

Preliminary Evaluation of the Ultracentrifugation Method for Extraction of Pore Fluids from Sedimentary Rocks

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ABSTRACT

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Abstract

The compositions of pore fluids within deep sedimentary rock formations are required for near-field performance and safety assessment calculations for deep geologic repositories and for models involving groundwater transport or evolution. Few direct methods are currently available for the extraction of pore fluids from low permeability sedimentary formations. In the current study, the ultracentrifugation technique was applied to extract pore fluids directly from argillaceous limestones of the Cobourg Formation.

The argillaceous limestone core samples used in this study were obtained from a borehole drilled in August, 2006 at the St. Mary's Cement property near Bowmanville in southwestern Ontario. The cores were vacuum-sealed within 30 minutes of core recovery and stored in a refrigerator at 4°C until analysis. Pore fluid was extracted by spinning core pieces at a rate of 15,000 rpm under controlled conditions of temperature and pressure, according to a protocol originally developed for volcanic tuffs by the U.S. Geological Survey and adapted in this study for application to sedimentary rocks. Despite the very low water contents determined for the limestones (0.3 to 2.5 wt.%), between 0.03 and 0.75 g of pore fluid were extracted using ultracentrifugation from one subsample of a core taken at a depth of 50.09 m and from 5 subsamples of a core taken at 73.86 m. Relative to the total water available in the sample as determined from the gravimetric water content, the portion of fluid extracted from the samples ranged from 0.6 to 6.8%. The pore fluid yields are much lower than those obtained in previous studies where centrifugation was applied to volcanic tuffs (23 to 46%) or to a chalk formation (40 to 95%) and likely reflects the lower porosity of the argillaceous limestones and/or lower connectivity between pores.

The total dissolved solids (TDS) content of pore fluids extracted from 5 subsamples of one core from a depth of 73.86 m ranged from 4,400 to 52,500 mg/L. Pore fluid extracted from a subsample of core from a depth of 50.09m had an intermediate TDS value of 10,100 mg/L. The concentrations of both Ca²⁺ and Na⁺ were observed to increase with increasing Cl⁻ concentration (the Na/Ca ratio also increased), whereas the Br/Cl ratio decreased. In two sequential extractions on a single subsample of core, the quantity of fluid extracted after 4 hours of spinning in the second extraction was more than twice that extracted during the first, 2 hour extraction step. Decreases in the major ion concentrations by factors between 0.7 and 3.4 were observed between the two extraction steps; well beyond the analytical uncertainty of ±10%. This observation suggests that the variations observed in pore fluid composition do not reflect in-situ variations, but rather may be the result of changes in pore fluid composition that occurred prior to (e.g. by evaporation) or during ultracentrifugation as the result of an ion filtration process. It is not possible to conclude whether one or both of these processes affected the extracted pore fluid compositions. Future studies of water content changes during core transport and storage could be used to explore the importance of evaporation. Additionally, multiple sequential extractions from single core samples and comparison with pore fluids

extracted using an independent method and/or groundwaters sampled in close proximity could be used to further examine how representative the extracted pore fluids are of in-situ pore fluids.

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1. INTRODUCTION

Sedimentary rocks, such as those in southern Ontario, possess many characteristics that are favourable for a deep geologic repository (DGR) for the long-term isolation of used nuclear fuel, including the potential presence of reducing mineral phases and diffusion-controlled transport (e.g. Mazurek 2004). Several hydrogeochemical lines of evidence indicate that deep groundwaters in the Paleozoic sedimentary rock formations underlying southern Ontario have remained undisturbed, despite long-term perturbations on geologic time scales (Mazurek 2004). For example, with the exception of groundwaters collected from shallow levels within the sedimentary sequence, high salinities (200-300 g/L Total Dissolved Solids (TDS)) coupled with water and strontium isotopic signatures indicate long groundwater residence times.

The composition of groundwaters and pore fluids in sedimentary rock formations is required for near-field performance and safety assessment calculations for deep geologic repositories and for models involving groundwater transport or evolution. Mazurek (2004) identified low-permeability shale and limestone formations within the sedimentary sequence underlying southwestern Ontario, which are potentially suitable host rocks for a deep geologic repository. Resaturation of a repository constructed in these types of formations will likely be predominantly by diffusion of pore fluids from within the host rock matrix. This mechanism was proposed for repository resaturation in the crystalline rocks investigated in the Used Fuel Research program conducted by AECL (Gascoyne et al. 1996). Subsequent testing in the Underground Research Laboratory (URL) in southeastern Manitoba demonstrated that matrix pore fluids will seep into boreholes within unfractured rock over time (Gascoyne 2004).

To date, information on the composition of saline waters from within the deep flow systems in southwestern Ontario has been limited to samples of groundwater associated with hydrocarbons collected from producing wells (e.g. Dollar et al. 1991; Weaver et al. 1995; Hobbs et al. 2008). It is thought that the compositions of water within the rock matrix (matrix pore fluids) of sedimentary formations will likely have compositions similar to those of the groundwaters associated with the oil and gas reservoirs. However, direct information on the compositions of the pore fluids from these formations is required to verify this hypothesis.

The purpose of this study is to investigate the application of a high-speed centrifugation technique for the extraction and determination of matrix pore fluid compositions in sedimentary rocks, in collaboration with researchers from the U. S. Geological Survey (USGS). The USGS began developing methods for extracting pore fluid from welded tuffs (volcanic rocks) using centrifugation methods in 2001 (Yang et al. 2003). For the welded tuffs, pore fluid is extracted by spinning approximately 150 to 200 g of core, which has been broken into 1 to 3 cm pieces, at a rate of 15,000 rpm under thermostatically controlled conditions, with the sample maintained at atmospheric pressure. Sample preparation is performed in less than 10 minutes to minimize the evaporation of pore fluid. Samples are then spun for up to 6 hours, at which time the extracted pore fluid is collected and analyzed (it was found that centrifuging for longer times did not result in collection of any additional fluids).

To date, ultracentrifugation methods have been applied to extract pore fluid from welded tuffs with water contents as low as 3 percent (Scofield 2006). However, pore fluids extracted from several adjacent core intervals may need to be combined in order to obtain sufficient amount for analysis (typically 0.1 g to 2.5 g) of major and trace ions and water isotopes (oxygen and hydrogen). In the current study, initial testing of the ultracentrifugation technique as a potential

method for extracting pore fluid from argillaceous carbonate rocks was conducted. To our knowledge, this is the first application of this technique to such rocks.

2. PREVIOUS APPLICATIONS OF CENTRIFUGATION

Studies of pore fluids in tuffs, shales, mudstones and unconsolidated sediments such as soils and glacial till, have shown that the fluid composition can be determined by a number of techniques. These techniques and their application have been described in detail in a Nuclear Energy Agency/Organization for Economic Co-operation and Development report (NEA 2000).

This section reviews and documents the ultracentrifugation method as it has been applied to other rock types (Edmunds and Bath 1976, Bath and Edmunds 1981, Dahlgren et al. 1997, Scofield 2006). Possible challenges and limitations of applying this method to argillaceous limestones and shales are discussed.

2.1 TUFFACEOUS AND GRANITIC ROCKS

The ultracentrifugation technique has been developed and applied successfully by the US Geological Survey (USGS) at Denver, Colorado, to extract pore fluids from tuffaceous rocks from the Yucca Mountain site, Nevada (Peterman and Marshall 2002). Early USGS pore fluid studies at Yucca Mountain relied on uniaxial compression techniques for extraction from nonwelded and zeolitized tuffs. This technique could not be used for densely welded tuffs because their greater strength would not allow collapse of the pores and expulsion of the pore fluid. Because approximately 80 percent of the rocks in the unsaturated zone at Yucca Mountain are densely welded, the ultracentrifuge method was adopted to more fully characterize the dissolved ion and isotopic compositions and spatial evolution of pore fluid from infiltration at the surface to the water table.

Scofield (2006) evaluated the efficiency of extraction (quantity of pore fluid extracted relative to the total amount present) for both the uniaxial compression and ultracentrifugation methods. The possibility of chemical fractionation during compressional extractions with increasing load and sequential ultracentrifugation was also investigated. In a series of test samples of nonwelded tuffs, Scofield (2006) reported extraction efficiencies of approximately 40% for samples with moisture contents of approximately 19% using uniaxial compression. Aliquots of water extracted from two nonwelded samples using this method showed some dissolved ion variability with increased load and compression, notably in Ca^{2+} and Cl^- concentrations. In contrast, successive splits obtained by ultracentrifugation showed only minor differences (typically less than 20 percent of the analyte concentrations) in dissolved ion concentrations (Scofield 2006). For the ultracentrifugation technique, extraction efficiencies for two samples of densely welded tuff units were also approximately 40%, despite the much lower moisture contents of the densely welded units (8 to 9%). An extraction efficiency of 26% was reported for extraction from a non-welded tuff by ultracentrifugation with a moisture content of 20%.

Preliminary experiments have been conducted on crystalline rock in collaboration with the USGS, AECL and the University of Waterloo to compare the relative benefits of the following four techniques for characterizing pore fluid compositions: 1) ultracentrifugation of broken rock pieces; 2) out-diffusion of pore fluids into deionized water; 3) crush and leach; and 4) direct sampling of seepages entering into boreholes. Granitic rocks from six boreholes at the 420m

level of the Atomic Energy Canada Limited Underground Research Laboratory (URL) in the Lac du Bonnet granite batholith, southeastern Manitoba, were used for the comparative analysis.

Approximately 0.05 to 0.1 mL of fluid was extracted by ultracentrifuging ~250g of saturated, freshly broken rock. In most cases, sufficient pore fluid for analysis of major ions (~0.05 mL) was obtained. The pore fluids collected by ultracentrifugation showed variable concentrations between cores, but replicate analyses had good agreement (within $\pm 10\%$), demonstrating the reproducibility of the technique. Evidence of the accuracy of the ultracentrifugation technique was demonstrated by its comparability with traditional out-diffusion methods, since both techniques yielded TDS values of ~ 20 g/L for the samples from the 420 m level of the URL (See Table 1).

