
7	$\text{K}_3\text{Br}_3 + \text{K}^+ = \text{K}_4\text{Br}_3^+$	-0.244	0.57			8.602E-14
7	$\text{K}_3\text{Br}_2^+ + \text{KBr} = \text{K}_4\text{Br}_3^+$	-0.056	0.88			8.627E-14
8	$\text{K}_4\text{Br}_3^+ + \text{Br}^- = \text{K}_4\text{Br}_4$	-0.013	0.97		3.425E-16	
8	$\text{K}_3\text{Br}_4^- + \text{K}^+ = \text{K}_4\text{Br}_4$	0.104	1.27		3.407E-16	
8	$\text{K}_3\text{Br}_3 + \text{KBr} = \text{K}_4\text{Br}_4$	-0.076	0.84		3.376E-16	
9	$\text{K}_4\text{Br}_4 + \text{Br}^- = \text{K}_4\text{Br}_5^-$	-0.357	0.44	1.775E-18		
9	$\text{K}_3\text{Br}_4^- + \text{KBr} = \text{K}_4\text{Br}_5^-$	-0.066	0.86	6.000E-19		
8	$\text{K}_4\text{Br}_3^+ + \text{K}^+ = \text{K}_5\text{Br}_3^{+2}$	-0.553	0.28			1.807E-15
8	$\text{K}_4\text{Br}_2^{+2} + \text{KBr} = \text{K}_5\text{Br}_3^{+2}$	0.084	1.21			1.786E-15
9	$\text{K}_5\text{Br}_3^{+2} + \text{Br}^- = \text{K}_5\text{Br}_4^+$	0.413	2.59			1.917E-17
9	$\text{K}_4\text{Br}_4 + \text{K}^+ = \text{K}_5\text{Br}_4^+$	-0.125	0.75			1.916E-17
9	$\text{K}_4\text{Br}_3^+ + \text{KBr} = \text{K}_5\text{Br}_4^+$	0.045	1.11			1.908E-17
10	$\text{K}_5\text{Br}_4^+ + \text{Br}^- = \text{K}_5\text{Br}_5$	-0.119	0.76		5.973E-20	

Table B9. Seawater compositions at various stages of evaporation (McCaffrey et al., 1987) used to calculate the amount of Cl^- and Br^- in positive and neutral ion clusters.

Degree of seawater evaporation	Cl^-	Br^-	K^+	Na^+
	concentration (mmol/kgw)			
0.95	579	0.883	10.7	497
0.98	585	0.917	11.1	497
1.10	594	0.931	12	506
1.17	649	0.99	13.2	582
1.75	947	1.49	17.9	839
2.26	1210	1.77	21.9	1010
2.68	1440	2.24	26.6	1220
3.16	1790	2.85	34.8	1600
3.53	2030	3.05	39.2	1710
4.36	2490	3.75	46.8	2160
6.07	3500	5.36	62.3	2930
6.91	3870	5.84	72.3	3360
8.45	4900	7.33	90.5	4170
8.62	4900	7.22	87.7	4210

Table B9 cont.				
Degree of seawater evaporation	Cl ⁻	Br ⁻	K ⁺	Na ⁺
	concentration (mmol/kgw)			
9.03	4900	7.57	91.4	4220
10.5	5670	8.8	112	5000
11.0	5880	9.38	109	4830
12.6	5910	10.8	115	4700
13.2	5750	11.9	152	5020
15.1	6040	12.7	157	4740
16.4	5820	13.8	180	4670
17.6	5720	14.6	190	4480
20.1	5980	16.7	208	4140
20.4	6010	17.4	212	4130
23.4	6080	19.5	249	4110
23.6	5980	20.8	242	3960
25.4	6080	19.5	253	3810
26.8	5850	23	278	3720
31.4	5920	26.4	330	3320
32.8	5960	28.7	339	3170
34.0	5830	28.2	342	3190
36.8	5890	29.9	379	3060
39.4	5930	33.1	402	2830
40.4	5860	34.3	417	2630
43.5	5740	35.6	443	2310
44.8	6030	38.4	449	2270
48.9	5800	40.1	495	1960
58.1	6100	48.2	591	1370
58.6	6260	48.1	588	1500
63.6	6230	51.8	637	1,160
66.2	6620	59	632	842
69.2	6470	59.8	754	712
72.9	7130	66.1	782	825
78.8	7380	71.6	712	545
87.9	7500	77.7	565	413
87.9	6890	74.8	348	553
93.3	7500	77.3	311	500
97.1	7800	82.8	597	428
98.1	5990	77.4	125	169

Table B5. Porewater concentrations in Michigan Basin, Opalinu Clay, and Lorraine Group Shale samples extracted by the paper absorption method. Values used in ion clustering calculations. These values were not reported as they were manipulated during ion clustering calculations to force the calculation error to 0.

Sample Name	Br ⁻	Cl ⁻	K ⁺	Na ⁺
	mol/kgw			
Michigan Basin				
334	0.004	0.8	0.08	0.6
383	0.016	1.8	0.04	0.5
421	0.034	1.9	0.04	0.3
431	0.055	3.6	0.03	0.2
463	0.037	1.4	0.09	0.7
496	0.059	2.9	0.03	0.2
520	0.052	2.3	0.04	0.4
530	0.051	2.5	0.04	0.3
572	0.050	2.7	0.04	0.3
626	0.054	2.6	0.04	0.3
634	0.042	2.0	0.04	0.4
658	0.020	1.2	0.06	0.6
662	0.030	1.9	0.04	0.4
707	0.032	1.5	0.06	0.6
723	0.018	0.8	0.10	1.2
Opalinus Clay				
75	0.00055	0.299	0.0038	0.270
82	0.00003	0.026	0.0041	0.064
83	0.00001	0.014	0.0031	0.052
100	0.00009	0.054	0.0042	0.119
115	0.00019	0.117	0.0036	0.157
128	0.00029	0.160	0.0055	0.214
144	0.00048	0.239	0.0062	0.316
178	0.00073	0.401	0.0053	0.370
204	0.00076	0.390	0.0050	0.378
Lorraine Group Shales				
F7-1	0.0012	0.2627	0.0000	0.259
F7-2	0.0014	0.2991	0.0000	0.296
F8-1	0.0001	0.0512	0.0000	0.068
F8-2	0.0001	0.0482	0.0000	0.087
F20-1	0.0030	0.4943	0.0000	0.433
F20-2	0.0018	0.3078	0.0000	0.271
F20-3	0.0017	0.30114	0.0000	0.261
444-1	0.0013	0.21620	0.0000	0.282

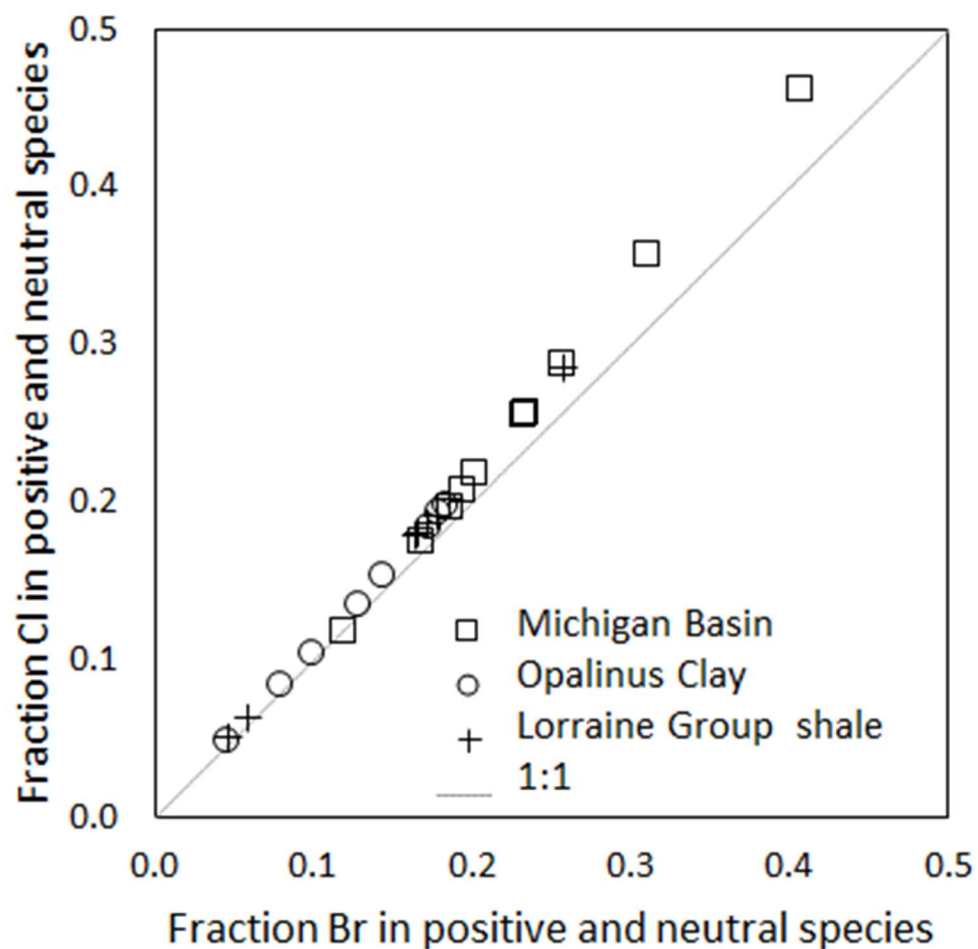


Figure B1. Fraction of Cl^- and Br^- occurring in the form of positively charged and neutral ion pairs and clusters. Calculations are for porewaters extracted by the paper absorption method from Michigan Basin, Opalinu Clay, and Lorraine Group Shale samples using K_{assoc} values from Chen and Pappu (2007, Appendix B). This data was not reported due to manipulation of values required to minimize the error in reported calculations. Manipulation involved decreasing concentrations to account for evaporation of porewater during core handling.

Table B61. Hydrated anion radii (pm) reported in the by Ohtaki and Radnai (1993) and Smirnov (2013).

F ⁻		Cl ⁻		Br ⁻		I ⁻	
Smirnov	Ohtaki	Smirnov	Ohtaki	Smirnov	Ohtaki	Smirnov	Ohtaki
0.23	0.269	0.34	0.325	0.355	0.321	0.368	0.361
0.3	0.262	0.325	0.313	0.345	0.336	0.364	0.37
0.26	0.262	0.329	0.31	0.332	0.329	0.364	0.37
0.264	0.292	0.328	0.313	0.337	0.334	0.356	0.363
0.267	0.26	0.321	0.323	0.33	0.332	0.371	0.358
0.288	0.267	0.345	0.319	0.343	0.34	0.364	0.358
0.26	0.264	0.319	0.31	0.333	0.34	0.355	0.355
0.275	0.263	0.316	0.329	0.336	0.312	0.375	0.359
0.262	0.26	0.32	0.319		0.333		0.36
0.254	0.23	0.3225	0.32		0.335		0.37
0.261	0.33	0.336	0.3175		0.349		0.37
0.253	0.222	0.318	0.316		0.345		0.36
0.26	0.264	0.315	0.31		0.32		0.357
0.257		0.34	0.32				0.354
0.266			0.31				0.36
0.265			0.32				
0.266			0.31				
0.26			0.32				
0.278			0.315				
			0.313				
			0.3145				
			0.3165				
			0.325				
			0.325				
			0.312				
			0.32				
			0.32				
			0.326				
			0.32				
			0.313				
			0.32				
			0.314				
			0.308				
			0.317				
			0.32				
			0.32				

Table B8. Mercury injection porosimetry measurements of pore throat diameters of an Opalinus clay sample quantified by Houben et al. (2013).

pore throat diameter (nm)	measurement		average	Standard deviation
	1	2		
5.2	1.63	1.4	0.015	0.002
5.6	2.3	1.1	0.017	0.008
6.5	0.8	1.6	0.012	0.006
6.9	3.25	1.75	0.025	0.011
7.4	2.5	1.6	0.021	0.006
8	2.9	3.2	0.031	0.002
8.7	5.8	4.2	0.050	0.011
9.6	5.2	4.2	0.047	0.007
13	4.4	2.75	0.036	0.012
18	4.9	3.3	0.041	0.011
21	2.1	1.15	0.016	0.007
25	9.6	7.1	0.084	0.018
31	4.1	1.75	0.029	0.017
33	11.9	7.6	0.098	0.030
39	1.5	0.75	0.011	0.005
40	9.7	7.9	0.088	0.013
46	3.8	3.9	0.039	0.001
55	1.75	2.4	0.021	0.005
65	1.6	1.75	0.017	0.001
75	0	1.4	0.007	0.010
82	0	1.25	0.006	0.009
90	0	1	0.005	0.007
100	0	1	0.005	0.007

References

- Houben, M. E., Desbois, G., and Urai, J. L. (2013). Pore morphology and distribution in the Shaly facies of Opalinus Clay (Mont Terri, Switzerland): Insights from representative 2D BIB–SEM investigations on mm to nm scale. *Applied Clay Science*, 71, 82–97. <https://doi.org/10.1016/j.clay.2012.11.006>
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Petrology, 57, 928–938. <https://doi.org/10.1306/212F8CAB-2B24-11D7-8648000102C1865D>