Crush-leach tests demonstrated that leach time did not significantly affect soluble salt (Cl^{-1}) leaching, irrespective of grain size. However, the concentrations of leachable salts increased as grain size decreased, which may be partly due to increased contributions from fluid inclusions during crushing to finer grain sizes. Salinities of the seepage fluids directly obtained from boreholes were about four times as saline (TDS of 58-85 g/L) as the values obtained by out-diffusion and ultracentrifugation (Table 1). Two possible explanations of this discrepancy were suggested: i) evaporation of seepage fluids entering into the boreholes resulted in the higher salinities in those samples compared to out-diffusion and ultracentrifugation methods; or ii) drill water entered into the permeable pathways within the cores during drilling and resulted in dilution of the pore fluids measured using out-diffusion and ultracentrifugation. While the reason for this discrepancy cannot be definitively attributed at this time, electrical conductivity and chemical and stable isotopic data ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) indicated that the early seepage waters were diluted by drill water and that several days were required for the drill water to be removed. In addition, a pronounced shift in $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of fluids in the boreholes, which could be taken as evidence of an evaporation effect, was not seen. It was recommended that future drilling efforts focused on measurements of pore fluid compositions add a tracer to drill fluids so that quantification of drilling-related dilution can be quantified.

The relative benefits and limitations of each of the techniques for extracting matrix pore fluid from crystalline rock were compared. The comparable results between out-diffusion and ultracentrifugation (Table 1) suggested that ultracentrifugation offers considerable promise as a new tool for pore fluid characterization. The benefits of the ultracentrifugation technique are that: i) it has a short experimental timeframe; ii) it is not dependent on porosity measurements; iii) it allows for direct sampling of pore fluids; and iv) stable isotopic measurements of the extracted pore fluids can also be made, if large enough quantities of pore fluid are obtained, because no deionized water is added to the sample.

The crush-leach method also has merit, particularly if grain-size leaching profiles show distinctive changes in slope that may be used to distinguish pore fluids on grain boundaries from isolated fluid inclusions in quartz grains. The laboratory out-diffusion method may also be useful in determining the composition and amounts of matrix pore fluids, without the complication of extracting fluid inclusions but, because of the time required to develop a diffusion profile, it would be slower than centrifugation and crush-leach methods.

Table 1: Comparison of total dissolved solids (g/L) for crystalline rocks from the AECL Underground Research Laboratory measured using different pore fluid extraction techniques.

Pore Fluid Extraction Technique	Total Dissolved Solids (g/L)
Ultracentrifugation	15 to 22
Out-diffusion	10 to 39
Sampling of borehole seepage	58 to 85

2.2 UNCONSOLIDATED SEDIMENTS

The determination of pore fluid composition in sediments has been an area of intensive research over the last 50 years. In this context, pore fluid compositions are a tool to quantify the ability of sediments to trap toxic species, where the presence and concentration of different species can be determined from the composition of accompanying pore fluids. In unconsolidated sediments, four methods are typically used to determine the composition of pore fluids: dialysis, vacuum filtration, squeezing and centrifugation. In a review of these methods, Bufflap and Allen (1995) found that centrifugation gave the most reproducible and acceptable results and was generally the simplest method to apply. This was supported by the findings of Winger et al. (1998) and other reports therein. Pore fluid collected by in-situ methods such as dialysis or use of 'peepers' (vessels containing de-oxygenated, de-ionised water fitted with a semi-permeable membrane) were regarded as giving the most representative concentrations of ionic constituents. In contrast, the vacuum (suction/filtration), centrifugation and squeezing methods require greater disturbance of the pore fluid and its surroundings. Despite these disturbances, the centrifuge method was favoured for extraction of pore fluids from unconsolidated sediments, primarily because of its ease of application.

To extract the pore fluids by centrifugation, sediments are normally homogenised, placed in centrifuge vessels and centrifuged at 4°C. A low temperature is required to minimize evaporation and the potential for chemical reaction between sediments and pore fluids that will cause changes in pH and dissolved SiO₂. It is also important to prevent redox reactions which could occur between iron minerals and O₂ in the vessel during the extraction procedure. This is best accomplished by the use of headspace gases such as N₂ or Ar (Bufflap and Allen 1995).

2.3 SEDIMENTARY ROCKS

In comparison to unconsolidated sediments, relatively little has been done to extract pore fluids from sedimentary rocks using centrifugation methods. Previous experimental work in the oil industry has focused on the study of fluid saturation in relation to pore fluid pressure in porous hydrocarbon and groundwater reservoir rocks. The emphasis has therefore been on the rock physical properties rather than obtaining chemical analysis of the fluids.

In a study by Edmunds and Bath (1976) on theoretical and practical aspects of centrifuge extraction of pore fluids, two types of high speed centrifuge were used, which attained speeds of 4,000 and 14,000 rpm, respectively. The relationship between centrifuge speed and its

ability to draw pore fluids from their cavities was shown to be dependent on the capillary pressure in a pore and the distance to the centre of the rotor (i.e. the 'g' force). Figure 1 shows the relationship between rotor speed and capillary pressure. They show that for a rotor speed of 7,000 rpm, complete draining of pores as small as 0.1 μm in size might be expected. For a rotor speed of 15,000 rpm (as used in the present study) complete draining of pores with radii as small as 0.03-0.05 μm should be possible, assuming the pore spaces are interconnected.

Further application of the centrifuge technique was demonstrated by Bath and Edmunds (1981) in their study of the composition of connate waters in the Upper Cretaceous Chalk beds in eastern England. Because of the high porosity of the chalk (greater than 40% in some cases) a centrifuge force of only 2,000 g was required and approximately 40 to 50% of the total moisture content was extracted. Both the major and minor elements concentrations and the isotopic (^2H and ^{18}O) contents of the fluids were determined. On the basis of results from their previous study (Edmunds and Bath 1976), Bath and Edmunds (1981) reported that fractionations observed in the cation concentrations may introduce errors of up to $\pm 10\%$ in the extracted fluid compositions relative to the actual in-situ pore fluid composition within the chalk. In contrast, similar testing conducted to examine the effect of centrifuging on the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ compositions of the extracted water showed no significant fractionation effects (Bath and Edmunds 1981).

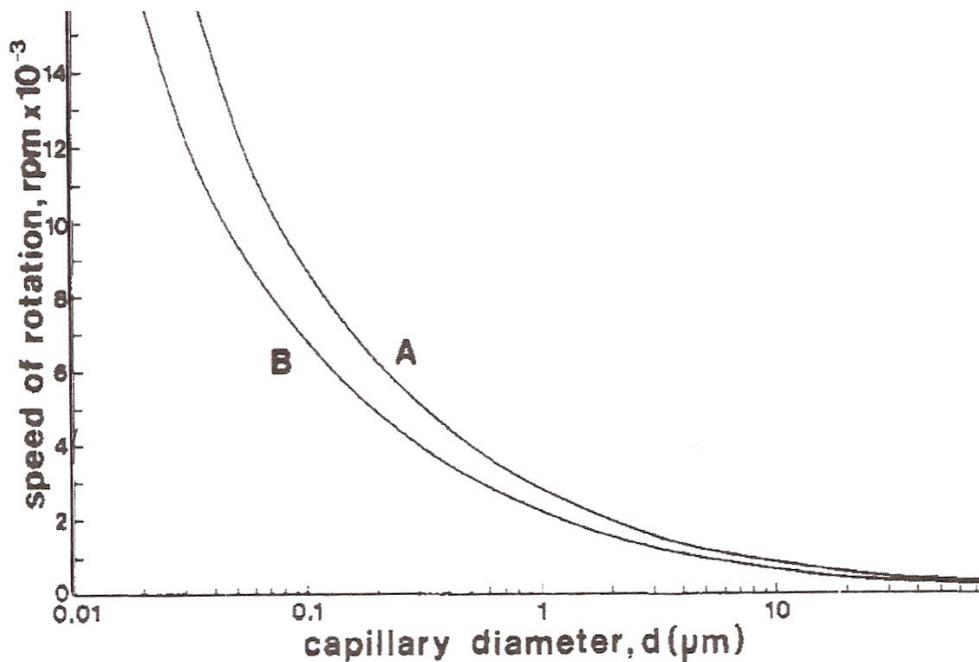


Figure 1: Curves showing relationship between speeds of rotation and minimum capillary size in the centrifugation equipment used by Edmunds and Bath (1976). Curves A and B show the effect of tension (force) midway (A) and at the maximum distance (B, 11.1 cm) to the centre of rotation (modified from Edmunds and Bath 1976).

2.4 POTENTIAL FOR ION FILTRATION PROCESSES

It is well known that compacted clays and shales can act as semi-permeable membranes that can restrict the movement of ionic species while allowing unrestricted passage of neutral species (such as water molecules). Under conditions where there is no hydraulic pressure differential to force advective flow of groundwater through the clay membrane, movement of water molecules through the membrane will take place by diffusion, in the direction from low salinity to high salinity. In the absence of flow outlets, pressure in the higher salinity zone will increase. This effect is known as osmosis and, in sedimentary basins containing saline waters and brines, may cause significant pressure differentials to develop across clay-rich strata. This may apply on the large scale, over basinal distances, but also could occur in the laboratory during the application of pore fluid extraction techniques, when fluids are forced out of the rock matrix under a strong hydraulic gradient.

3. METHODS

The technique of centrifuging a limestone core sample to extract pore fluids is a development of the USGS procedures for sampling pore fluids in the tuffs of Yucca Mountain, Nevada (Scofield 2006). The procedure as applied to limestones is described in detail in Appendix A.

3.1 CORE PRESERVATION

The core samples used in this study were obtained from the Cobourg Formation, an argillaceous limestone, from a borehole drilled in August, 2006 at the St. Mary's Cement property near Bowmanville, Ontario. The cores were vacuum-sealed within 30 minutes of core recovery and stored in a refrigerator at 4°C. Vacuum-sealed cores from depths of 54.35, 67.87 and 68.28 m below ground surface (BGS) were stored for approximately 2 months before being shipped to the USGS. Samples were transferred by overnight express from Ottawa, Ontario, by INTERA Engineering Ltd., on November 27, 2006 and received by the US Geological Survey in Denver, Colorado, on November 28, 2006. The samples were not refrigerated during shipping. Upon receipt at the USGS, the samples were examined and found to be in good condition, with vacuum seals intact. After examination, the samples were refrigerated at 9°C until analysis, approximately one week later. Additional core samples were later obtained from depths of 50.09 m and 73.86 m for use in additional pore fluid extraction tests (Section 4.2).