Ohtaki, Hitoshi., and Radnai, Tamas. (1993). Structure and dynamics of hydrated ions. *Chemical Reviews*, 93(3), 1157–1204. <https://doi.org/10.1021/cr00019a014>

Smirnov, P. (2013). Structural parameters of the nearest surrounding of halide ions in the aqueous electrolyte solutions. *Russian Journal of General Chemistry*, 83(8), 1469–1481. <https://doi.org/10.1134/S107036321308001X>

Appendix C: Supplementary information for Chapter 4

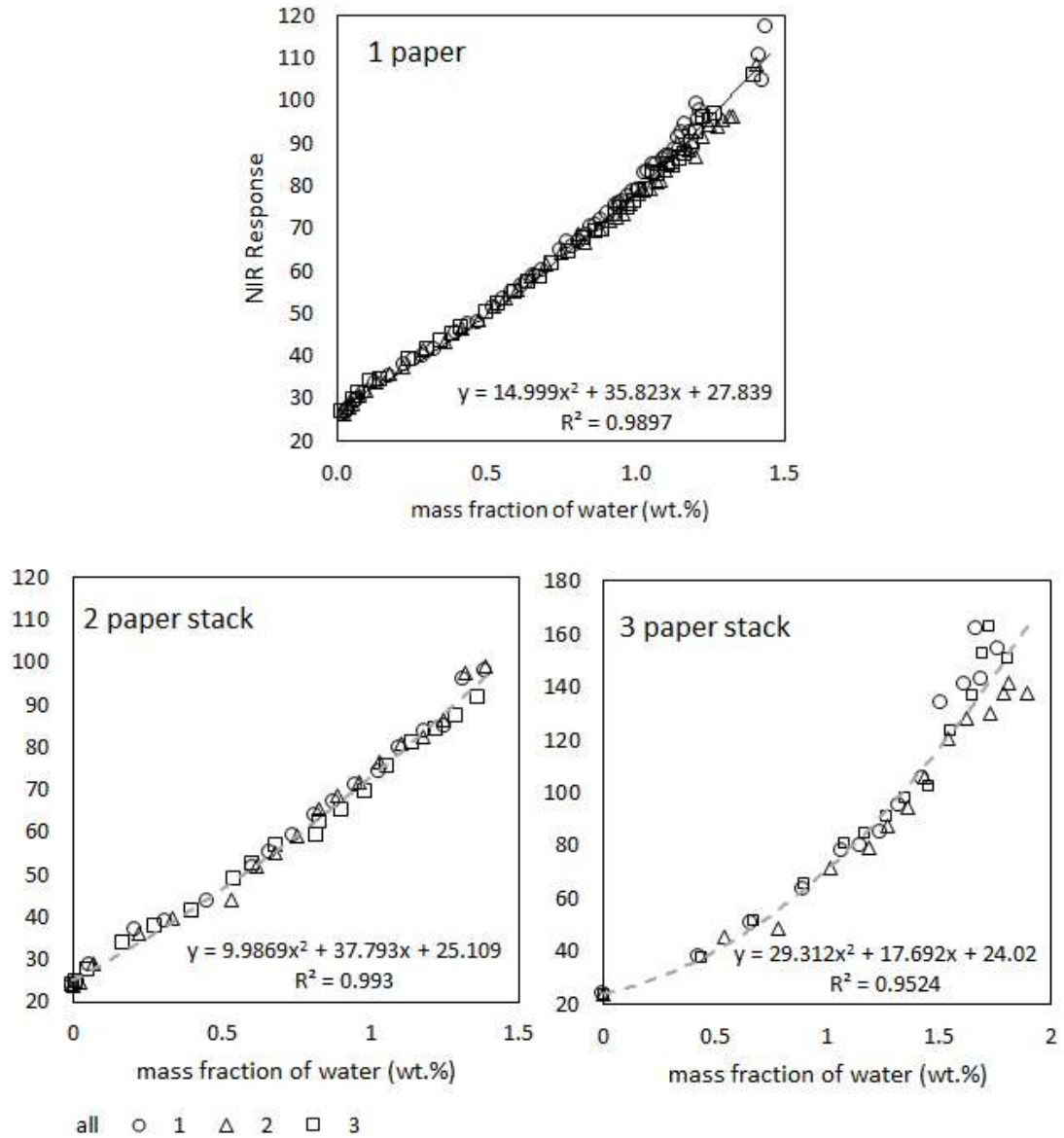


Figure C1. Relationship between reflectance NIR response and moisture content of a stack of 1, 2, and 3 Whatman[®] 1 CHR papers and the resulting calibration curves used. Only water evaporation curves were used due to the low salinity and relatively large masses of porewater extracted.

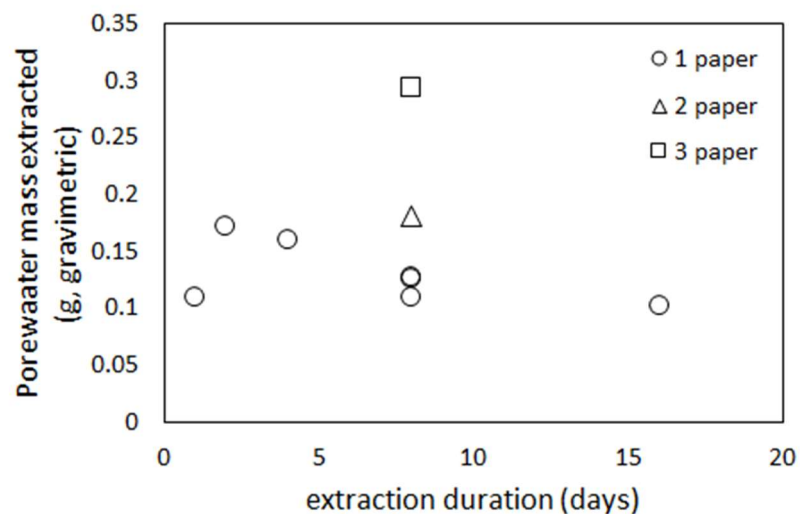


Figure C2. Preliminary measurements determining the duration of time needed to equilibrate absorbing papers with porewater. Mass of porewater was extracted from a Champlain Sea mud sample from 18 mbgs over different durations and using stacks of one, two, and three papers.

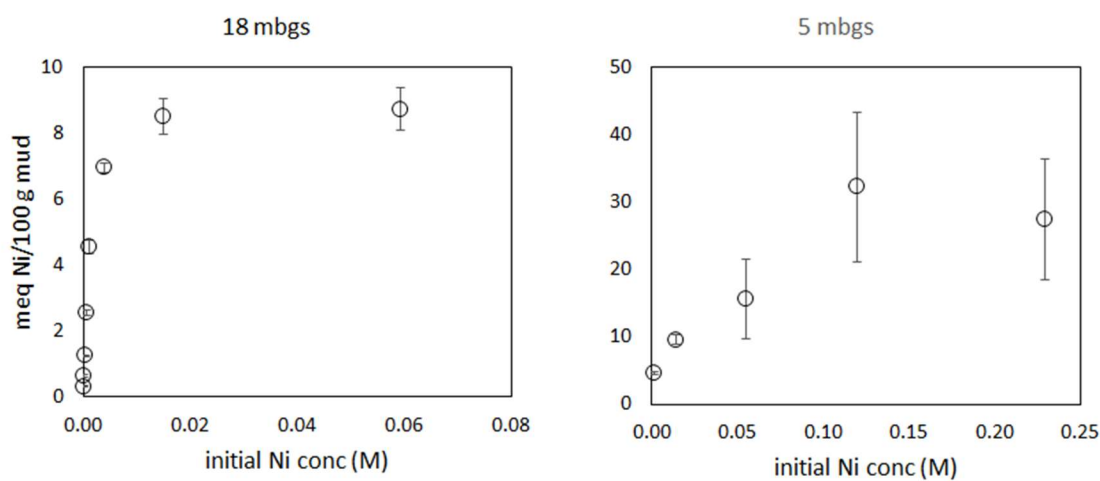


Figure C3. Ni sorption isotherms collected at 18 and 5 m bgs.

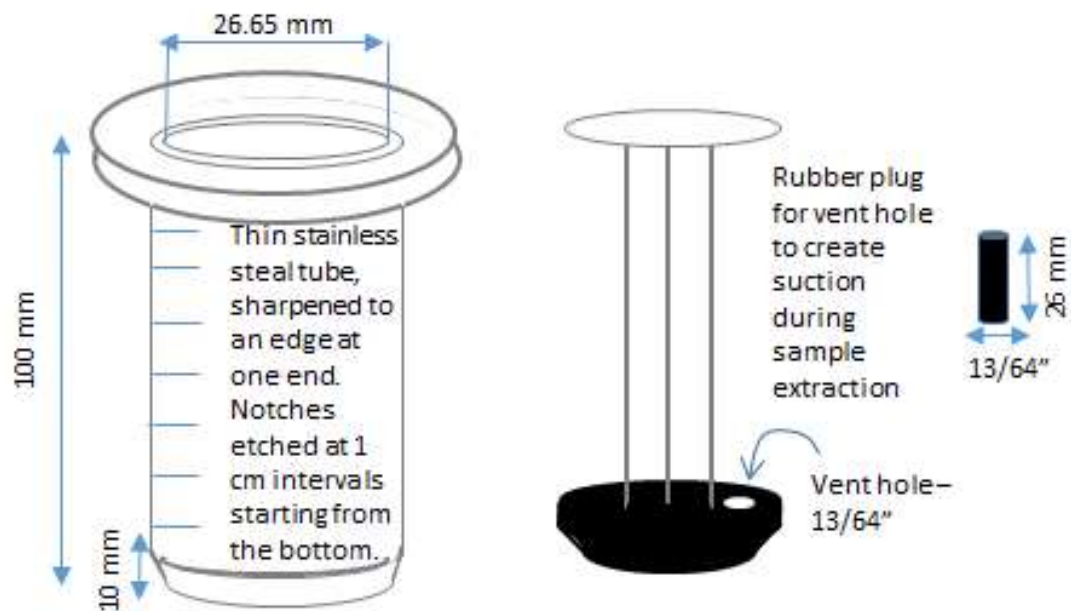


Figure C4. Design for fixed volume porosity sampler.

Table C9. Reflectance NIR check standards.

date	Blank			Low			High		
	measurement	average	standard deviation	measurement	average	standard deviation	measurement	average	standard deviation
28-Sep-19	25.3	25.2	0.1	26.1	26.1	0.1	40.1	40.0	0.1
	25.2			26.2			40.0		
	25.2			26.1			40.0		
28-Sep-19	25.2	25.2	0.0	26.1	26.1	0.1	40.0	40.0	0.1
	25.2			26.1			40.0		
	25.2			26.2			39.9		
01-Oct-19	25.2	25.2	0.0	26.2	26.2	0.1	40.0	40.1	0.0
	25.2			26.2			40.0		
	25.2			26.1			39.9		
02-Oct-19	25.2	25.3	0.1	26.1	26.1	0.0	40.1	40.1	0.1
	25.3			26.1			40.1		
	25.3			26.1			40.1		
04-Oct-19	25.1	25.1	0.1	26.2	26.1	0.1	40.0	40.0	0.1
	25.1			26.1			40.1		
	25.2			26.1			40.1		
08-Oct-19	25.2	25.2	0.1	26.2	26.1	0.1	40.1	40.0	0.1
	25.2			26.1			40.0		
	25.1			26.1			40.0		
16-Oct-19	25.2	25.2	0.0	26.2	26.2	0.1	40.0	40.1	0.1
	25.2			26.2			40.0		
	25.2			26.1			40.1		
17-Jan-20	25.2	25.2	0.0	26.2	26.1	0.1	40.1	40.6	0.1
	25.2			26.1			40.1		
	25.2			26.1			40.0		
17-Jan-20	25.2	25.2	0.0	26.0	26.0	0.0	40.6	39.9	0.0
	25.2			26.0			40.5		
	25.2			26.0			40.6		
17-Jan-20	25.2	25.2	0.0	26.1	26.1	0.0	39.9	40.1	0.1
	25.2			26.1			39.9		
	25.2			26.1			39.9		
21-Jan-20	25.2	25.2	0.0	26.1	26.1	0.0	40.0	39.9	0.0
	25.2			26.1			40.2		
	25.2			26.1			40.1		
09-Feb-20	25.2	25.2	0.0	26.1	26.1	0.0	39.9	40.0	0.1
	25.2			26.1			39.9		
	25.2			26.1			39.9		
10-Feb-20	25.2	25.2	0.0	26.0	26.1	0.1	40.0	39.9	0.1
	25.2			26.1			39.9		
	25.2			26.1			39.9		

Table C1. cont.									
date	Blank			Low			High		
	measurement	average	standard deviation	measurement	average	standard deviation	measurement	average	standard deviation
11-Feb-20	25.3	25.3	0.0	26.1	26.1	0.0	40.0	40.0	0.1
	25.3			26.1			40.0		
	25.3			26.1			39.9		
12-Feb-20	25.2	25.2	0.0	26.1	26.1	0.1	39.9	39.9	0.0
	25.2			26.1			39.9		
	25.2			26.0			39.9		
13-Feb-20	25.2	25.2	0.0	26.0	26.1	0.1	40.0	40.0	0.0
	25.2			26.1			40.0		
	25.2			26.1			40.0		
18-Feb-20	25.2	25.2	0.0	26.2	26.2	0.0	39.9	39.9	0.0
	25.2			26.2			39.9		
	25.2			26.2			39.9		
19-Feb-20	25.2	25.2	0.0	26.0	26.1	0.1	39.9	39.9	0.1
	25.2			26.1			39.8		
	25.2			26.1			39.9		
24-Feb-20	25.2	25.2	0.0	26.2	26.2	0.0	40.4	40.4	0.1
	25.2			26.2			40.5		
	25.2			26.2			40.4		
25-Feb-20	25.2	25.2	0.0	26.0	26.1	0.1	40.1	40.1	0.1
	25.2			26.1			40.0		
	25.2			26.1			40.1		
26-Feb-20	25.2	25.2	0.0	26.1	26.1	0.0	40.0	40.0	0.0
	25.2			26.1			40.0		
	25.2			26.1			40.0		
27-Feb-20	25.2	25.2	0.0	26.2	26.2	0.1	40.2	40.2	0.0
	25.2			26.2			40.2		
	25.2			26.1			40.2		
28-Feb-20	25.2	25.2	0.0	26.1	26.1	0.0	40.0	40.0	0.0
	25.2			26.1			40.0		
	25.2			26.1			40.0		
02-Mar-20	25.2	25.2	0.0	26.1	26.1	0.0	40.1	40.0	0.1
	25.2			26.1			40.0		
	25.2			26.1			40.0		
03-Mar-20	25.2	25.2	0.0	26.1	26.1	0.0	40.1	40.1	0.1
	25.2			26.1			40.0		
	25.2			26.1			40.1		
04-Mar-20	25.2	25.2	0.0	26.1	26.1	0.0	40.0	40.0	0.1
	25.2			26.1			40.0		
	25.2			26.1			40.1		

Table C1. cont.									
	Blank			Low			High		
date	measurement	average	standard deviation	measurement	average	standard deviation	measurement	average	standard deviation
05-Mar-20	25.2	25.2	0.0	26.1	26.1	0.0	40.0	40.0	0.0
	25.2			26.1			40.0		
	25.2			26.1			40.0		
08-Mar-20	25.2	25.2	0.0	26.1	26.0	0.1	40.0	40.0	0.0
	25.2			26			40.0		
	25.2			26			40.0		
09-Mar-20	25.2	25.2	0.0	26.1	26.1	0.0	40.0	40.0	0.0
	25.2			26.1			40.0		
	25.2			26.1			40.0		
10-Mar-20	25.2	25.2	0.0	26.1	26.1	0.0	40.0	40.0	0.0
	25.2			26.1			40.0		
	25.2			26.1			40.0		
11-Mar-20	25.2	25.2	0.0	26.1	26.1	0.1	39.9	39.9	0.1
	25.2			26.1			39.9		
	25.2			26			40.0		
12-Mar-20	25.2	25.2	0.0	26.1	26.1	0.0	40.0	40.0	0.0
	25.2			26.1			40.0		
	25.2			26.1			40.0		
14-Mar-20	25.2	25.2	0.0	26.1	26.1	0.1	40.0	40.1	0.1
	25.2			26.2			40.1		
	25.2			26.1			40.1		
19-Mar-20	25.3	25.3	0.0	26.1	26.1	0.1	40.0	40.2	0.2
	25.3			26.2			40.3		
	25.3			26.1			40.2		
24-Mar-20	25.2	25.2	0.0	26.1	26.1	0.1	40.0	39.9	0.1
	25.2			26			39.8		
	25.2			26.1			40.0		
25-Mar-20	25.2	25.2	0.1	26.1	26.1	0.0	40.0	40.0	0.0
	25.2			26.1			40.0		
	25.3			26.1			40.0		
01-Nov-20	25.2	25.2	0.0	26.2	26.2	0.1	40.1	40.1	0.0
	25.2			26.2			40.1		
	25.2			26.1			40.1		
02-Nov-20	25.3	25.3	0.0	26.2	26.2	0.0	40.0	40.0	0.0
	25.3			26.2			40.0		
	25.3			26.2			40.0		
03-Nov-20	25.3	25.3	0.0	26.3	26.3	0.0	40.0	40.0	0.0
	25.3			26.3			40.0		
	25.3			26.3			40.0		

Table C1. cont.									
	Blank			Low			High		
date	measurement	average	standard deviation	measurement	average	standard deviation	measurement	average	standard deviation
05-Nov-20	25.2	25.2	0.0	26.3	26.3	0.1	40.0	40.1	0.1
	25.2			26.2			40.1		
	25.2			26.3			40.1		
08-Nov-20	25.3	25.3	0.0	26.2	26.2	0.0	39.9	40.0	0.1
	25.3			26.2			40.1		
	25.3			26.2			39.9		
09-Nov-20	25.3	25.3	0.0	26.2	26.2	0.0	40.1	40.1	0.1
	25.3			26.2			40.2		
	25.3			26.2			40.1		
10-Nov-20	25.3	25.3	0.0	26.2	26.2	0.0	40.2	40.2	0.0
	25.3			26.2			40.2		
	25.3			26.2			40.2		
16-Nov-20	25.2	25.2	0.0	26.2	26.2	0.0	40.2	40.2	0.1
	25.2			26.2			40.1		
	25.2			26.2			40.2		
17-Nov-20	25.3	25.2	0.1	26.2	26.2	0.1	39.9	39.9	0.0
	25.2			26.3			39.9		
	25.2			26.2			39.9		
19-Nov-20	25.2	25.2	0.1	26.1	26.2	0.1	40.1	40.1	0.0
	25.3			26.3			40.1		
	25.2			26.1			40.1		
20-Nov-20	25.2	25.2	0.1	26.2	26.1	0.1	39.8	39.9	0.1
	25.3			26.1			39.9		
	25.2			26.1			39.9		
20-Nov-20	25.2	25.2	0.0	26.1	26.2	0.1	39.9	40.0	0.1
	25.2			26.2			40.0		
	25.2			26.2			40.0		
23-Nov-20	25.2	25.2	0.0	26.1	26.2	0.1	40.0	40.1	0.1
	25.2			26.2			40.1		
	25.2			26.2			40.1		
24-Nov-20	25.2	25.2	0.0	26.1	26.1	0.1	40.5	40.4	0.1
	25.2			26.2			40.4		
	25.2			26.1			40.4		
30-Nov-20	25.2	25.2	0.1	26.1	26.1	0.0	40.0	40.0	0.0
	25.3			26.1			40.0		
	25.2			26.1			40.0		

Table C2. Limit of detection (LOD) and accuracy and precision of replicate (n) measurements of certified reference standards (high (ES-H3) and low (ES-L2) concentration groundwater and seawater) and a calibration check standard of all ICP-OES analyses.

		Na ⁺ ppm	Mg ²⁺ ppm	S ppm	K ⁺ ppm	Ca ²⁺ ppm	Ni ²⁺ ppm
July 1, 2020 – Centrifuge porewater							n = 5
ES-H3	LOD	0.609	0.000	0.017	0.000	0.000	
	precision	0%	0%	N/A	0%	0%	
	accuracy	6%	11%	N/A	31%	8%	
ES-L2	precision	16%	0%	N/A	1%	0%	
	accuracy	37%	1%	N/A	5%	9%	
CHK std	precision	0%	1%	N/A	N/A	0%	
	accuracy	1%	2%	N/A	N/A	3%	
December 1, 2020 – Centrifuge and paper absorption porewater							n = 10
ES-H3	LOD	0.0004	0.0000	0.0229	0.0095	0.0003	
	precision	1%	0.7%	N/A	1%	1%	
	accuracy	2%	2%	N/A	41%	8%	
ES-L2	precision	4%	7%	N/A	4%	4%	
	accuracy	11%	18%	N/A	10%	10%	
CHK std	precision	N/A	2%	N/A	N/A	3%	
	accuracy	N/A	1%	N/A	N/A	2%	
July 23, 2021 – Cation exchange capacity							n = 10
Exchangeable cation sites							
ES-H3	LOD	0.01	0.00	0.02	0.07	0.00	0.00
	precision	3%	3%	N/A	3%	3%	3%
	accuracy	11%	4%	N/A	68%	27%	5%
ES-L2	precision	4%	3%	N/A	12%	3%	78%
	accuracy	10%	2%	N/A	51%	37%	419%
CHK std	precision	2%	2%	4%	3%	3%	3%
	accuracy	3%	4%	2%	3%	4%	4%
August 1, 2021 – Crush and leach							n = 11
ES-H3	LOD	0.01	0.00	0.02	0.04	0.00	
	precision	1%	1%	N/A	1.4%	2%	
	accuracy	9%	26%	N/A	89%	18%	
ES-L2	precision	2%	1%	N/A	5%	2%	
	accuracy	7%	22%	N/A	302%	27%	
Seawater	precision	2%	2%	1%	2%	2%	
	accuracy	12%	22%	6%	107%	15%	

Table C3. Limit of detection (LOD) and accuracy and precision of replicate (n) measurements of certified reference standards (seawater) ICP-MS analyses in basic medium.

		Cl ⁻ ppm	Br ⁻ ppb	I ppb
June 2021 - Paper absorption and centrifuge				n = 13
Seawater 100x	LOD	0.13	0.07	0.06
	precision	3%	1%	2%
	accuracy	0%	4%	76%
October 2021 - Centrifuge and crush and leach				n = 12
Seawater 500x	LOD	0.10	0.12	0.04
	precision	1%	1%	4%
	accuracy	2%	2%	48%
Seawater 100x	precision	1%	1%	10%
	accuracy	2%	2%	49%

Table C10. Limit of detection (LOD) and accuracy and precision of replicate (n) measurements of certified reference standards (high (ES-H3) and low (ES-L2) concentration groundwater and seawater) and a calibration check standard of all ICP-MS analyses in acidic medium.

		Ba ²⁺ ppb	Br ⁻ ppb	Ca ²⁺ ppm	Cl ⁻ ppm	K ⁺ ppb	Li ⁺ ppb	Mg ²⁺ ppb	Na ⁺ ppm	Rb ⁺ ppb	Sr ²⁺ ppb	Ni ²⁺ ppb
November 5, 2019 – extraction duration and paper number test												n = 5
ES-H3	LOD	0.18	4.31	0.01	0.76	23.07	0.18	0.67	0.01	0.16	0.02	
	precision	N/A	6%	5%	3%	3%	N/A	1%	1%	N/A	2%	
	accuracy	N/A	2%	1%	1%	19%	N/A	1%	6%	N/A	4%	
May 6, 2020 – CEC sorption isotherm (18 m bgs)												n = 6
ES-H3	LOD	0.00	0.79		0.37	2.48	0.00	0.00		0.00	0.00	0.03
	precision	3%	N/A		N/A	2%	2%	3%		2%	1%	2%
	accuracy	9%	N/A		N/A	2%	7%	5%		50%	20%	4%
Seawater	precision	2%	2%		6%	7%	14%	2%		8%	4%	N/A
	accuracy	50%	3%		14%	0%	55%	5%		20%	10%	N/A
July 1, 2020 – centrifuge porewater												n = 5
ES-H3	LOD	0.01	0.30		0.03	4.22	0.00	0.01		0.00	0.00	
	precision	1%	N/A		N/A	N/A	1%	N/A		N/A	1%	
	accuracy	4%	N/A		N/A	N/A	19%	N/A		N/A	5%	
ES-L2	precision	N/A	N/A		N/A	7.7%	N/A	1.3%		N/A	N/A	
	accuracy	N/A	N/A		N/A	14%	N/A	9%		N/A	N/A	
Seawater	precision	21%	0.0%		0.0%	1.8%	1.5%	1.0%		N/A	2.4%	
	accuracy	53%	0%		0%	7%	4%	2%		N/A	1%	
CHK std	precision	0.9%	N/A		N/A	N/A	N/A	5.1%		N/A	1.4%	
	accuracy	31%	N/A		N/A	N/A	N/A	22%		N/A	9%	
October 1, 2020 – centrifuge porewater												n = 5
ES-H3	LOD	0.01	0.60		0.02	4.81	0.01	0.01		0.00	0.00	
	precision	3%	N/A		N/A	N/A	1%	0%		N/A	2%	
	accuracy	6%	N/A		N/A	N/A	20%	0%		N/A	5%	