3.2 SAMPLE PREPARATION

The samples were opened immediately prior to analysis and pieces of core were broken from each section, quickly weighed and placed in centrifuge cups. The cups were balanced and placed in the centrifuge rotor (the total weight of sample is between 200 g and 250 g). The rotor was spun for at least 5 hours at 15,000 rpm (approximately 20,000 g force). The pore fluid collection tubes were then removed and the weight of the extracted pore fluid recorded. The centrifuged limestone pieces were then weighed and placed in an oven for at least 48 hours at 120°C for determination of the gravimetric water content.

3.3 PORE FLUID EXTRACTION

Two different techniques were used in this study to extract pore fluid; ultracentrifugation and vacuum distillation. The ultracentrifugation technique described in section 3.3.1 was the most widely tested. However, the quantity of pore fluid extracted using ultracentrifugation was often insufficient for measurement of the chemical composition and in all cases was insufficient for the measurement of the stable isotopic composition ($\delta^{18}\text{O}$, $\delta^2\text{H}$) of the fluids. Therefore, the vacuum distillation method (section 3.3.2) was also applied to selected subsamples of core in an attempt to extract pore fluid for analysis of stable oxygen and hydrogen isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$).

3.3.1 Centrifugation

As part of the present study, a technique for extracting low-volume pore fluid samples was employed. A detailed protocol for this method is included in Appendix A2.1. The centrifuge cups containing the limestone samples were weighed before and after centrifuging. If the volume of pore fluid extracted was too small to collect with a pipette, the sample was diluted with deionized water placed directly into the centrifuge cups to give sufficient volume to allow collection by pipette. The sample was then filtered and stored in a low-volume sample vial. This method has worked well in the past for core samples with low water contents (such as granite cores, Section 2.1).

Several techniques were tested to enhance pore fluid recovery, including i) using different size fractions of core rubble (Appendix A2.2); ii) centrifuging the samples at different temperatures (Appendix A2.3); and iii) and performing a “quick-leach” on a centrifuged sample and comparing it to a quick-leach from a fresh sample (Section 4.3 and Appendix A2.4).

3.3.2 Vacuum Distillation

For all core samples examined in this study, the quantity of water extracted by ultracentrifugation was insufficient for analysis of stable isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$). Therefore, a vacuum distillation technique was applied to extract pore fluids from several fresh core samples and the stable oxygen and hydrogen compositions of the extracted waters were measured. The vacuum distillation method employed in this study by the USGS is described in Appendix A3.

3.4 WATER CONTENT

The gravimetric water content was determined using two different methods; by i) drying the centrifuged rock or fresh (saturated) rock samples in an oven for > 48 hours at 120° C; or ii) vacuum distillation of a fresh rock sample at 130° C for 6 hours.

For gravimetric water contents determined by oven drying, the total quantity of water in the sample in grams is calculated from the difference between the initial weight of the rock sample (immediately after preparation and before centrifugation) and the final weight of the rock sample after oven drying. In the vacuum distillation experiments, the weight of water collected during distillation (or the water yield) is taken as the total quantity of water in the rock. The final weight of the rock at the end of the vacuum distillation procedure is also required in order to

calculate the gravimetric water content.

The gravimetric water content in weight percent is then calculated as:

$$\text{Water content} = \frac{\text{total weight of water removed from rock (g)}}{\text{dry weight of the rock (g)}} \times 100\%$$

The assumption implicit in this calculation is that all water in the connected pore spaces of the rock was removed during oven drying or vacuum distillation. In the vacuum distillation experiments, the validity of this assumption was tested after distillation by placing the core sample in an oven at approximately 130° C for an additional 72 hours to check for further water loss (Appendix A3).

3.5 ANALYTICAL METHODS

Major ions were analyzed using a Dionex Model ICS 2000 ion chromatograph (IC). Minor and trace elements were analyzed using a Thermo Electron Model PQ3 inductively-coupled plasma mass spectrometer (ICP-MS). Specific conductance was measured using a Horiba Twin Conductivity Meter B-173.

The minimum volume of sample for analysis of major ions is 1.0 mL. A sample volume of 0.2 mL is required for measuring specific conductance. In this study, the amount of extracted pore fluid is measured gravimetrically and ranged from 0.011 g to 0.075 g. The pore fluid samples were initially diluted to a volume of at least 1.2 mL and the weight of water added was recorded. This provided sufficient volume for measurements of conductivity and to determine if the sample needed to be diluted further before analysis. A second dilution was required to provide enough volume for analysis of minor and trace elements.

4. RESULTS

Using ultracentrifugation, very little water could be extracted from the argillaceous limestone samples examined in this study. Upon unpacking, the argillaceous limestone cores were found to be dry on the outside. The core cleaved easily along bedding planes, but was very hard and impenetrable perpendicular to the bedding planes.

The results of various tests and evolution of the ultracentrifuge method are described in the sections below. Pore fluid was extracted and analyzed in two phases as described in Section 4.1. The data for from both of these phases are reported in Table 2.

4.1 PORE FLUID COLLECTION

4.1.1 Initial Attempts

Seven centrifuge tests were conducted in the first stage of this project to adapt and evaluate the ultracentrifuge method to limestone samples. In these initial tests, fluid was only obtained from one sample (68.28c), which had the highest water content (2.5%). Due to the low fluid yield from these initial samples, additional samples were requested by the USGS for use in subsequent pore fluid extraction tests.

4.1.2 Additional Core Samples

Two additional core samples of argillaceous limestone from the Cobourg Formation sampled at depths of 50.09 and 73.86 m BGS were shipped by overnight express from Ottawa, Ontario by Intera Engineering Ltd. on January 15, 2007 and received by the US Geological Survey in Denver, Colorado on January 18, 2007.

Two subsamples of the core from 50.09 m were centrifuged for 6 hours. Only the extraction test performed on sample 50.09b produced pore fluid (0.02 g, Table 2). Extraction tests were conducted on five separate subsamples of the core from 73.86 m. Four of these subsamples were centrifuged for 6 hours (subsamples a, d, e and f in Table 2). The extraction tests performed on the fifth subsample produced two pore fluid samples. A volume of 0.031 g of pore fluid was collected after a two hour spin (73.86b, Table 2). The centrifuge cups were immediately reattached and the subsample was centrifuged for another 4 hours. After 6 hours of total spin time, another 0.064 g of pore fluid was extracted from two of the three centrifuge cups (73.86c, Table 2).

Extracted pore fluids were analyzed for specific conductance, major ions and trace metals. As in the first phase of the study, the extracted pore fluid volumes were very small and usually only present in one or two of the three centrifuge cups. A 3-decimal place balance was used to record the weights and to perform dilutions.

4.2 WATER CONTENT

The gravimetric water contents determined for subsamples of each core examined in this study are given in Table 2. The analytical uncertainty in the calculated water contents is $\pm 0.1\%$.

The gravimetric water contents determined for cores from different depths ranged from 0.3 to 2.5%. Variations in water contents are also observed for subsamples taken from each core (Table 2). For core samples from depths of 54.25, 67.87 and 68.28 m, attempts to extract pore fluid by ultracentrifugation were unsuccessful. The water contents determined for subsamples of these cores ranged from 1.3% to 1.6% in the sample from 54.24 m, from 0.3% to 0.8% in the sample from 67.87 m and from 1.9% to 2.5% in core sample 68.28. Small amounts of water were extracted from core samples taken at depths of 73.86 m and 50.09 m, despite their relatively low, average gravimetric water contents (0.6% and 1.6%, respectively; Table 2). The differences in gravimetric water content determined for subsamples of a single core ranged from 0.1 to 0.9 wt. %.

Table 2: Summary of results of pore fluid extraction attempts for the limestone samples. Extraction time was 6 hours, unless otherwise indicated.

Extraction Date	Sample Interval	Extraction Method	Wt. of Dry Rock (g)	Total Wt. of H ₂ O in Sample* (g)	Gravimetric water content Wt. %	H ₂ O Extracted using UC (g)
3/7/07	50.09a	UC	217.38	3.33	1.5	Nd
3/9/07	50.09b	UC	216.85	3.45	1.6	0.020
12/18/06	54.35a	UC	207.00	3.26	1.6	Nd
12/19/06	54.35b	D	415.4	5.6	1.4	3.5
12/19/06	54.35c	D	419.9	5.3	1.3	3.4
11/30/06	67.87a	UC	217.09	1.00	0.5	Nd
12/6/06	67.87b	UC	221.31	0.58	0.3	Nd
12/7/06	67.87c	D	506.7	4.0	0.8	3.1
12/11/06	68.28a	UC	208.32	4.90	2.4	Nd
12/12/06	68.28b	UC	215.90	4.35	2.0	Nd
12/13/06	68.28c	UC	203.91	5.17	2.5	<0.03
12/15/06	68.28d	UC	206.66	4.41	2.1	Nd
12/14/06	68.28e	D	469.0	8.8	1.9	6.1
12/27/06	68.28f	UC	201.48	3.20	1.6	Nd
1/22/07	73.86a	UC	209.43	1.24	0.6	Nd
1/24/07	73.86b	UC (2 hr spin)	223.58	1.40	0.6	0.031
1/24/07	73.86c	UC (6 hr spin)	223.58	1.40	0.6	0.064
1/26/07	73.86d	UC	225.52	1.30	0.6	0.075
2/12/07	73.86e	UC	268.78	1.39	0.5	0.072
2/13/07	73.86f	UC	221.73	1.36	0.6	0.011

UC: ultracentrifugation method

D: vacuum distillation method

* For samples extracted using ultracentrifugation, the gravimetric water content was determined by oven drying at 120 °C, as described in section 3.4.

There is good agreement between the water content measurements obtained using vacuum distillation and those determined gravimetrically (Table 2) for those core samples to which both methods were applied. A comparison of the total quantity of water extracted from subsamples of core taken from the same depths (extracted using both the ultracentrifugation and vacuum distillation techniques) indicates that the total volume of water extracted was significantly higher when the vacuum distillation technique was applied (Table 2). This reflects the greater mass of rock used in the vacuum distillation extractions (approximately twice that used in the ultracentrifugation tests).

4.3 PORE FLUID COMPOSITION

During the initial tests conducted as part of this study, it was possible to extract a minute amount of pore fluid from only one interval of core, the 68.28 m argillaceous limestone sample, which had the highest gravimetric water content (2.5%) of all the samples (section 4.1; Table 2,

sample interval 68.28c). The volume of pore fluid was insufficient to withdraw from the centrifuge cup. Instead, it was diluted to 0.48 g, collected and subsequently diluted further to 0.925 g. It was not possible to determine an accurate dilution factor for this sample, because the weight of the pore fluid extracted was not known. On the basis of the approximate concentrations, the salinity of the pore fluid is consistent with a Ca-Na-Cl type water (data not shown).