Table C4. cont.												
		Ba ²⁺	Br [−]	Ca ²⁺	Cl [−]	K ⁺	Li ⁺	Mg ²⁺	Na ⁺	Rb ⁺	Sr ²⁺	Ni ²⁺
		ppb	ppb	ppm	ppm	ppb	ppb	ppb	ppm	ppb	ppb	ppb
ES-L2	precision	N/A	N/A		N/A	6%	N/A	6%		N/A	N/A	
	accuracy	N/A	N/A		N/A	23%	N/A	1%		N/A	N/A	
Seawater	precision	12%	0%		0%	1%	3%	1%		N/A	4%	
	accuracy	14%	0%		0%	6%	2%	2%		N/A	3%	
CHK std	precision	2%	N/A		N/A	N/A	N/A	5%		N/A	1%	
	accuracy	8%	N/A		N/A	N/A	N/A	9%		N/A	6%	
January 1, 2021– paper absorption porewater												
CEC sorption isotherm (5 m bgs)												
ES-H3	LOD	0.00	0.97		0.01	2.42	0.00	0.01		0.00	0.00	
	precision	1%	N/A		N/A	N/A	1%	N/A		N/A	1%	
	accuracy	23%	N/A		N/A	N/A	14%	N/A		N/A	4%	
ES-L2	precision	N/A	N/A		N/A	15%	0%	1%		N/A	0%	
	accuracy	N/A	N/A		N/A	15%	0%	8%		N/A	0%	
Seawater	precision	N/A	0%		0%	4%	2%	2%		N/A	2%	
	accuracy	N/A	0%		0%	18%	6%	6%		N/A	21%	
CHK std	precision	2%	N/A		N/A	N/A	N/A	4%		N/A	2%	
	accuracy	5%	N/A		N/A	N/A	N/A	36%		N/A	14%	
August 10, 2021 – Crush and leach												
n = 11												
ES-H3	LOD	0.04	0.76		0.34	0.00	0.10	0.00		0.14	0.01	
	precision	1%	N/A		N/A	N/A	2%	N/A		N/A	1%	
	accuracy	8%	N/A		N/A	N/A	13%	N/A		N/A	4%	
ES-L2	precision	N/A	N/A		N/A	40%	N/A	2%		N/A	N/A	
	accuracy	N/A	N/A		N/A	29%	N/A	3%		N/A	N/A	
Seawater	precision	N/A	0%		0%	2%	7%	2%		9%	1%	
	accuracy	N/A	0%		0%	3%	11%	4%		20%	2%	

Table C4. cont												
		Ba ²⁺ ppb	Br [−] ppb	Ca ²⁺ ppm	Cl [−] ppm	K ⁺ ppb	Li ⁺ ppb	Mg ²⁺ ppb	Na ⁺ ppm	Rb ⁺ ppb	Sr ²⁺ ppb	Ni ²⁺ ppb
Aug 17, 2021– Cation exchange capacity												
Exchangeable cation sites												
		n = 10										
ES-H3	LOD	0.08	1.61		0.19	0.04	0.36	0.00		0.40	0.02	
	precision	3%	N/A		N/A	N/A	4%	N/A		N/A	2%	
	accuracy	12%	N/A		N/A	N/A	17%	N/A		N/A	5%	
ES-L2	precision	N/A	N/A		N/A	46%	0%	4%		N/A	N/A	
	accuracy	N/A	N/A		N/A	56%	0%	9%		N/A	N/A	
Seawater	precision	N/A	0%		0%	5%	28	2%		15%	2%	
	accuracy	N/A	0%		0%	11%	19%	5%		98%	3%	

C1. Example of Match! Software report for sample 019 (12mBGS)

Match! Phase Analysis Report

Sample: 019

Sample Data

File name	019.txt
File path	C:/Users/thinkpad/Dropbox/PAM/Bilberry Creek/XRD
Data collected	Feb 27, 2022 19:57:11
Data range	1.960° - 71.940°
Original data range	2.000° - 71.980°
Number of points	3500
Step size	0.020
Rietveld refinement converged	No
Alpha2 subtracted	No
Background subtr.	Yes
Data smoothed	Yes
2theta correction	-0.04°
Radiation	X-rays
Wavelength	1.541874 Å

Matched Phases

Index	Amount (%)	Name	Formula sum
A	40.6	Orthoclase	Al1.02 K O8 Si2.98
B	28.3	Albite	Al Na O8 Si3
C	15.7	Quartz	O2 Si
D	5.3	Amphibole	Al2.3 Ca1.94 F0.26 Fe2.76 H2.12 K1.9 Mg1.8 Na1.56 O23.74 Si6.08 Ti0.06
E	4.6	Biotite	Al F H K Mg3 O11 Si3
F	2.6	Chlorite	Al0.865 Fe0.255 H4 Mg2.292 O9 Si1.588
G	2.3	Vermiculite	C12 H2 Al1.43 Fe0.48 Mg2.37 N2 O16 Si2.72
H	0.5	Anorthoclase	Al1.1 Ca0.1 K0.27 Na0.63 O8 Si2.9
	5.4	Unidentified peak area	

Amounts calculated by RIR (Reference Intensity Ratio) method

Elemental composition of sample (identified crystalline phases only)

Element	Amount (weight %)
O	50.39%
Si	33.33%
Al	8.42%
K	7.27%
Na	2.84%
Mg	1.88%
Fe	1.07%
C	0.59%
Ca	0.51%
F	0.21%
N	0.11%
H	0.08%
LE (sum)	51.38%

Matching entry details

A: Orthoclase (40.6 %)*

Formula sum	Al1.02 K O8 Si2.98
Entry number	96-900-0305
Figure-of-Merit (FoM)	0.614292*
Total number of peaks	586
Peaks in range	328
Peaks matched	123
Intensity scale factor	0.41*
Space group	C 1 2/m 1
Crystal system	Monoclinic
Unit cell	lI a= 8.5450 Å b= 12.9670 Å c= 7.2010 Å β= 116.000 °
I/Ic	0.72
Calc. density	2.578 g/cm ³
Reference	Phillips M. W., Ribbe P. H., "The structures of monoclinic potassium-rich feldspars Note: variety adularia", American Mineralogist 58 , 263-270 (1973)

B: Albite (28.3 %)*

Formula sum	Al Na O8 Si3
Entry number	96-900-2199
Figure-of-Merit (FoM)	0.693587*
Total number of peaks	500
Peaks in range	500
Peaks matched	190
Intensity scale factor	0.29*
Space group	C -1
Crystal system	triclinic (anorthic)
Unit cell	a= 8.1700 Å b= 12.8110 Å c= 7.1410 Å α= 93.790° β= 116.530 ° γ= 88.090 °
I/Ic	0.74
Calc. density	2.610 g/cm ³
Reference	Meneghinello E., Alberti A., Cruciani G., "Order-disorder process in the tetrahedral sites of albiteSample: 1060- 6dNote: this sample of feldspar is from Stintino, Sardinia, Italy", American Mineralogist 84 , 1144-1151 (1999)

C: Quartz (15.7 %)*

Formula sum	O2 Si
Entry number	96-901-2601
Figure-of-Merit (FoM)	0.825613*
Total number of peaks	140
Peaks in range	36
Peaks matched	32
Intensity scale factor	0.65*
Space group	P 31 2 1
Crystal system	trigonal (hexagonal axes)
Unit cell	a= 4.9140 Å c= 5.4060 Å
I/Ic	2.97
Calc. density	2.648 g/cm ³
Reference	Hazen R. M., Finger L. W., Hemley R. J., Mao H. K., "High-pressure crystal chemistry and amorphization of alpha-quartzLocality: syntheticSample: P = 1 bar", Solid State Communications 72 , 507-511 (1989)

D: Amphibole (5.3 %)*

Formula sum	Al2.3 Ca1.94 F0.26 Fe2.76 H2.12 K1.9 Mg1.8 Na1.56 O23.74 Si6.08 Ti0.06
Entry number	96-900-1549
Figure-of-Merit (FoM)	0.584904*
Total number of peaks	600
Peaks in range	396
Peaks matched	139
Intensity scale factor	0.05*
Space group	C 1 2/m 1
Crystal system	monoclinic

Unit cell	a= 9.8950 Å b= 18.1190 Å c= 5.3320 Å β= 105.170 °
I/Ic	0.64
Calc. density	3.629 g/cm ³
Reference	Oberti R, Ungaretti L, Cannillo E, Hawthorne F C, "The mechanism of Cl incorporation in amphiboleSample: Cl(0)Locality: Nuptse Glacier moraine, Everest Massif, Nepal", American Mineralogist 78 , 746-752 (1993)
E: Biotite (4.6 %)*	
Formula sum	Al F H K Mg3 O11 Si3
Entry number	96-900-0026
Figure-of-Merit (FoM)	0.667818*
Total number of peaks	226
Peaks in range	226
Peaks matched	128
Intensity scale factor	0.06*
Space group	P -1
Crystal system	triclinic (anorthic)
Unit cell	a= 5.3000 Å b= 5.3000 Å c= 60.0000 Å α= 90.000° β= 90.000 ° γ= 120.000 °
I/Ic	1.00
Calc. density	2.862 g/cm ³
Reference	Hendricks S. B., Jefferson M. E., "Polymorphism of the micas with optical measurements", AmericanMineralogist 24 , 729-771 (1939)
F: Chlorite (2.6 %)*	
Formula sum	Al0.865 Fe0.255 H4 Mg2.292 O9 Si1.588
Entry number	96-901-0167
Figure-of-Merit (FoM)	0.550823*
Total number of peaks	600
Peaks in range	305
Peaks matched	115
Intensity scale factor	0.03*
Space group	C 1 2/m 1
Crystal system	monoclinic
Unit cell	a= 5.2930 Å b= 9.1680 Å c= 14.1900 Å β= 96.790 °
I/Ic	0.72
Calc. density	2.777 g/cm ³
Reference	Zanazzi P. F., Montagnoli M., Nazzareni S., Comodi P., "Structural effects of pressure on monoclinic chlorite: a single-crystal studyLocality: Alpe Raguzzolo, Val Malenco, Italy Sample: P = 2.28 GPa", American Mineralogist 92 , 655-661 (2007)
G: Vermiculite (2.3 %)*	
Formula sum	C12 H2 Al1.43 Fe0.48 Mg2.37 N2 O16 Si2.72
Entry number	96-900-0209
Figure-of-Merit (FoM)	0.607643*
Total number of peaks	614
Peaks in range	377
Peaks matched	161
Intensity scale factor	0.08*
Space group	C 1 2 1
Crystal system	monoclinic
Unit cell	a= 5.3300 Å b= 9.1800 Å c= 17.4500 Å β= 97.000 °
I/Ic	2.44
Calc. density	2.467 g/cm ³
Reference	Kanamaru F., Vand V., "The crystal structure of a clay-organic complex of 6-amino hexanoic acid andvermiculite", American Mineralogist 55 , 1550-1561 (1970)
H: Anorthoclase (0.5 %)*	
Formula sum	Al1.1 Ca0.1 K0.27 Na0.63 O8 Si2.9
Entry number	96-901-3311
Figure-of-Merit (FoM)	0.619348*

Total number of peaks	506
Peaks in range	506
Peaks matched	194
Intensity scale factor	0.00*
Space group	C -1
Crystal system	triclinic (anorthic)
Unit cell	a= 7.8900 Å b= 12.7200 Å c= 6.9600 Å α = 92.460° β = 116.530 ° γ = 90.830 °
I/Ic	0.66
Calc. density	2.855 g/cm ³
Reference	Nestola F., Curetti N., Benna P., Ivaldi G., Angel R., Bruno E., "Compressibility and high-pressure behavior of Ab ₆₃ Or ₂₇ An ₁₀ anorthoclase Locality: Torino, Italy Note: P = 6.0 GPa", The Canadian Mineralogist 46 , 1443-1454 (2008)

(*)2theta values have been shifted internally for the calculation of the amounts, the intensity scaling factors as well as the figure-of-merit (FoM), due to the active search-match option 'Automatic zero point adaption'.

Candidates

Name	Formula	Entry No.	FoM
Anorthoclase	Al K _{0.25} Na _{0.75} O ₈ Si ₃	96-900-0858	0.3117
Potassium tecto- alumotrisilicate (Orthoclase)	Al K O ₈ Si ₃	96-101-1206	0.2990
ammonium chlorite	Cl H ₄ N O ₂	96-220-5377	0.2950
Oneillite	Ca _{5.31} Ce _{3.24} Cl _{2.16} Fe _{4.28} K La ₂ Mn _{11.16} Na ₄₁ Nb ₃ Nd O _{230.31} Pr _{0.27} Si ₇₅ Y Zr ₁₀	96-901-0549	0.2945
Orthoclase	Al K O ₈ Si ₃	96-900-6347	0.2920
Orthoclase	Al K O ₈ Si ₃	96-900-6348	0.2889
Merrillite	Ca ₉ Fe _{0.2} Mg _{0.8} Na _{0.23} O ₂₈ P _{6.24}	96-901-0118	0.2880
Orthoclase	Al K O ₈ Si ₃	96-900-6349	0.2852
barium chlorite hydrate	Ba Cl ₂ H ₇ O _{7.5}	96-201-4931	0.2834
Vermiculite	C ₁₂ H ₂ Al _{1.43} Fe _{0.48} Mg _{2.37} N ₂ O ₁₆ Si _{2.72}	96-900-0209	0.2782
Biotite	Al _{1.207} Fe _{0.4} K _{1.906} Mg _{0.512} Mn _{0.007} Na _{0.034} O ₁₂ Si _{2.808} Ti _{0.067}	96-900-1583	0.2769
Amphibole	Al _{2.3} Ca _{1.94} F _{0.26} Fe _{2.76} H _{2.12} K _{1.9} Mg _{1.8} Na _{1.56} O _{23.74} Si _{6.08} Ti _{0.06}	96-900-1549	0.2754
Biotite	Al _{1.62} F _{0.04} Fe _{1.5} H _{1.8} K _{0.96} Mg _{0.76} Na _{0.04} O _{11.96} Si _{2.72} Ti _{0.22}	96-900-2302	0.2742
Biotite	Al _{1.78} Cl _{0.04} F _{0.16} Fe _{1.48} H _{1.56} K _{0.98} Mg _{0.7} Na _{0.02} O _{11.8} Si _{2.72} Ti _{0.16}	96-900-2304	0.2722
Biotite	Al Fe H ₂ K Mg ₂ O ₁₂ Si ₃	96-900-1266	0.2709
strontium chlorite	Cl ₂ O ₄ Sr	96-220-7381	0.2590
Orthoclase	Al _{1.02} K O ₈ Si _{2.98}	96-900-0305	0.2587
Amarillite	Fe H ₁₂ Na O ₁₄ S ₂	96-901-2893	0.2669
Illite	Al ₂ H ₂ K O ₁₂ Si ₄	96-901-3724	0.2662
Biotite	Al _{1.9} Fe _{1.44} H _{1.54} K _{0.95} Mg _{0.84} Na _{0.05} O ₁₂ Si _{2.64} Ti _{0.16}	96-900-2307	0.2619
Illite	Al ₂ H ₂ K O ₁₂ Si ₄	96-901-3722	0.2597
Biotite	Al _{1.84} Ba _{0.02} Ca _{0.02} Fe _{1.54} H _{1.6} K _{0.96} Mg _{0.7} Na _{0.03} O ₁₂ Si _{2.64} Ti _{0.2}	96-900-2306	0.2596
Illite	Al ₂ H ₂ K O ₁₂ Si ₄	96-901-3721	0.2578
Merrillite	Ca _{9.45} Fe _{0.22} Mg _{0.78} O ₂₈ P ₇	96-901-6664	0.2557
Biotite	Al _{1.27} Ca _{0.007} Cr _{0.006} Fe _{0.942} K _{0.915} Mg _{1.476} Mn _{0.024} Na _{0.015} O ₁₂ Si _{2.736} Ti _{0.39}	96-900-1352	0.2538
Biotite	Al _{1.999} K _{0.5} Mg _{2.001} O ₁₂ Si ₃	96-900-0469	0.2531
Biotite	Al Fe H ₂ K Mg ₂ O ₁₂ Si ₃	96-900-1269	0.2509
Biotite	Al _{1.249} Ca _{0.009} Cr _{0.006} Fe _{1.239} K _{0.968} Mg _{1.401} Mn _{0.024} Na _{0.02} O ₁₂ Si _{2.832} Ti _{0.231}	96-900-1353	0.2505
Biotite	Al Fe K Mg ₂ O ₁₂ Si ₃	96-900-1267	0.2495
Biotite	Al _{1.9} Ba _{0.01} Ca _{0.03} F _{0.32} Fe _{1.38} H _{1.56} K _{0.96} Mg _{0.73} Na _{0.02} O _{11.68} Si _{2.68} Ti _{0.14}	96-900-2303	0.2477

Biotite	Al1.428 Ca0.001 Cr0.006 Fe1.296 K0.914 Mg1.245 Mn0.009 Na0.022 O12 Si2.764Ti0.198	96-900-1354	0.2476
Biotite	Al1.96 Fe1.36 H1.56 K0.98 Mg0.72 Na0.02 O12 Si2.68 Ti0.16	96-900-2305	0.2476
Tweddillite	Al1.43 Ca Fe0.257 H Mn1.313 O13 Si3 Sr	96-900-9523	0.2472
Biotite	Al1.208 Fe1.392 K Mg1.161 O12 Si2.792 Ti0.276	96-900-0744	0.2470
Biotite	Al Fe H2 K Mg2 O12 Si3	96-900-1265	0.2470
Biotite	Al1.24 Fe1.4 H1.64 K0.98 Mg0.71 Na0.02 O12 Si1.36 Ti0.16	96-900-2308	0.2432
Biotite	Al Fe H2 K Mg2 O12 Si3	96-900-1268	0.2425
Potassium iron dimagnesium phylloaluminosilicate dihydroxide (Biotite)	Al Fe H2 K Mg2 O12 Si3	96-100-0039	0.2416
Hillite	Ca2 H4 Mg0.377 O10 P2 Zn0.623	96-900-4787	0.2409
Chlorite	H4 Mg3 O9 Si2	96-900-0159	0.2407
Chlorite	Al0.865 Fe0.255 H4 Mg2.292 O9 Si1.588	96-901-0170	0.2395
Biotite	Al1.369 Ca0.03 Cr0.048 Fe0.39 K0.955 Mg2.166 Mn0.021 Na0.015 O12 Si2.856Ti0.144	96-900-1347	0.2384
Biotite	Al1.216 Fe1.215 K0.946 Mg1.545 Mn0.018 Na0.032 O12 Si2.784 Ti0.225	96-900-1584	0.2383
Illite	Al2 H2 K O12 Si4	96-901-3723	0.2383
Chlorite	Al0.865 Fe0.255 H4 Mg2.292 O9 Si1.588	96-901-0169	0.2378
Illite	Al2 H2 K O12 Si4	96-901-3719	0.2365
Biotite	Al3.3 Fe3.512 K2 Mg7.164 O48 Si5.68 Ti1.344	96-900-0845	0.2341
Leadhillite	C2 H2 O12 Pb4 S	96-900-3815	0.2327
Illite	Al2 H2 K O12 Si4	96-901-3720	0.2327
Merrillite	Ca9.443 Fe0.065 Mg0.935 O28 P6.964	96-901-0494	0.2318
Vermiculite	C12 Mg3 N4 O12 Si4	96-900-0119	0.2305
Leadhillite	C2 H2 O12 Pb4 S	96-901-4065	0.2303
and 46 others...			

Search-Match

Settings

Reference database used	COD-Inorg 2021.12.14
Automatic zeropoint adaptation	Yes
Downgrade entries with low scaling factors	Yes
Minimum figure-of-merit (FoM)	0.60
2theta window for peak corr.	0.30 deg.
Minimum rel. int. for peak corr.	0
Parameter/influence 2theta	0.50
Parameter/influence intensities	0.50
Parameter multiple/single phase(s)	0.50

Criteria for entries added by user

Reference:

Entry number: 96-900-1549;96-900-1665;96-900-3815;96-900-4787;96-900-4919;96-900-7429;96-900-7612;96-900-9523;96-900-9666;96-901-0118;96-901-0494;96-901-0549;96-901-1123;96-901-1745;96-901-1746;96-901-2893;96-901-3719;96-901-3720;96-901-3721;96-901-3722;96-901-3723;96-901-3724;96-901-3733;96-901-3985;96-901-4065;96-901-6664;96-201-4618;96-201-4619;96-201-4931;96-220-5377;96-220-7380;96-220-7381;96-900-0159;96-900-4189;96-901-0164;96-901-0165;96-901-0166;96-901-0167;96-901-0168;96-901-0169;96-901-0170;96-101-1206;96-900-0162;96-900-0163;96-900-0305;96-900-0312;96-900-0856;96-900-0857;96-900-0858;96-900-0859;96-900-0860;96-900-0861;96-900-6347;96-900-6348;96-900-6349;96-901-3309;96-901-3310;96-901-3311;96-100-0037;96-900-0010;96-900-0017;96-900-0061;96-900-0119;96-900-0147;96-900-0209;96-901-5236;96-

100-0039;96-900-0026;96-900-0468;96-900-0469;96-900-0744;96-900-0843;96-900-0844;96-900-0845;96-900-1265;96-900-1266;96-900-1267;96-900-1268;96-900-1269;96-900-1347;96-900-1348;96-900-1349;96-900-1350;96-900-1351;96-900-1352;96-900-1353;96-900-1354;96-900-1583;96-900-1584;96-900-2302;96-900-2303;96-900-2304;96-900-2305;96-900-2306;96-900-2307;96-900-2308

Peak List

No.	2theta [°]	d [Å]	I/I0 (peak height)	Counts (peak area)	FWHM	Matched
1	10.48	8.4414	31.07	14.14	0.1200	D,E,G
2	12.46	7.1041	29.65	22.49	0.2000	F
3	19.26	4.6085	23.95	25.43	0.2800	A,B,E,F,G,H
4	19.64	4.5202	28.70	13.06	0.1200	D,E,F,G,H
5	20.86	4.2585	155.38	94.29	0.1600	A,C,D,E,F,G,H
6	22.02	4.0367	205.57	124.74	0.1600	B,D,E,F,G
7	22.96	3.8736	38.49	40.87	0.2800	A,B,D,E,F,G,H
8	23.58	3.7731	115.57	87.67	0.2000	A,B,E,G,H
9	24.30	3.6629	115.83	87.86	0.2000	B,D,E,F,H
10	25.16	3.5396	47.24	64.49	0.3600	A,E,F,H
11	25.56	3.4851	74.31	90.19	0.3200	A,B,E,F,G,H
12	26.64	3.3462	1000.00	606.83	0.1600	B,C,D,E,G,H
13	27.10	3.2905	90.19	656.75	1.9200	A,D,E,F,H
14	27.94	3.1934	474.25	503.63	0.2800	B,H
15	28.28	3.1558	44.03	86.83	0.5200	B,D,E,G,H
16	29.82	2.9962	57.54	61.11	0.2800	A,B,D,E,G
17	30.42	2.9385	117.93	143.13	0.3200	A,B,D,F,H
18	30.84	2.8994	60.13	54.73	0.2400	A,B,E,G,H
19	31.40	2.8490	36.11	43.83	0.3200	B,E,H
20	33.00	2.7144	76.20	57.80	0.2000	B,D,E,H
21	34.10	2.6293	78.83	155.48	0.5200	B,D,E,F,G,H
22	34.50	2.5998	71.58	119.45	0.4400	A,D,E,G,H
23	35.06	2.5595	111.38	202.76	0.4800	A,B,D,E,F,G,H
24	36.56	2.4579	122.35	74.24	0.1600	A,B,C,D,E,G,H
25	37.66	2.3886	54.56	49.66	0.2400	A,B,D,E,F,G,H
26	39.46	2.2837	89.83	40.88	0.1200	A,B,C,D,E,F,G,H
27	40.30	2.2380	36.49	16.61	0.1200	A,B,C,D,E,F,G,H
28	41.24	2.1891	29.21	17.73	0.1600	A,B,D,E,F,G,H
29	41.72	2.1650	48.67	44.30	0.2400	A,B,D,E,F,G,H
30	42.44	2.1300	78.65	47.73	0.1600	A,B,C,D,E,F,G,H
31	44.92	2.0180	41.88	76.25	0.4800	A,B,D,E,F,G,H
32	45.78	1.9820	50.35	45.83	0.2400	A,B,C,D,E,F,G,H
33	49.20	1.8520	33.83	20.53	0.1600	A,B,D,E,F,G,H
34	50.12	1.8201	142.89	86.71	0.1600	A,B,C,D,E,F,G,H
35	50.68	1.8013	40.19	48.78	0.3200	A,B,C,D,F,G,H
36	51.32	1.7803	34.53	10.48	0.0800	A,B,D,E,F,G,H
37	54.86	1.6735	50.60	23.03	0.1200	A,B,C,F,G,H
38	55.32	1.6607	26.07	15.82	0.1600	A,B,C,D,F,G,H
39	59.94	1.5433	145.52	110.38	0.2000	A,B,C,D,F,G,H
40	61.62	1.5052	29.52	26.87	0.2400	A,B,D,F,G,H
41	64.00	1.4548	31.01	14.11	0.1200	A,B,C,D,F,G,H
42	67.72	1.3837	57.08	25.98	0.1200	A,C,D,F,G,H
43	67.90	1.3804	34.89	79.39	0.6000	A,C,D,F,G,H
44	68.30	1.3733	70.41	53.41	0.2000	A,C,D,F,G,H