For subsamples from core 73.86, Table 3 includes analysis of most of the major ions. No fluid could be extracted from subsample 73.86a. Notably, the fluids collected from the same subsample after 2 hours of centrifugation (73.86b) and after an additional 4 hours of centrifugation (total centrifugation time 6 hours, 73.86c), have different chemical compositions. The fluid extracted after the first 2 hours (73.86b) has a higher salinity than that collected after an additional 4 hours of centrifugation (73.86c in Table 3). Fluids extracted from the remaining three subsamples of core 73.86 (d, e and f) by ultracentrifugation for 6 hours also show a wide range of TDS values between 4,400 and 29,700 mg/L.

The concentrations of Na^+ and Ca^{2+} in the extracted pore fluids are plotted against Cl^- in Figure 2. These fluids were extracted from several subsamples of the core sampled from a depth of 73.86 m, and for one additional pore fluid extracted from a core from depth of 50.09 m (50.09b in Table 3). In pore fluids extracted from subsamples of core 73.86, chloride concentrations range from 2,750 to 32,500 mg/L. With increasing Cl^- concentration, Na^+ concentrations increase from 179 to 9,850 mg/L and Ca^{2+} concentrations increase from 970 to 6,560 mg/L (Figure 2a).

Table 3: Results of analyses of extracted pore fluids [TDS= total dissolved solids calculated from dissolved ion concentrations]. *Results are for fluids extracted from separate subsamples, with the exception of 73.86b and c, which are sequential extractions from a single subsample.

Elements and Ions	Fluid Sample ID (number indicates depth of core in mBGS) and Extraction Date						Quick-Leach Sample/Date	
	73.86b*	73.86c*	73.86d	73.86e	73.86f	50.09b	OSI-68.28-1	OSI-68.28-2
	1/24/2007	1/24/2007	1/26/2007	2/12/2007	2/13/2007	3/9/2007	12/27/2006	12/27/2006
	Ionic Charge Balance (%)							
	0.6	-0.5	0.9	0.6	0.8	0.0	10.2	11.0
	Milligrams per Litre						Milligrams per Kilogram	
TDS	52550	22850	29700	4375	17570	10050	380	600
Na	9,850	2,730	4,520	179	1,260	403	103	171
K	214	157	167	27	245	99.3	4.9	8.6
Ca	6,560	3,760	4,370	972	3,460	2,180	39.7	59.7
Mg	2140	1220	1410	304	1090	624	10.9	15.3
NH ₄	57	28	31	5.7	14	17	--	--
Cl	32,500	14,300	18,400	2,750	10,900	6,340	213	333
SO ₄	155	33	74	6.4	34	17	1.0	1.8
HCO ₃	<700	354	<400	89	365	242	3.7	5.9
NO ₃	34	78	68	60	35	21	--	--
F	<6	<3	<3	<0.6	<3	<1	--	--
Br	343	202	223	47	167	106	3.3	5.2
PO ₄	14	5.2	6.5	<1.0	<3.9	<2	--	--
SiO ₂	<30	<20	<20	<20	<200	--	--	--
Li	6.8	4.0	4.7	1.0	3.6	--	--	--
Be	<0.02	<0.02	<0.02	<0.02	<0.2	--	--	--
B	<1	<1	1.02	<1	<8	--	--	--
Al	<0.6	<0.5	<0.5	<0.5	13.4	--	--	--
V	0.109	0.060	0.055	<0.02	<0.2	--	--	--
Cr	<0.1	<0.09	<0.09	<0.09	<0.7	--	--	--
Mn	0.239	0.105	0.149	0.028	0.380	--	--	--
Co	0.039	0.016	0.024	<0.03	<0.2	--	--	--
Ni	<0.3	<0.3	<0.3	<0.3	<2	--	--	--
Cu	<0.05	<0.05	<0.05	<0.05	<0.4	--	--	--
Zn	2.42	3.13	3.19	0.66	11.3	--	--	--
As	<0.07	<0.06	<0.06	<0.06	<0.5	--	--	--
Se	0.220	0.106	0.110	<0.1	<0.8	--	--	--
Sr	264	154	173	41.7	147	--	--	--
Rb	0.214	0.145	0.159	0.014	<0.08	--	--	--
Mo	<0.01	<0.01	<0.01	<0.01	<0.08	--	--	--
Ag	<0.08	<0.07	<0.07	<0.07	<0.5	--	--	--
Cd	<0.02	<0.02	<0.02	0.029	<0.2	--	--	--
Sb	<0.02	<0.02	<0.02	<0.02	<0.2	--	--	--
Ba	0.384	0.444	0.347	<0.3	<2	--	--	--
Pb	0.043	0.025	0.054	0.106	0.529	--	--	--
Th	<0.004	<0.003	<0.003	<0.003	<0.02	--	--	--
U	<0.004	<0.003	<0.003	<0.003	<0.02	--	--	--

In Figure 2b, the concentrations of the ions are plotted in milliequivalents per litre (meq/L). Ca^{2+} is dominant in all extracted fluids, with two exceptions: i) the fluid extracted from subsample 73.86d with approximately 500 meq/L Cl^- has approximately equal concentrations of Ca^{2+} and Na^+ ; and ii) the fluid extracted from subsample 73.86b after two hours of spinning, in which sodium is the dominant cation. Although Na^+ concentrations exceed Ca^{2+} concentrations in sample 73.86b, in the fluid extracted from the same sample spun after an additional 4 hours of ultracentrifugation (i.e. total spin time of 6 hours; 73.86c), higher Ca^{2+} than Na^+ concentrations were observed, similar to the other extracted pore fluids. The one pore fluid extracted from core sample 50.09 also appears to fit the trend observed in Na^+ and Ca^{2+} concentrations as a function of Cl^- concentration (Figure 2a and b). This fluid has one of the lower Cl^- concentrations measured (6340 mg/L), and the dominant cation in this fluid is calcium (Figure 2b), as observed for the lower salinity fluids (<500 meq/L) from subsamples of core 73.86.

The variation in the Na to Ca ratio of the extracted pore fluids as a function of Cl^- concentration is shown in Figure 3. Na^+ is the dominant cation in the higher salinity fluids. The variation of the Br/Cl ratio with Cl^- concentrations for extracted fluids from all core sections is shown in Figure 4. The Br/Cl ratio decreases as the amount of Cl^- in the pore fluid increases. By comparison to the Na/Ca ratios observed in Figure 3, the Na/Ca ratio is the highest in the pore fluid with the lowest Br/Cl ratio.

In contrast to the difference in Na^+ and Ca^{2+} trends with Cl^- concentration, the relationship between Ca^{2+} and Mg^{2+} is almost constant over the entire Cl^- concentration (Figure 5). The Ca/Mg ratio varies between 1.85 and 1.95 in fluids extracted from subsamples of core 73.86. A slightly higher Ca/Mg ratio of 2.1 is calculated in the fluid extracted from core 50.09b.

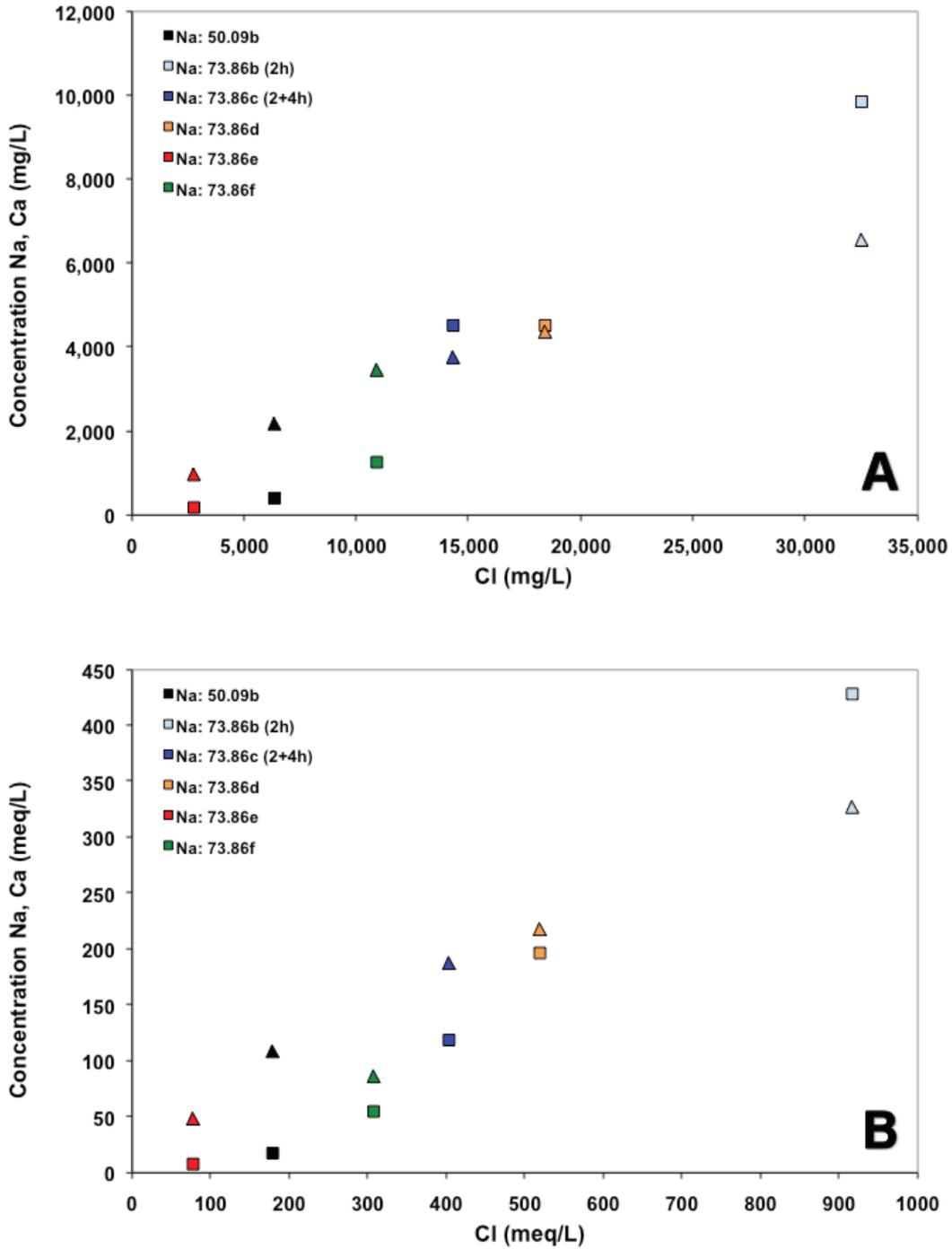


Figure 2: Variation and trends in Na⁺ (squares) and Ca²⁺ (triangles) concentrations as a function of Cl⁻ concentrations in units of mg/L (A) and meq/L (B) for pore fluids extracted by ultracentrifugation from limestone core sections 50.09 and 73.86 (corrected pore fluid concentrations from Table 3).