Integrated Profile Areas

Based on calculated profile

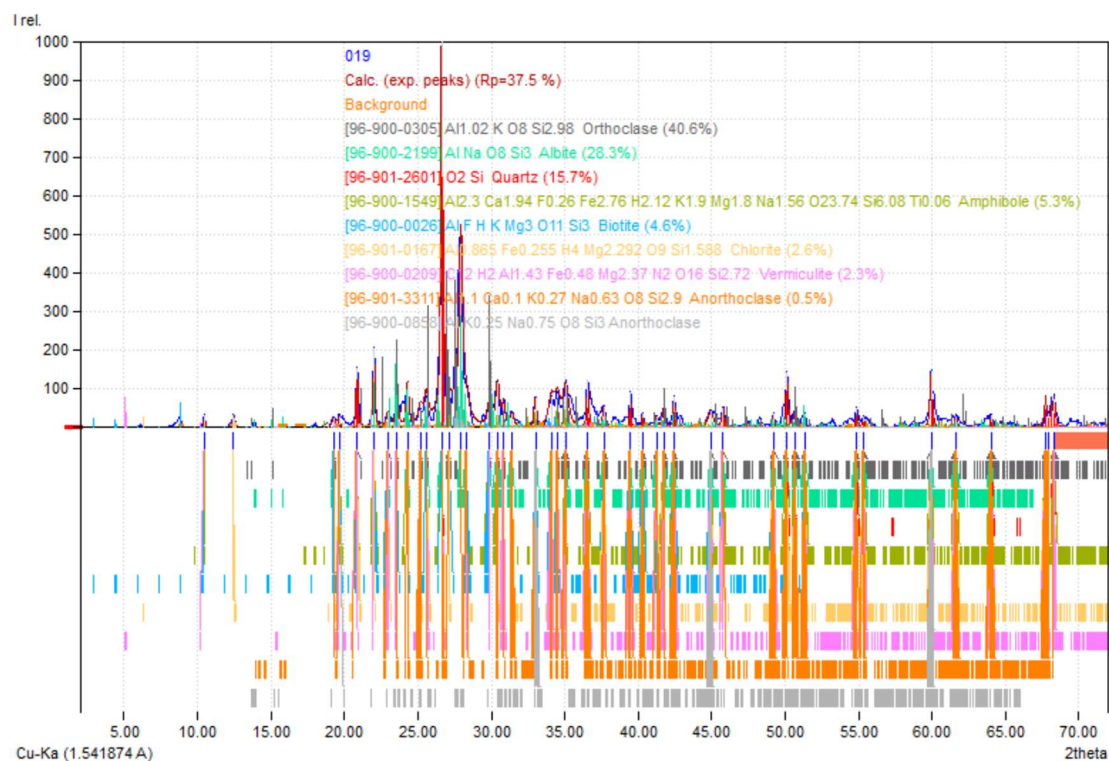
Profile area	Counts	Amount
Overall diffraction profile	283448	100.00%

Background radiation	25743	9.08%
Diffraction peaks	257705	90.92%
Peak area belonging to selected phases	242347	85.50%
Peak area of phase A (Orthoclase)	78220	27.60%
Peak area of phase B (Albite)	70634	24.92%
Peak area of phase C (Quartz)	50116	17.68%
Peak area of phase D (Amphibole)	19277	6.80%
Peak area of phase E (Biotite)	10376	3.66%
Peak area of phase F (Chlorite)	7383	2.60%
Peak area of phase G (Vermiculite)	5321	1.88%
Peak area of phase H (Anorthoclase)	1020	0.36%
Unidentified peak area	15358	5.42%

Peak Residuals

Peak data	Counts	Amount
Overall peak intensity	4286	100.00%
Peak intensity belonging to selected phases	4281	99.88%
Unidentified peak intensity	5	0.12%

Diffraction Pattern Graphics



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Appendix D: Supplementary information for Chapter 5

D1. Experimental design for testing porewater solute adsorption to Whatman® 1 CHR

The purpose of this experiment is to determine if the discrepancy in porewater concentrations between PAM and centrifuge extraction methods can be explained by adsorption of ions to the paper. This discrepancy can be seen in Figure 4.3 for Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} . Sorption isotherms for I^- , Br^- , Cl^- , SO_4^{2-} , F^- , Na^+ , Ca^{2+} , K^+ , Mg^{2+} , Sr^{2+} , Ba^{2+} , Al^{3+} , Fe^{2+} , Li^+ , Rb^+ , Ni^{2+} , Mn^{2+} , and B^{3+} to the paper pH 5, 7, and 9 is proposed.

D1.2. Method design

D1.2.1. Synthetic porewater recipe

The synthetic porewater (SPW) recipe was generated from maximum porewater concentration values obtained by the centrifuge method from mud samples examined in Chapter 4 (Table D1). The elemental concentrations of Rb^+ , Ni^{2+} , and Li^+ have been increased by a factor of 25 so that the salt mass can be measured gravimetrically. Salts of B^{3+} , Ba^{2+} , and are not readily available, so certified reference standards will be used diluted from 1000 to 2 ppm. The elemental concentration of Ba^{2+} has been increased by a factor of 25 and F^- and B^{3+} by a factor of 2.5 so that the standards can be dispensed using 20 uL pipette then quantified gravimetrically. The proposed SPW was modeled using PHREEQC to ensure dissolution of all solutes

Table D11. SPW recipe based on porewater concentrations obtained by centrifuge from mud samples presented in Chapter 4.

Maximum concentration in porewater			
element	Centrifuge mmol/kgw	Paper absorption mmol/kgw	SPW mmol/kgw
Al ³⁺	0.0538	0.0394	0.0102
B ³⁺	0.1736	0.2140	1.7399
Ba ²⁺	0.0010	0.0007	0.0137
Br ⁻	0.1876	0.1540	0.1538
Ca ²⁺	5.3300	5.4429	0.3359
Cl ⁻	97.2298	85.2944	7.0503
Fe ²⁺	0.1723	0.0360	0.0118
I ⁻	0.0101	N/A	0.0387
K ⁺	1.5926	1.5247	0.1979
Li ⁺	0.0051	0.0035	0.0445
Mg ²⁺	6.9024	4.9246	0.5037
Mn ²⁺	0.0586	0.0340	0.0649
Na ⁺	92.6835	100.129	5.4958
Ni ²⁺	0.0001	0.0006	0.0123
Rb ⁺	0.0001	0.0001	0.0166
SO ₄ ²⁻	4.9160	3.3768	0.0394
Sr ²⁺	0.0219	0.0110	0.1218
F ⁻	0.1068	N/A	0.425
SPW recipe			
Salt	Molar mass	g per kgw	
RbCl	120.918	0.020	
NiNO ₃	120.693	0.0148	
LiBr	86.844	0.0387	
AlCl ₃	133.332	0.0135	
SrCl ₂ · 6H ₂ O	276.52	0.3367	
KI	165.998	0.0642	
CaCl ₂ · 2H ₂ O	146.978	0.4937	
Mn(OH) ₂	88.938	0.0577	
MgSO ₄ · 6H ₂ O	228.361	0.0577	
Na ₂ S ₂ O ₃	158.11	0.6110	
MgCl ₂ · 6H ₂ O	167.755	0.8010	
NaBr	102.894	0.1125	
Fe(III)Cl ₃ · 6H ₂ O	270.195	0.0318	
KCl	74.548	0.1187	
NaCl	58.44	2.9220	
No salts available. Use certified standards diluted to 2 ppm (from 1000 ppm)			
element	mmol/kgw	mL per kgw	
B ³⁺	0.1850	0.0940	
Ba ²⁺	0.0146	0.0188	
F ⁻	0.1052	0.0404	

Table D12. PHREEQC output of saturation indices of SPW recipe presented in Table D1.

-----Saturation indices-----				
Phase	SI**	log IAP	log K(298 K,1 atm)	
Al(OH)3(a)	-3.02	7.78	10.80	Al(OH)3
Alunite	-7.98	-9.38	-1.40	KAl3(SO4)2(OH)6
Anhydrite	-4.19	-8.47	-4.28	CaSO4
Aragonite	-4.07	-12.41	-8.34	CaCO3
Barite	0.28	-9.56	-9.84	BaSO4
Calcite	-3.93	-12.41	-8.48	CaCO3
Celestite	-2.25	-8.91	-6.66	SrSO4
CH4(g)	-61.36	-64.17	-2.80	CH4
CO2(g)	-3.50	-4.97	-1.47	CO2 Pressure 0.0 atm, phi 1.000
Dolomite	-7.56	-24.65	-17.09	CaMg(CO3)2
Fe(OH)3(a)	0.31	5.20	4.89	Fe(OH)3
FeS(ppt)	-55.96	-59.88	-3.92	FeS
Fluorite	0.02	-10.58	-10.60	CaF2
Gibbsite	-0.33	7.78	8.11	Al(OH)3
Goethite	6.20	5.20	-1.00	FeOOH
Gypsum	-3.89	-8.47	-4.58	CaSO4:2H2O
H2(g)	-20.95	-24.05	-3.10	H2
H2O(g)	-1.50	-0.00	1.50	H2O
H2S(g)	-59.66	-67.65	-7.99	H2S
Halite	-6.07	-4.50	1.57	NaCl
Hausmannite	-14.59	46.44	61.03	Mn3O4
Hematite	14.41	10.40	-4.01	Fe2O3
Jarosite-K	-7.91	-17.12	-9.21	KFe3(SO4)2(OH)6
Mackinawite	-55.23	-59.88	-4.65	FeS
Manganite	-6.38	18.96	25.34	MnOOH
Melanterite	-7.73	-9.94	-2.21	FeSO4:7H2O
O2(g)	-41.39	-44.29	-2.89	O2
Pyrite	-88.15	-106.63	-18.4	8FeS2
Pyrochroite	-6.68	8.52	15.20	Mn(OH)2
Pyrolusite	-11.97	29.41	41.38	MnO2:H2O
Rhodochrosite	-2.00	-13.13	-11.13	MnCO3
Siderite	-2.99	-13.88	-10.89	FeCO3
Strontianite	-3.58	-12.85	-9.27	SrCO3
Sulfur	-44.69	-39.81	4.88	S
Sylvite	-6.84	-5.94	0.90	KCl
Witherite	-4.94	-13.50	-8.56	BaCO3

D1.2.2. Paper to SPW ratio

A paper to SPW ratio is chosen to ensure both workable solution volumes and quantifiable changes in solute masses during sorption. The ratio has been chosen porewater Ba^{2+} as a representative element (Figure 4.8) and the average paper mass used for porewater extraction from the Champlain muds (0.39 g).

Approximately $0.0014 \mu\text{g Ba}^{2+}$ can be expected to sorb to 0.39 g of paper (three 4.5 cm diameter papers) if a 1 ppb Ba^{2+} solution is used and a 5 mL aliquot of 1 ppb Ba^{2+} will contain $0.005 \mu\text{g Ba}^{2+}$. This should result in 31% of the Ba^{2+} contained in the SPW sorbing to the paper so 12.8:1 (or 5 mL SPW to 0.39 g paper) should be quantifiable.

D1.2.3. Dilution factors

The average limit of detection for Ba^{2+} is 0.3 ppb for three ICP-MS analyses. The highest Ba^{2+} concentration in the Champlain mud was 188 ppm and the SPW contains 1880 ppb Ba^{2+} . Dilutions of 33 x and 50 x will yield Ba^{2+} concentrations of 57 ppb and 38 ppb respectively. Assuming 31 % sorption, then at the low concentration 26 ppb should remain in the solution. This is above the detection limit.

D1.2.4. pH adjustment

Adsorption will be conducted at three pHs: 5, 7, and 9. The pH 5 solution will be buffered with acetate buffer and for pHs 7 and 9, Tris buffer will be used. Buffer recipes are as follows:

- For 10 mL at pH 5.0 and a 0.1 M buffer, 0.055 g of sodium acetate and 0.020 g of acetic acid is needed.
- For 0 mL at pH 7.1 and a 0.01 M buffer, 0.0144 g of Tris HCl and 0.0010 g of Tris is needed.

- For 10 mL at pH 9 and a 0.01 M buffer, 0.0018 g of Tris HCl and 0.0107 g of Tris is needed.

D1.2.5. Equilibration duration

A 24 hour equilibration duration is recommended.

D1.3. Method summary

- Make SPW according to above recipe (10x concentrated).
- Dilute SPW to 3 dilutions (full strength, 33x and 50x) making 100 mL of each solution.
- Adjust the pH of 30 mL of each diluted solution with the appropriate buffer.
- Place weighed paper in a 15 mL centrifuge tube.
- Add a 5 mL aliquot of solution to the paper making sure the paper is submerged.
- Equilibrate for 24-hours.
- Filter the liquid through a 0.45 μ m filter and prepare for ICP-MS analysis.
- Prepare original solution in the same way as the soaking solutions.

D2. Calibration of transmission NIR spectrometer for measurement of porewater samples smaller than 35 mg

The transmission near infrared (NIR) apparatus was designed to quantify the water content of a 4.5 cm diameter Whatman[®] 1 CHR paper. It consists of a vertical stack of two opaque tubes with an optically pure quartz lined sample slot in between, a NIR light source (tungsten-halogen light source, Thorlabs QTH10) on the bottom, and an NIR spectrometer (Ocean Optics NIR Quest) connected by a 600 μm diameter fiber optic cable at the top (Figure D1).

As the light source warms up, it can reach a temperature of 50 °C. Liquid water NIR absorption is temperature dependent (Langford et al., 2001), so a constant sample temperature is maintained at 22 to 23 °C using a cooling coil located between the light source and the sample. During instrument use, water is circulated through the cooling coil around the bottom black tube. The instrument was calibrated using the same evaporation technique as described by Celejewski et al., (2014, Figure D2)

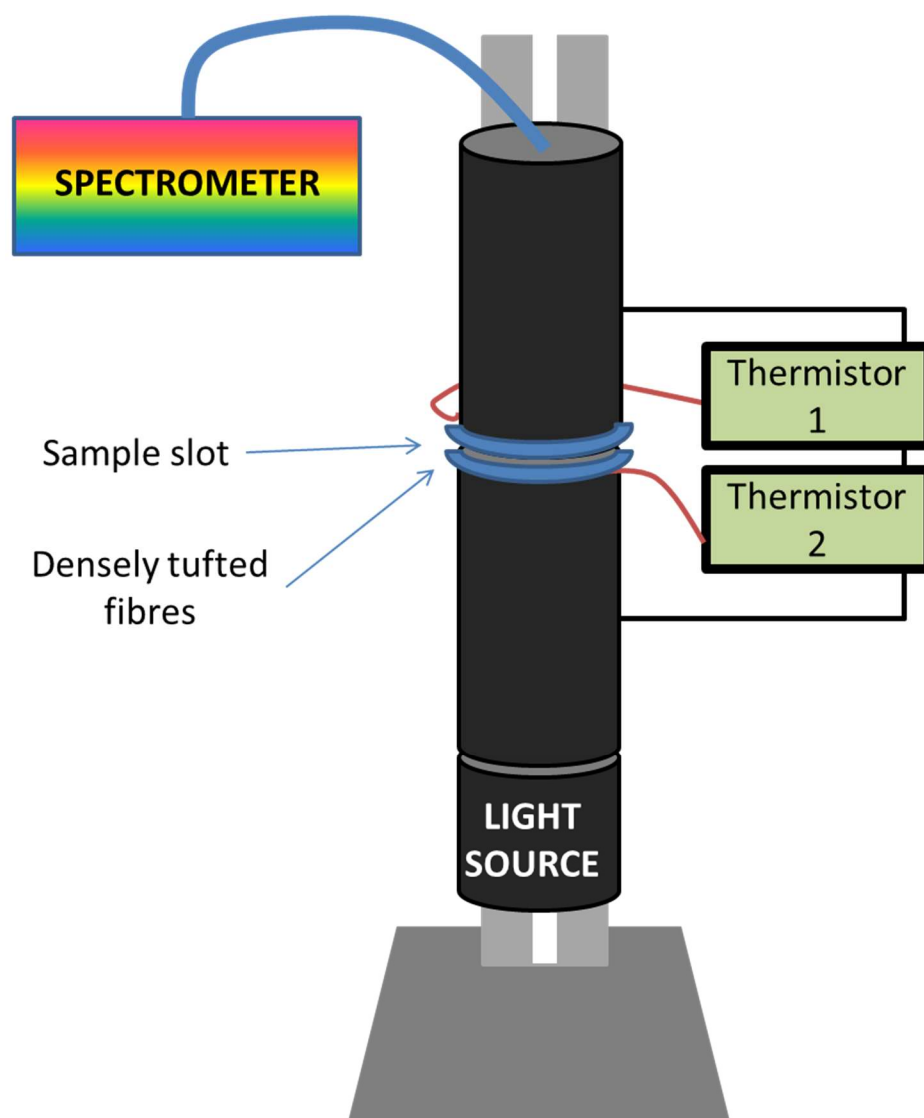


Figure D1. Diagram of transmission NIR apparatus.

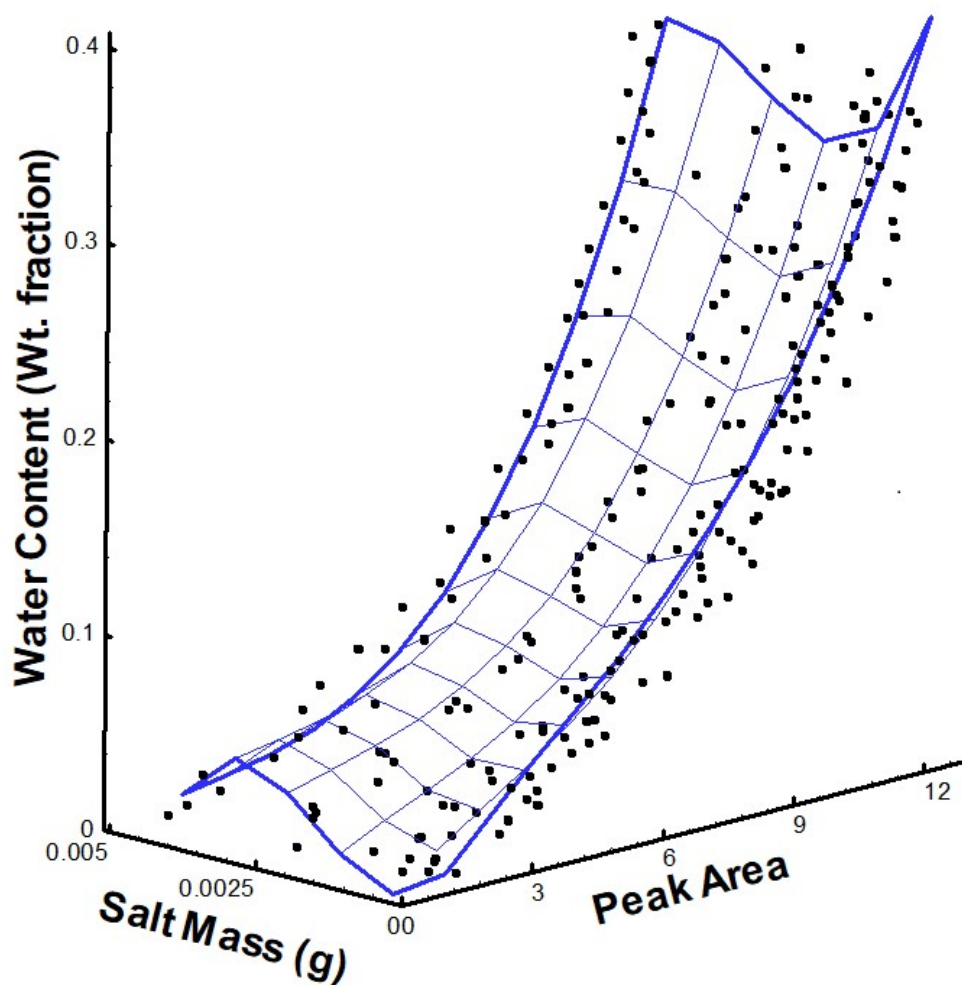


Figure D2. Calibration surface of transmission NIR, correlating paper water content (wt. %) and salt mass (g) to the absorption peak.

Table D3. Equation and error statistics of transmission NIR spectrometer calibration surface (summary of zunzun.com output).

$z = a + bx + cy + dx^2 + fy^2 + gx^3 + hy^3 + ixy + jx^2y + kxy^2$			
Fitting target of lowest sum of squared absolute error = 3.028079E-01			
a	-1.69E-02	Absolute	Error
b	-3.47E+01	Minimum:	-0.158
c	2.90E-02	Maximum:	0.068
d	3.22E+04	Mean:	0.000
f	-2.21E-03	Std error of mean	0.002
g	-5.11E+06	Median:	0.000
h	2.16E-04	Variance:	0.001
i	-1.05E+01	Standard deviation	0.032
j	1.07E+03	Skew:	-1.029
k	3.70E-01	Kurtosis:	3.086

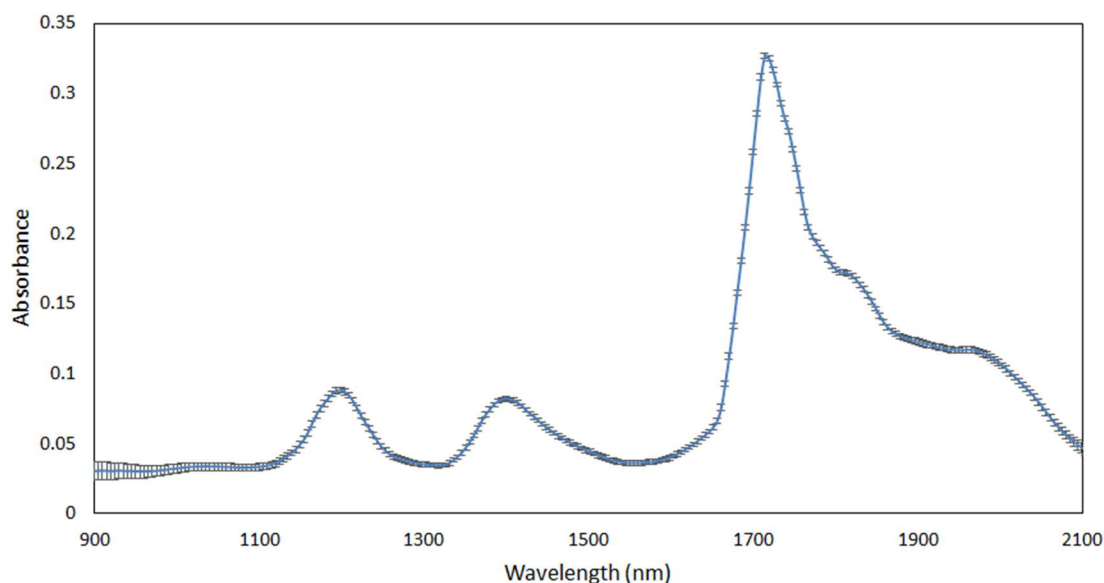


Figure D3. Polystyrene check standards measured during calibration of transmission NIR. Error bars represent standard deviation.

Table D4. Data used for transmission NIR spectrometer calibration surfaces (zunzun.com input).

total salt mass (g)	Peak B area	Water content (% mass)	Predicted water content (% mass)	total salt mass (g)	NIR response	Water content (% mass)	Predicted water content (% mass)
0.0000	0.4060	0.0000	-0.0055	0.0003	1.6375	0.0049	0.0121
0.0000	2.2244	0.0059	0.0391	0.0003	1.1511	0.0134	0.0019
0.0000	2.2191	0.0074	0.0390	0.0003	2.6445	0.0191	0.0320
0.0000	3.5269	0.0215	0.0675	0.0003	4.2954	0.0513	0.0634
0.0000	3.5701	0.0357	0.0684	0.0003	4.8228	0.0647	0.0740
0.0000	1.9954	0.0398	0.0340	0.0003	6.4662	0.0782	0.1115
0.0000	2.0740	0.0422	0.0358	0.0003	5.3801	0.0924	0.0858
0.0000	2.0857	0.0430	0.0360	0.0003	7.8531	0.1104	0.1517
0.0000	4.2537	0.0483	0.0832	0.0003	8.3952	0.1246	0.1703
0.0000	2.9322	0.0551	0.0547	0.0003	9.1584	0.1576	0.2000
0.0000	5.1439	0.0706	0.1033	0.0003	6.0008	0.1965	0.1000
0.0000	3.6031	0.0714	0.0691	0.0003	5.3626	0.2436	0.0854
0.0000	4.5400	0.0827	0.0895	0.0003	8.8161	0.2541	0.1862
0.0000	4.4288	0.0877	0.0871	0.0003	9.3114	0.2811	0.2064

Table D4 cont.							
total salt mass (g)	Peak B area	Water content (% mass)	Predicted water content (% mass)	total salt mass (g)	NIR response	Water content (% mass)	Predicted water content (% mass)
0.0000	6.0534	0.0944	0.1257	0.0003	11.5644	0.2818	0.3254
0.0000	5.2423	0.0992	0.1056	0.0003	11.8655	0.3162	0.3451
0.0000	5.3642	0.1044	0.1085	0.0003	12.3718	0.3731	0.3805
0.0000	6.5722	0.1107	0.1396	0.0003	1.0279	0.0088	-0.0009
0.0000	6.0565	0.1172	0.1258	0.0003	2.8272	0.0250	0.0354
0.0000	6.5301	0.1315	0.1385	0.0003	3.3115	0.0447	0.0445
0.0000	7.6067	0.1322	0.1709	0.0003	4.6302	0.0650	0.0700
0.0000	6.7917	0.1477	0.1459	0.0003	5.1610	0.0884	0.0810
0.0000	7.4276	0.1555	0.1651	0.0003	6.6458	0.1103	0.1160
0.0000	7.6574	0.1568	0.1726	0.0003	7.8946	0.1390	0.1529
0.0000	6.9766	0.1591	0.1513	0.0003	8.5705	0.1609	0.1766
0.0000	8.2546	0.1840	0.1934	0.0003	9.3581	0.1926	0.2083
0.0000	8.7915	0.1865	0.2140	0.0003	7.3927	0.2122	0.1371
0.0000	7.6308	0.2122	0.1717	0.0003	10.1768	0.2326	0.2464
0.0000	8.8887	0.2132	0.2179	0.0003	10.3517	0.2477	0.2553
0.0000	8.8095	0.2184	0.2147	0.0003	10.7250	0.2786	0.2753
0.0000	9.1084	0.2355	0.2270	0.0003	11.2480	0.3111	0.3055
0.0000	9.5346	0.2447	0.2458	0.0003	11.4498	0.3367	0.3180
0.0000	9.1291	0.2607	0.2279	0.0003	11.4606	0.3669	0.3186
0.0000	8.9736	0.2630	0.2214	0.0003	1.1887	0.0148	0.0025
0.0000	10.2301	0.2717	0.2795	0.0003	1.5440	0.0249	0.0100
0.0000	9.2575	0.2903	0.2334	0.0003	3.8141	0.0466	0.0538
0.0000	9.9213	0.2935	0.2640	0.0003	5.0490	0.0555	0.0783
0.0000	10.7767	0.3175	0.3090	0.0003	5.0465	0.0765	0.0783
0.0000	10.7918	0.3328	0.3099	0.0003	7.4017	0.1101	0.1370
0.0000	11.1103	0.3415	0.3284	0.0003	8.1699	0.1325	0.1619
0.0000	9.7765	0.3472	0.2571	0.0003	9.0604	0.1572	0.1954
0.0000	11.5508	0.3707	0.3557	0.0003	9.6406	0.1751	0.2205
0.0000	10.4377	0.3753	0.2904	0.0003	10.5408	0.2050	0.2649
0.0000	11.5921	0.3805	0.3583	0.0003	11.0235	0.2356	0.2918
				0.0003	11.4450	0.2513	0.3173
				0.0003	11.6260	0.2730	0.3288
				0.0003	11.7733	0.2977	0.3384
				0.0003	12.1272	0.3283	0.3625
				0.0003	12.1272	0.3560	0.3625
0.0007	0.9687	0.0064	-0.0072	0.0013	2.9464	0.0242	0.0224
0.0007	1.1216	0.0123	-0.0043	0.0013	3.7555	0.0377	0.0330
0.0007	1.3121	0.0216	-0.0008	0.0013	4.6140	0.0182	0.0453
0.0007	1.3947	0.0213	0.0008	0.0013	5.7523	0.0634	0.0645