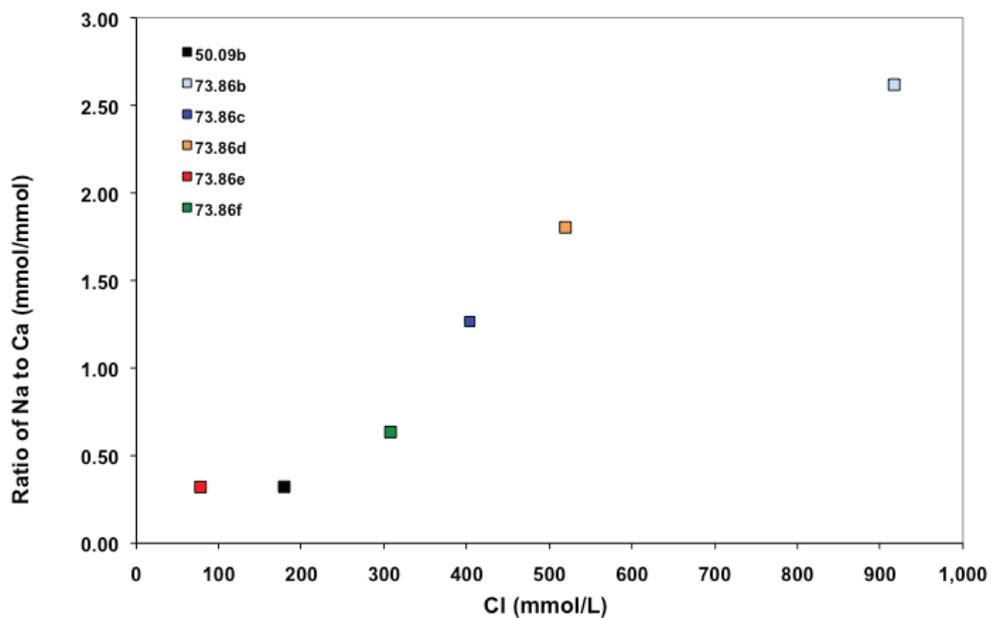


Figure 3: Diagram showing the increase in the Na/Ca ratio in the extracted fluid from core section 73.86 as a function of increasing salinity. Note that values plotted are calculated fluid concentrations after correction for dilution with deionised water.

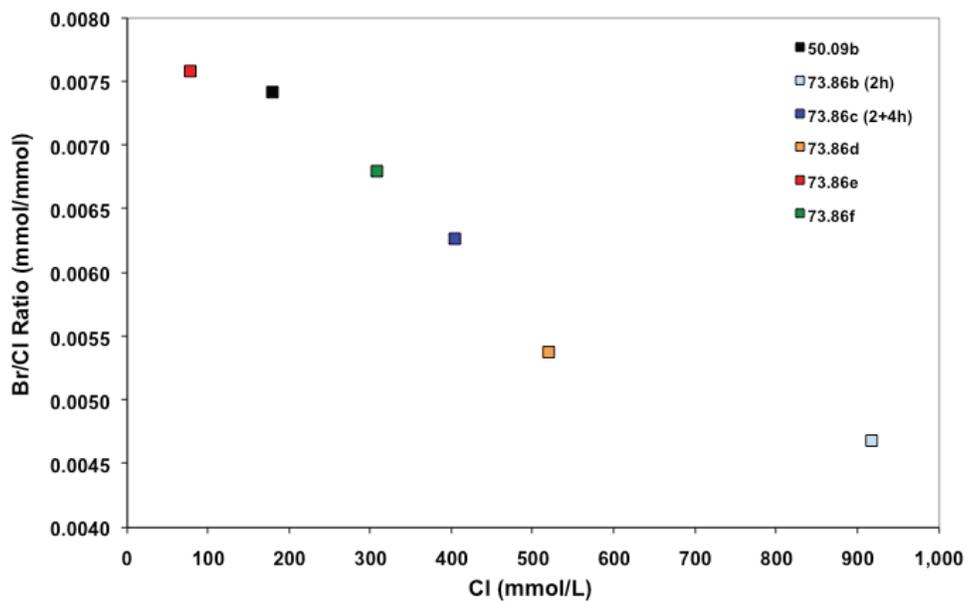


Figure 4: Variation of Br/Cl ratio with Cl⁻ concentration

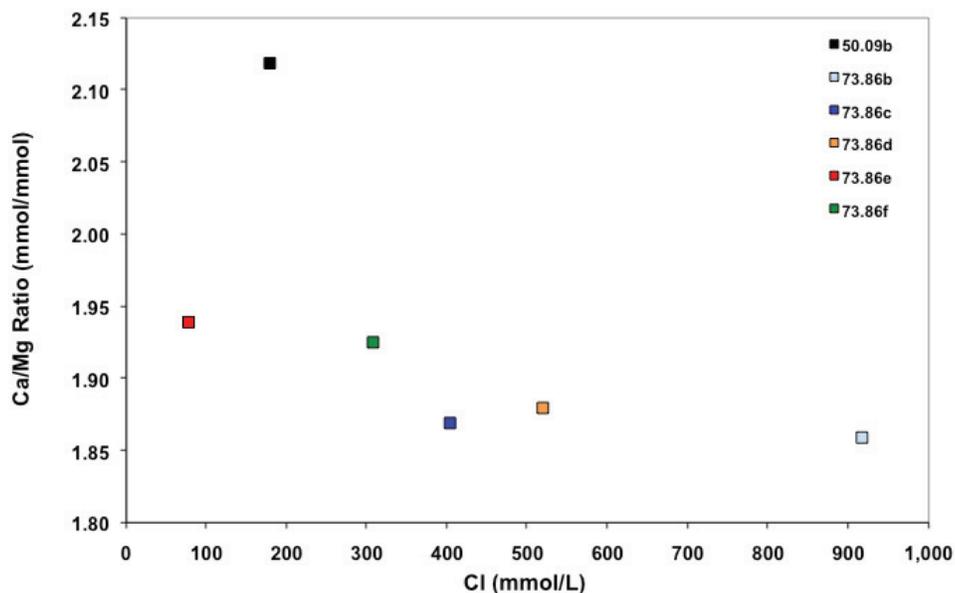


Figure 5: Diagram showing consistency of Ca/Mg ratio for extracted pore fluids from all core sections.

Stable Water Isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$)

The vacuum distillation technique was applied to extract water from 4 subsamples of core; two subsamples of core 54.35, and one from each of cores 67.87 and 68.28 (Table 2). The stable isotopic compositions ($\delta^{18}\text{O}$, $\delta^2\text{H}$) of the extracted waters are presented in Table 4. The $\delta^{18}\text{O}$ values determined for the extracted waters range from -8.6 to -10.0‰ and the average $\delta^2\text{H}$ values range between -52.7 and -54.7‰. The analytical uncertainties in the reported $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are 0.2 and 2‰, respectively.

Table 4: Stable hydrogen and oxygen isotopic compositions determined for waters extracted from subsamples of core using vacuum distillation.

Sample Interval	Average $\delta^2\text{H}$ (‰ SMOW)	Number of $\delta^2\text{H}$ measurements	$\delta^{18}\text{O}$ (‰ SMOW)
54.35b	-52.7	2	-10.0
54.35c	-53.7	2	-9.1
67.87c	-52.8	2	-8.6
68.28e	-54.7	4	-9.9

4.4 "QUICK LEACH" RESULTS

A sample from the 68.28 m core was used to test the proposed 'quick leach' method. While this sample was being centrifuged, a quick-leach of the remnants of the same sample was performed by placing the remnants in a 40 mL beaker and dripping 8.6 mL of deionized water onto 74.8 g of the limestone fragments (just enough to cover the sample) for 5 minutes. A pipette was used to collect a sample aliquot which was then filtered and stored in a 1.5 mL vial, labelled "OSI-68.28.1" (Table 3). After 6 hours of centrifuging of the sample from the same interval, no pore fluid was observed. The centrifuged sample was removed from the centrifuge cups and a quick leach was performed in the same manner as before, this time by dripping 12.2 mL of deionized water onto 120.7 g of the limestone fragments. This sample was labelled as "OSI-68.28.2" (Table 3).

The quick-leach samples (OSI-68.28.1 and OSI-68.28.2 on 12/27/2006) were not diluted and several ion concentrations were beyond the maximum of the calibration curve of the ion chromatograph, but were not high enough to overwhelm the IC detector. The charge balances were 10.2% and 11%. The compositions of the two quick leach samples were very similar to each other, indicating that there was no change in the accessible fluids and/or salts available for leaching as a result of centrifuging of the rock sample.

5. DISCUSSION

The fluids extracted by ultracentrifugation show considerable variation in terms of quantity and composition, as shown by the results presented in Table 2 and Table 3 (sections 4.2 and 4.3, respectively). These variations are discussed in the following sections.

5.1 QUANTITY OF FLUID EXTRACTED

The gravimetric water contents of the core samples taken from depths between 50.09 and 73.86 m ranges from a low of 0.3% to a high of 2.5%, as shown in Figure 6 (see also Table 2). Generally, the water contents determined for subsamples of the same core are similar; the difference in the water contents determined for subsamples of cores 50.09 and 73.86 are within the measurement uncertainty of ± 0.1 wt.%. For subsamples of cores from depths of 54.35, 67.87 and 68.28, the standard deviations in the water content measurements are ± 0.2 , 0.3 and 0.3 wt.%, respectively. Good agreement is observed between the gravimetric water contents determined by drying at 120 °C for 48 hours and those determined using vacuum distillation at approximately 130 °C for 6 hours for four cores from depths of 54.35, 67.87 and 68.28 m (Table 2). This suggests that the variations in water content observed between cores from different depths are not simply an artefact of the experimental method applied.

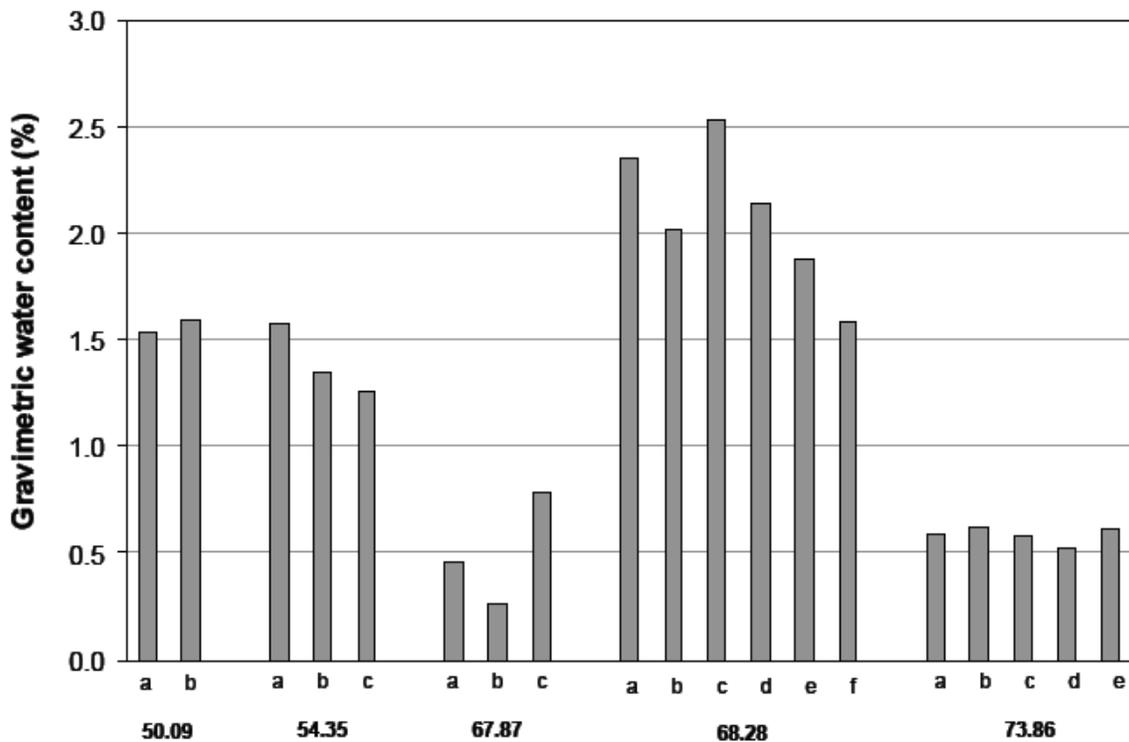


Figure 6: Variations in the water content determined by drying at 120 °C in samples of limestone core, according to sampling depth in meters.

Differing quantities of fluid were extracted from subsamples from the same core centrifuged for the same length of time (6 hours). The extraction test on subsample 73.86d produced a pore fluid volume of 0.075 g from two of the three centrifuge cups after a 6-hour spin. Subsample 73.86e produced a similar pore fluid volume of 0.072 g. However, only 0.011 g were extracted from subsample 73.86f, and no fluid was extracted from subsample 73.86a (Table 2) after 6 hours of centrifuging. These differences in the quantity of water extracted from subsamples of the same core can not be attributed to differences in water content, because as discussed above, the measured water contents determined for subsamples of core 73.86 were the same within the analytical uncertainty of 0.1 wt.% (Figure 6).

The quantity of fluid extracted sequentially from a subsample of core from a depth of 73.86 was different in the two extraction steps examined. A total of 0.031g of fluid was extracted during the first 2 hours of centrifuging (73.86b). After an additional 4 hours in the second centrifugation step, approximately twice as much fluid (an additional 0.064g) had been extracted (73.86c) from the same rock sample. Taken together, a total of 0.095g of fluid was extracted from this one subsample of core 73.86 over the 6 hour total centrifugation time. This is more than was extracted from the other four subsamples (a, d, e and f) using a single centrifugation step of 6 hours.

In Table 5, the quantity of fluid extracted using ultracentrifugation is compared to the total water available in the sample as determined by drying at 120 °C for 48 hours. The calculated approximate yield, or approximate percentage of the total amount of pore fluid removed from each subsample by ultracentrifugation is also given.

Table 5: Comparison of quantities of fluid extracted using ultracentrifugation to total amount of pore fluid available.

Sample ID	Total weight of pore fluid in sample (drying at 120 °C) ¹ (g)	Wt. of pore fluid extracted by ultracentrifugation ¹ (g)	Approx. % of total pore fluid removed
50.09b	3.45	0.020	0.6
73.86b (2h)	1.40	0.031	2.2
73.86c (2 + 4 h)	1.40	0.064	6.8*
73.86d	1.30	0.075	5.8
73.86e	1.39	0.072	5.2
73.86f	1.36	0.011	0.8

*Calculated using the total quantity of water removed in both sequential extraction steps (73.86b,c)

¹Values as reported in Table 2

The percentages of pore fluid removed using ultracentrifugation are small (0.6 to 7%) relative to the total quantity of pore fluid in the rock sample as determined by drying at 120 °C.

Edmunds and Bath (1976) noted that as with any extraction method, centrifugation will only extract a fraction of the total pore fluid. The quantity of pore fluid extracted from the argillaceous limestones in the current study is low compared to quantities reported for volcanic tuffs, where 26% to 45% of the available pore fluid was extracted using ultracentrifugation (Scofield 2006). In the case of the chalk examined by Edmunds and Bath (1976), 85 to 95% of the pore fluid was extracted using centrifugation (14,000 rpm). The centrifuge conditions, the

initial degree of saturation of the rock and the intergranular physical properties (e.g. pore size distribution, interconnectivity of pores) of the rock will influence the fraction of pore fluid which can be extracted (Edmunds and Bath, 1976). The lower pore fluid yields observed in the current study are likely a result of the lower porosity of the argillaceous limestones and/or lower connectivity between pores.

The important question with respect to interpreting the chemical compositions of the extracted fluids is whether or not the partial extracts of pore fluid obtained are representative of the “bulk” pore fluid composition in the rock. This is considered in conjunction with observations on the chemical compositions of the extracted pore fluids in section 5.3.

5.2 COMPOSITION OF EXTRACTED FLUIDS

The Total Dissolved Solids (TDS) content of the extracted pore fluids varies between 4,400 and 52,500 mg/L (Table 3). For samples from which fluid could be extracted, there is no apparent correlation between water content and TDS, as shown in Figure 7. This figure also highlights the observation that although the water content determined for five different subsamples of core 73.86 was essentially the same (0.5 to 0.6 wt. %), the TDS contents of the fluids extracted from the subsamples varied substantially from 4,400 to 52,500 mg/L.

In addition to the large variability in TDS observed between subsamples of the same core extracted for the same length of time (subsamples d, e and f from core 73.86), large variations in salinity were also observed within the single subsample of core that was centrifuged twice; first for 2 hours and then for an additional 4 hours. After the first 2 hours of centrifugation, 0.031 g of fluid with a TDS of 52,550 mg/L (73.86b in Figure 7) had been extracted. After four additional hours of centrifuging, slightly more than twice as much water was extracted (0.064 g; 73.86c in Figure 7). The salinity of this second fluid is much lower, with a TDS of only 22,800 mg/L. Decreases in the concentrations of all major cations and anions are also observed with the progressive centrifugation of the subsample to extract pore fluids 73.86b and 73.86c. The molar concentrations of the dominant ions determined in these fluids are compared in Table 6. Examination of the dominant ions, Na^+ , Ca^{2+} and Cl^- , shows that the concentration decreases observed in the sequential extractions are well beyond the analytical uncertainty in these values of $\pm 10\%$.

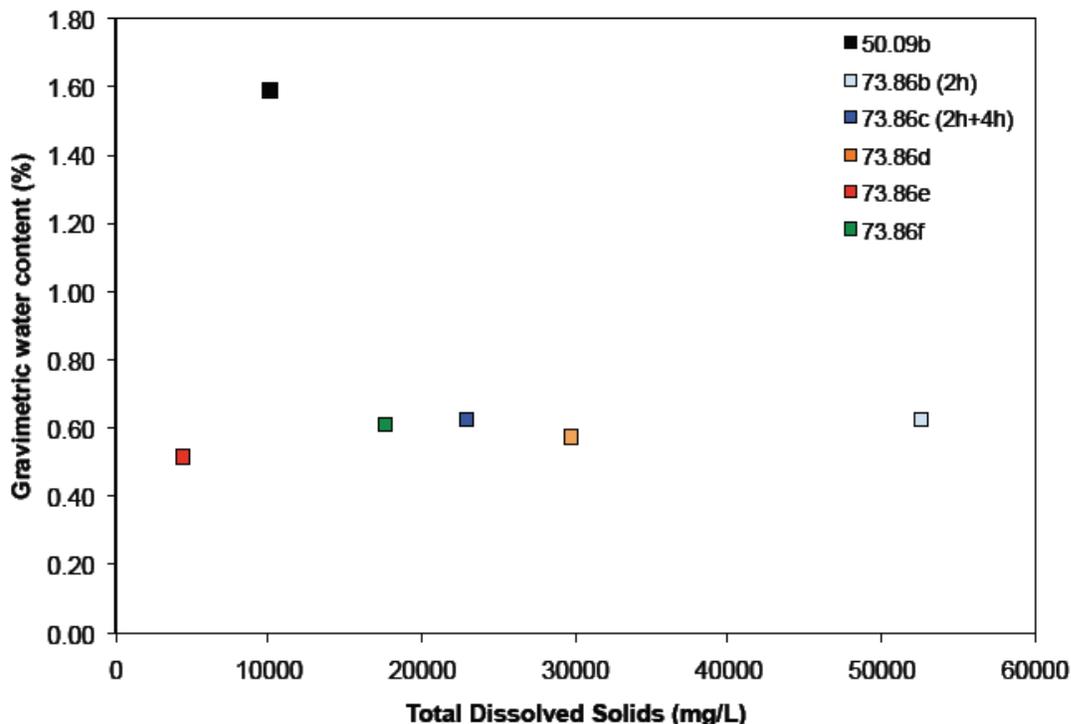


Figure 7: Relationship between water content of core subsamples and salinity, reported as TDS in mg/L. Fluids 73.86b and c were extracted from the same subsample of core after a total extraction time of 2 and 6 hours, respectively.