Table D4 cont.							
total salt mass (g)	Peak B area	Water content (% mass)	Predicted water content (% mass)	total salt mass (g)	NIR response	Water content (% mass)	Predicted water content (% mass)
0.0007	1.8600	0.0351	0.0090	0.0013	7.1190	0.1068	0.0946
0.0007	2.6333	0.0269	0.0220	0.0013	7.2305	0.0876	0.0974
0.0007	3.0051	0.0414	0.0281	0.0013	7.4418	0.1253	0.1031
0.0007	3.4379	0.0352	0.0353	0.0013	8.9541	0.1445	0.1523
0.0007	4.1584	0.0601	0.0474	0.0013	9.4648	0.1823	0.1728
0.0007	4.1672	0.0626	0.0475	0.0013	9.8457	0.2699	0.1896
0.0007	4.6425	0.0787	0.0559	0.0013	10.3235	0.1901	0.2126
0.0007	4.6518	0.0541	0.0562	0.0013	10.8491	0.2101	0.2405
0.0007	5.2010	0.0735	0.0664	0.0013	11.2043	0.2336	0.2610
0.0007	5.7034	0.0677	0.0767	0.0013	11.2713	0.2934	0.2650
0.0007	5.8391	0.0996	0.0794	0.0013	12.2537	0.3226	0.3298
0.0007	6.2287	0.0945	0.0881	0.0013	12.3585	0.3454	0.3374
0.0007	6.9497	0.1002	0.1060	0.0013	12.4120	0.3639	0.3414
0.0007	7.3702	0.1118	0.1174	0.0013	1.1016	0.0116	-0.0020
0.0007	7.5927	0.1422	0.1239	0.0013	2.3109	0.0359	0.0143
0.0007	7.7280	0.1299	0.1280	0.0013	3.3171	0.0442	0.0272
0.0007	7.7788	0.1175	0.1298	0.0013	4.4376	0.0525	0.0426
0.0007	8.1710	0.1387	0.1424	0.0013	5.8911	0.0735	0.0670
0.0007	8.7327	0.1676	0.1621	0.0013	6.7913	0.0924	0.0863
0.0007	8.9544	0.1591	0.1708	0.0013	8.0308	0.1263	0.1200
0.0007	9.0740	0.1422	0.1754	0.0013	8.5665	0.1413	0.1378
0.0007	9.3783	0.1574	0.1879	0.0013	9.1448	0.1835	0.1594
0.0007	9.3813	0.1877	0.1880	0.0013	9.3577	0.1579	0.1680
0.0007	9.5440	0.3280	0.1951	0.0013	10.4806	0.2415	0.2203
0.0007	9.6292	0.1916	0.1991	0.0013	10.6397	0.2159	0.2287
0.0007	9.9122	0.2123	0.2118	0.0013	10.7157	0.2769	0.2328
0.0007	9.9418	0.2595	0.2132	0.0013	11.7892	0.3107	0.2975
0.0007	9.9453	0.2059	0.2136	0.0013	11.8415	0.3823	0.3009
0.0007	9.9568	0.1972	0.2139	0.0013	11.8904	0.3507	0.3042
0.0007	10.4084	0.2631	0.2363	0.0013	11.9894	0.3311	0.3110
0.0007	10.4579	0.2331	0.2391	0.0013	-0.0637	-0.0440	-0.0204
0.0007	10.5704	0.2139	0.2448	0.0013	3.1573	-0.0119	0.0251
0.0007	10.6682	0.2370	0.2501	0.0013	4.8333	0.0214	0.0486
0.0007	10.7190	0.2505	0.2530	0.0013	4.8662	0.0140	0.0491
0.0007	10.8253	0.2452	0.2587	0.0013	6.0303	0.0392	0.0697
0.0007	11.0965	0.2678	0.2744	0.0013	7.2492	0.0629	0.0976
0.0007	11.2952	0.2897	0.2862	0.0013	8.5093	0.0889	0.1357
0.0007	11.5286	0.3101	0.3007	0.0013	8.5510	0.1148	0.1371
0.0007	11.5756	0.2982	0.3034	0.0013	9.7733	0.1311	0.1859

Table D4 cont.

total salt mass (g)	Peak B area	Water content (% mass)	Predicted water content (% mass)	total salt mass (g)	NIR response	Water content (% mass)	Predicted water content (% mass)
0.0007	11.7236	0.3388	0.3132	0.0013	10.1441	0.1422	0.2033
0.0007	11.8088	0.3864	0.3188	0.0013	10.5320	0.1630	0.2229
0.0007	11.8285	0.3623	0.3201	0.0013	10.9659	0.1786	0.2467
0.0007	12.0880	0.3571	0.3375	0.0013	11.2054	0.1949	0.2606
0.0007	12.2191	0.3832	0.3468	0.0013	11.8865	0.2542	0.3039
0.0007	12.2193	0.2935	0.3468	0.0013	12.0623	0.2801	0.3159
0.0007	12.4898	0.3296	0.3665	0.0013	12.2208	0.3105	0.3271
0.0007	12.5892	0.3535	0.3739	0.0013	12.2643	0.3246	0.3302
0.0007	12.6209	0.3709	0.3763	0.0013	12.2878	0.3557	0.3319
				0.0013	12.3396	0.3743	0.3357
0.0025	1.2984	0.0182	0.0278	0.0046	0.6854	-0.0058	0.0080
0.0025	2.7945	0.0286	0.0387	0.0047	0.9558	0.0059	0.0035
0.0025	3.1579	0.0366	0.0415	0.0045	1.1073	0.0116	0.0180
0.0025	4.8562	0.0541	0.0582	0.0045	1.7359	-0.0047	0.0201
0.0025	5.6438	0.0701	0.0692	0.0047	1.7480	0.0217	0.0062
0.0025	6.2129	0.0839	0.0789	0.0046	2.0184	0.0129	0.0126
0.0025	7.3240	0.1014	0.1031	0.0046	3.2219	0.0228	0.0191
0.0025	7.3843	0.1174	0.1046	0.0046	3.7989	0.0304	0.0238
0.0025	8.0404	0.1421	0.1231	0.0046	3.8831	0.0433	0.0245
0.0025	8.8187	0.1545	0.1494	0.0047	4.4134	0.0521	0.0252
0.0025	8.9296	0.1785	0.1536	0.0045	4.7064	0.0295	0.0416
0.0025	10.0144	0.2977	0.2004	0.0047	5.2987	0.0658	0.0378
0.0025	10.1844	0.2046	0.2088	0.0045	5.4346	0.0384	0.0523
0.0025	10.7026	0.2330	0.2364	0.0046	5.7817	0.0638	0.0511
0.0025	10.9837	0.2752	0.2525	0.0047	6.2943	0.0817	0.0575
0.0025	12.2849	0.3246	0.3399	0.0045	6.5304	0.0651	0.0745
0.0025	12.6206	0.3574	0.3659	0.0046	7.0436	0.0904	0.0812
0.0025	1.2971	0.0244	0.0287	0.0045	7.1555	0.0829	0.0911
0.0025	2.8198	0.0437	0.0396	0.0047	7.3983	0.1152	0.0879
0.0025	4.5975	0.0592	0.0557	0.0045	7.9503	0.0985	0.1167
0.0025	6.2938	0.0800	0.0809	0.0046	8.0640	0.1162	0.1149
0.0025	7.3370	0.1101	0.1039	0.0045	8.3912	0.1185	0.1334
0.0025	8.1497	0.1333	0.1270	0.0047	8.4728	0.1402	0.1275
0.0025	8.7215	0.1542	0.1464	0.0046	8.9039	0.1428	0.1499
0.0025	9.4399	0.1843	0.1748	0.0047	9.1171	0.1646	0.1567
0.0025	9.9180	0.2152	0.1964	0.0045	9.3795	0.1490	0.1778
0.0025	10.4405	0.2291	0.2227	0.0046	9.5527	0.1573	0.1820
0.0025	10.7069	0.2507	0.2373	0.0047	9.6152	0.1851	0.1823
0.0025	11.1363	0.2800	0.2624	0.0045	9.8072	0.1653	0.2004

Table D4 cont.							
total salt mass (g)	Peak B area	Water content (% mass)	Predicted water content (% mass)	total salt mass (g)	NIR response	Water content (% mass)	Predicted water content (% mass)
0.0025	11.3620	0.3132	0.2765	0.0046	9.9643	0.1801	0.2049
0.0025	11.5784	0.3434	0.2906	0.0047	10.0306	0.2079	0.2059
0.0025	11.6321	0.3681	0.2942	0.0046	10.1569	0.2257	0.2162
0.0025	11.7378	0.3858	0.3014	0.0045	10.2335	0.1854	0.2249
0.0025	1.3801	0.0212	0.0294	0.0046	10.2854	0.2090	0.2241
0.0025	2.9517	0.0424	0.0406	0.0047	10.5271	0.2405	0.2368
0.0025	4.4217	0.0564	0.0538	0.0045	10.7187	0.2084	0.2555
0.0025	6.0182	0.0726	0.0759	0.0047	10.8433	0.2611	0.2581
0.0025	7.4134	0.0961	0.1059	0.0045	10.8953	0.2292	0.2674
0.0025	7.6868	0.1211	0.1133	0.0046	11.1891	0.2523	0.2851
0.0025	8.8117	0.1424	0.1497	0.0047	11.2301	0.2922	0.2860
0.0025	10.3895	0.1806	0.2201	0.0045	11.2788	0.2485	0.2946
0.0025	10.6962	0.1989	0.2367	0.0045	11.3845	0.3539	0.3025
0.0025	11.1809	0.2122	0.2652	0.0047	11.4071	0.3158	0.2994
0.0025	11.7878	0.2489	0.3048	0.0046	11.4814	0.2751	0.3071
0.0025	12.0540	0.2901	0.3237	0.0047	11.4852	0.3439	0.3054
0.0025	12.3821	0.3488	0.3482	0.0045	11.5132	0.2707	0.3123
0.0025	12.5486	0.3224	0.3612	0.0046	11.5994	0.3055	0.3163
0.0025	12.6994	0.3753	0.3732	0.0045	11.6224	0.3316	0.3207
				0.0045	11.6432	0.2952	0.3224
				0.0047	11.6659	0.3667	0.3198
				0.0045	11.7323	0.3836	0.3294
				0.0046	11.7843	0.3305	0.3312
				0.0046	11.8250	0.3624	0.3345
				0.0046	11.9356	0.3480	0.3437
				0.0046	12.0014	0.3868	0.3493

Curriculum Vitae

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Publications:

Celejewski, M., Barton, D., Al, T. 2018, Measurement of Cl^- : Br^- Ratios in the Porewater of Clay-Rich Rocks-A comparison of the Crush-and-Leach and the Paper-Absorption methods. *Geofluids*, 2018

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Celejewski, M., Clark, I., Al, T., A new method for extraction and characterization of porewater from low-permeability sedimentary rocks. 6th International Clay Conference, Brussels, Belgium, March 23-26, 2015. (Presentation).

Celejewski, M., Clark, I., Al, T., A new method for characterization of porewater chemistry in low-permeability sedimentary rocks, AGU Fall Meeting, San Francisco, CA, December 14-19, 2014. (Poster)

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Celejewski, M., Clark, I., Al, T., Characterization of porewater in low-permeability sedimentary rocks. GAC-MAC, Fredericton, Canada, May 21-23, 2014 (Presentation)

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