Table 6: Comparison of concentrations (in mmol/L) of selected ions in fluids extracted sequentially from the same subsample of core after 2 and 6 hours of centrifuging.

Ion or ion ratio	73.86b (2 hours) Concentration (mmol/L)	73.86c (2 + 4 hours) Concentration (mmol/L)	Difference (Factor)
Na ⁺	428	119	3.6
Ca ²⁺	164	94	1.7
Mg ²⁺	88.0	50.2	1.8
K ⁺	5.47	4.02	1.4
NH ₄ ⁺	3.16	1.55	2.0
Cl ⁻	917	403	2.3
HCO ₃ ⁻	--	5.80	--
Br ⁻	4.29	2.53	1.7
SO ₄ ²⁻	1.61	0.34	4.7
Na/Ca	2.62	1.27	2.0
Ca/Mg	1.86	1.87	1.0
Br/Cl	0.0047	0.0063	0.7

5.3 INITIAL INTERPRETATIONS

Two different interpretations of the results collected to date for the argillaceous limestone are explored in the following sections. We first consider whether or not the variations in the quantities of available pore fluids (i.e. water contents) and the chemical compositions of the extracted pore fluids might represent in-situ variations in water contents and pore fluid compositions. We then explore the evidence suggesting that the quantity and/or chemical compositions of the pore fluids may have been altered either during storage of the core or during ultracentrifugation.

5.3.1 Extracted pore fluids are representative of in-situ pore fluids

One possible interpretation of the observed variations in the quantity of pore fluid extracted and in the salinity and chemical composition of the pore fluid is that these reflect actual, in-situ variations in the amount and composition of pore fluid present within the rock matrix.

There is some experimental evidence to support the interpretation that the variation in water contents observed for core samples collected at different depths between 50 and 73 m are not simply an artefact of the experimental method applied. Water contents determined for cores taken from different depths using two different techniques (oven drying at 120 °C for 48 hours and vacuum distillation at 130 °C for 6 hours) were similar (Table 2). The reproducibility of the water contents determined for five subsamples of the same core (73.86m; Figure 6) was the same within the analytical uncertainty of 0.1%. However, these observations do not support the representativeness of the measured water contents with respect to in-situ values, because processes such as evaporation may have affected the cores prior to preservation or during storage of the preserved core.

A wide range of total salinity from approximately 4,400 to 52,500 mg/L TDS and chemical compositions (Table 3) were observed for fluids extracted from subsamples of the same core (73.86). This may imply centimetre-scale spatial heterogeneities in the in-situ pore fluid composition within the rock matrix. However, in order to substantiate this interpretation, a similar variation in pore fluid composition at the centimetre scale would need to be replicated using a different pore fluid extraction method. For example, Yang et al. 2003 reported variations at the decimetre to metre scale in the chemical composition of pore fluids extracted from volcanic tuffs. The chemical compositions of pore fluids extracted from adjacent core samples using two different methods, uniaxial or triaxial compression and ultracentrifugation, were found to be within the analytical error of 10 to 15% (with the exception of pH and SiO₂ for one zeolitic sample). The agreement between the chemical compositions determined using two independent methods supports the interpretation that the compositional variations observed by Yang et al. 2003 are present in-situ at the decimetre to metre scale.

Furthermore, the large variation observed in the total dissolved contents and chemical compositions of fluids extracted sequentially from a single subsample of core 73.86 (pore fluids 73.86b,c) can not be attributed to small-scale, in-situ heterogeneities in pore fluid composition. This observation suggests that the pore fluid composition may have been altered, either prior to or during extraction, as discussed below.

5.3.2 Quantities and compositions of pore fluids have been altered

Alternative explanations for the observed variations in the quantity and/or chemical composition of the extracted pore fluids involve external processes which may have affected the pore fluid prior to or during ultracentrifugation analysis. Two possible influences are considered in this section: i) evaporation of pore fluid from the core prior to analysis; and ii) fractionation as a result of ultracentrifugation.

Evaporation

Differences in water content and in the total salinity (TDS) of the extracted pore fluids may reflect partial drying of the core prior to analysis. In this case, water loss from the cores may have occurred during core retrieval, during the 30 minutes after drilling and before core preservation, or after the core had been preserved during the 2 or more months of refrigerated storage prior to analysis.

If partial drying had occurred, the first, shorter duration spin might access pore fluid which has been exposed to evaporation and precipitated salts may be re-dissolved, thereby increasing the TDS of the first portion of fluid extracted. The longer duration spin might then extract additional pore fluid from deeper within the core (but still within the connected porosity) which has not been influenced by evaporation. In general, this interpretation appears to be consistent with the extraction of higher salinity fluids during the first 2 hour spin of the subsample of 73.86 (extracted pore fluid 73.86b), followed by extraction of a more dilute pore fluid (73.86c) during a second, 4 hour extraction from the same subsample. In this case, the higher Na/Ca and lower Br/Cl ratios measured in the initially extracted fluids could represent the influence of halite precipitated in the outermost pores of the cores during evaporation of pore fluid and then redissolved into the pore fluid extracted during the first extraction step. However, we note that if the second, lower TDS (22,900 mg/L) pore fluid extracted is more representative of the in-situ pore fluid, the degree of evaporation required to reach halite saturation in the outermost pores would be high. Furthermore, the concentrations of all major ions are observed to decrease by factors ranging from 1.4 (Ca^{2+}) to 3.6 (Na^+) from the first to second pore fluid extracted. Re-dissolution of a series of soluble salts in the first extracted pore fluid would be required in order to explain the substantially higher concentrations of all major ions measured in the first fluid extracted.

If the variations in total salinity are the result of differential evaporation from the cores prior to analysis, a correlation between the water content of the core and the total dissolved solids content in the extracted pore fluid might be expected, such that as the total water content decreases, the salinity of the fluid increases. In this case, the wide range of TDS values between approximately 4,400 and 29,700 mg/L observed for fluids extracted from different subsamples of the same core (76.86d, e and f) might be explained by differential evaporation of the pore fluid in subsections of the same core. However as noted previously, the gravimetric water contents determined for the subsamples of this core are essentially constant (0.6 wt. %), despite large variations in TDS (Figure 7).

A detailed examination of the potential influence of evaporation on the chemical composition of the fluids extracted using ultracentrifugation would require fresh, preserved core. Water loss during transport and various core storage periods could be examined to determine the effectiveness and longevity of the core preservation methods. The potential effect of processes such as evaporation and/or interaction with drilling fluid on pore fluid composition could also be

investigated in preserved cores (fresh and older cores) by removing the outer 1 to 2 centimetres of the core. The outer rim material, which may have undergone some evaporation and/or interaction with drilling fluid, could then be analyzed separately from the inner core material.

Fractionation

In previous studies by Yang et al. (2003) and Scofield (2006), little or no fractionation of solutes was observed during extraction of pore fluids from volcanic tuffs using ultracentrifugation. Scofield (2006) examined the influence of sequential extractions made on the same sample of a non-welded volcanic tuff. The sample was initially spun for 1 hour and 5 ml of fluid were retrieved. The sample was then spun for an additional 5 hours, after which time an additional 2.4 ml of fluid had been extracted. The measured pH, specific conductance and major ion concentrations were found to be very similar in both fluids (Scofield 2006).

In contrast, in sequential extractions conducted on samples from the Upper English Chalk, Edmunds and Bath (1976) observed changes in the cation compositions of the extracted pore fluids (results for anions were not reported). As progressively more fluid was removed from a given sample, the concentrations of Na^+ and K^+ in the pore fluid decreased, with an up-turn or levelling off in the concentration observed in the final 10 to 20% of pore fluid removed. Calcium concentrations continued to decrease with progressive fluid extraction, whereas no changes were observed in the concentrations of Mg^{2+} and Sr^{2+} . For the chalk examined, it was estimated that the observed fractionation could introduce errors of up to $\pm 10\%$ with respect to the in-situ pore fluid compositions (Edmunds and Bath 1976; Bath and Edmunds 1981). However, it was also noted that the chalk was almost pure carbonate and that much greater fractionations may occur in rocks with higher clay mineral contents (Edmunds and Bath 1976).

In the current study, the changes in ion concentrations observed in pore fluids extracted from a single subsample of argillaceous limestone with sequential ultracentrifugation steps are significantly higher than those reported by Edmunds and Bath (1976) for the Upper English Chalk. Referring to Table 6, decreases are observed in all measured ions in the pore fluid extracted during the second extraction step relative to those measured in pore fluid from the first extraction step. For example, Na^+ concentrations in the second fluid extracted (73.86c) are lower by a factor of approximately 3.6 (or a decrease in concentration of $\approx 72\%$) compared to those extracted in the first extraction step (73.86b). Similarly, Cl^- concentrations in the second pore fluid extracted are a factor of 2.3 or approximately 56% lower than in the fluid recovered during the first step.

The chemical fractionation observed with sequential extractions may be the result of ion filtration during extraction. As discussed in section 2.4, argillaceous materials and in particular, compacted shales and clays, may act as semi-permeable membranes. During ultracentrifugation, solution is transported out of the rock material as a result of the applied tension, which varies as a function of distance from the rotor and centrifugal speed (Edmunds and Bath, 1976). If the rock material itself acts as a semi-permeable membrane, the movement of ionic species through the material will be restricted, whereas neutral water molecules will pass through the "membrane".

Using a simplifying assumption that the quantity of solutes removed during sequential extractions made on the same subsample from core 73.86 is the same and that the additional fluid removed by doubling the extraction time from 2 to 4 hours is pure water, a rough

predication of the salinity of the second pore fluid (i.e. 73.86c) can be made. The ratio of the quantity of fluid extracted during the two sequential spins is $0.031 \text{ g}/0.064 \text{ g} = 0.484$. Multiplying by the salinity for the first extraction, 52,550 mg/L gives an expected TDS of 25,430 mg/L. The measured salinity of the extracted pore fluid was 22,850 mg/L, which is within the 2σ error margins of the calculated TDS content ($\pm 10\%$). The similarity between the measured and predicted TDS of the fluid extracted during the second ultracentrifugation step combined with the decrease observed in the concentrations of the major ions between the first and second extraction steps may indicate that ion filtration is occurring in this material during ultracentrifugation.

To further evaluate the possibility that changes occurred in the pore fluid compositions during extraction by ultracentrifugation, the compositions of pore fluids extracted by ultracentrifugation and using other techniques should be compared. When such information is available, compositions of extracted pore fluids should also be compared the compositions of groundwater(s) sampled in close vicinity in order to evaluate how well the extracted pore fluids represent in-situ pore fluid compositions.

The potential influence of chemical fractionation could be further examined through a more extensive series of sequential extractions on the same subsample of core over different extraction times. This requires that enough fluid can be extracted for analysis of 3 or more subsamples with different extraction times (e.g. 2, 4 and 8 hours total extraction time), to explore the variability in pore fluid compositions.

5.4 STABLE ISOTOPIC COMPOSITIONS ($\delta^{18}\text{O}$, $\delta^2\text{H}$)

The fluid volumes extracted from the limestone cores using ultracentrifugation were insufficient for analysis of stable isotopic compositions; only major ion compositions were analyzed. Vacuum distillation is an alternative technique for extracting porewater from rock core. In the procedures applied in this study (Appendix A3), the samples are heated to approximately 130°C under vacuum and the extracted water is captured cryogenically over six hours. Using this technique, only water is extracted – any ions within the pore fluid remain in the rock core. While this method may provide sufficient water for analysis of stable isotopic compositions, it does not provide any information on the chemical composition of the pore fluid.

Vacuum distillation was used to extract waters from several subsections of cores taken at depths of between 54 and 68 mBGS. The average stable isotopic compositions of the extracted waters are presented in Table 4 and plotted in Figure 8. The Global Meteoric Water Line (GMWL) and the stable isotopic compositions of present-day meteoric waters within the Great Lakes Region as reported by Husain et al. (2004) are also plotted. The isotopic compositions of the extracted waters plot to the left and slightly above the GMWL. The $\delta^{18}\text{O}$ values of the extracted waters range between -8.6 and -12.9‰ , just overlapping the heavier end of the range measured in present-day meteoric waters (-11 to -9‰). The extracted waters have $\delta^2\text{H}$ values of between -55 and -53‰ , significantly heavier than present-day meteoric waters which have $\delta^2\text{H}$ values between -78 and -62‰ (Husain et al. 2004). If the stable isotopic signatures determined for the extracted waters are representative of in-situ values, then these results indicate that matrix porewaters have $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values which are different than present-day meteoric waters, despite the fact that the cores were sampled at relatively shallow depths (54 to 68 mBGS).

Insight into whether or not the stable isotopic compositions of the extracted waters are representative of in-situ values could be gained by comparison with the stable isotopic composition of local groundwaters. Ideally, these groundwaters would be sampled within the same formation or in close proximity, from the same borehole from which the core was taken. Groundwater samples were not collected as part of the drilling campaign to retrieve the core examined in this study, and therefore, such a comparison is not possible.

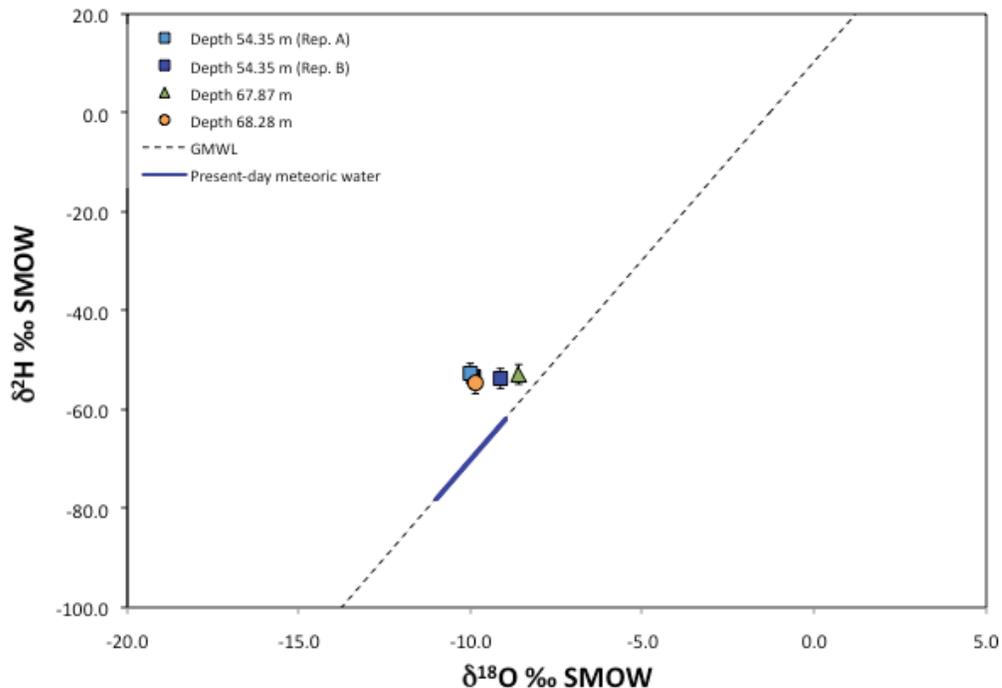


Figure 8: Stable oxygen and hydrogen isotopic compositions measured for porewaters extracted from the argillaceous limestone using the vacuum distillation technique. Stable isotopic compositions of present-day meteoric waters in the Great Lakes Region are from Husain et al. 2004. The analytical uncertainty of 2‰ in $\delta^2\text{H}$ is shown by the error bars. For $\delta^{18}\text{O}$, the analytical uncertainty of 0.2‰ is smaller than the symbols.

In several previous studies, vacuum distillation has been applied to extract porewaters for stable isotopic analyses from various argillaceous rock materials, including argillite from Touremire, France (Altinier et al. 2006; Savoye et al. 2006) and the Opalinus Clay, Switzerland (Gimmi et al. 2007; Rübél et al. 2002). Vacuum distillation was conducted at various temperatures including 50 °C (e.g. Altinier et al. 2006; Savoye et al. 2006), 105 °C (e.g. Altinier et al. 2006; Rübél et al. 2002) and 150 °C (Altinier et al. 2006). The stable isotopic compositions of the extracted waters were compared to stable isotopic values determined using

other porewater extraction methods and/or to water collected in nearby fractures. Values from vacuum distillation conducted at either 50 or 105 °C were found to be depleted in the heavy isotopes by 10 to 20‰ in $\delta^2\text{H}$ and approximately 3‰ in $\delta^{18}\text{O}$ when compared to isotopic compositions determined using other methods or when compared to groundwaters sampled in fractures at the same site (e.g. Gimmi et al. 2007). On the other hand, Altinier et al. 2006 found that the stable isotopic compositions determined for the porewaters from the Tournemire argillite extracted using vacuum distillation at 150 °C were consistent with values determined for nearby fracture fluids.

Using the data set generated as part of the current study, it is not possible to assess the effect of processes such as incomplete distillation during vacuum extraction at 130 °C on the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of the waters extracted from the Cobourg limestone. Such an assessment would require detailed studies including, for example, an examination of the stable isotopic compositions of waters extracted as a function of both extraction temperature and total extraction time.

6. CONCLUSIONS

The ultracentrifugation technique for the extraction of pore fluids has been applied to shallow limestones from the Bowmanville area, south-western Ontario. Preserved core samples from depths between 50 and 74 m were examined. Gravimetric water contents of the samples ranged from 0.3 to 2.5 wt.% and good agreement was observed between values determined on subsamples of the same core using two independent methods (oven drying for > 48 hours at 120 °C and vacuum distillation at 130 °C for 6 hours). The differences in gravimetric water contents determined for subsamples from a single core ranged from 0.1% up to 0.9 wt.%.

Despite the very low water contents (0.3 to 2.5%) of the core samples, small quantities (0.031 to 0.75 g) of pore fluid were extracted using ultracentrifugation from a subsample of core taken at a depth of 50.09 m and from 5 subsamples of a core taken at 73.86 m. Relative to the total water available in the sample as determined from the gravimetric water content, the portion of fluid extracted from the argillaceous limestones examined in this study ranged from 0.6 to 6.8%. This is much smaller portion than extracted in previous studies where 23 to 46% of the total water available was extracted from volcanic tuffs using ultracentrifugation (Scofield 2006) or the Upper English Chalk where 80 to 95% of the total water could be extracted using high-speed centrifugation (Edmunds and Bath, 1976) or 40 to 50% by centrifugation at 2000 rpm. The lower yields observed in the current study is likely a result of the lower porosity and/or lower pore connectivity within the argillaceous limestones.

The variation in the total dissolved solids (TDS) content of the extracted pore fluids ranged from 4,400 to 52,500 mg/L for pore fluids extracted from the 5 subsamples of one core from a depth of 73.86 m. The one pore fluid extracted from a subsample of core 50.09 had an intermediate TDS value of 10,100 mg/L. Differences in the chemical composition of the pore fluids were also observed. Based on a comparison of ion concentrations expressed in meq/L, Cl⁻ is the dominant anion in all pore fluids and Ca²⁺ is the dominant cation, except in the pore fluid with the highest salinity, in which Na⁺ was the dominant cation. The concentrations of both Ca²⁺ and Na⁺ were observed to increase with increasing Cl⁻ concentration and the Na/Ca ratio also increases, whereas the Br/Cl ratio decreases.

In two sequential extractions on a single subsample of core 73.86, the quantity of fluid extracted after 4 hours of spinning in the second extraction was more than twice that extracted during the first, 2 hour extraction step. Decreases in the major ion concentrations by factors between 0.7 and 3.4 were observed between the two extraction steps; well beyond the analytical uncertainty of ±10%. This observation suggests that the variations observed in pore fluid composition do not reflect in-situ variations, but rather may be the result of changes in pore fluid composition that occurred prior to or during ultracentrifugation. Two possible explanations were explored: i) the pore fluids were modified by evaporation prior to analysis; or ii) that the chemical changes observed in the pore fluid are induced during ultracentrifugation due to a process such as ion filtration. Based on the results of this study alone, it is not possible to conclude whether one or both of these processes affected the extracted pore fluid compositions. Future studies of fluid content changes during transport and storage could be used to explore the importance of evaporation, while multiple sequential extractions from single core samples and comparison with pore fluids extracted using an independent method and/or groundwaters sampled in close proximity could be used to further examine how representative the extracted pore fluids are of in-situ pore fluids.

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APPENDIX A: EXTRACTION OF PORE FLUID FROM LIMESTONE SAMPLES

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A.1 INTRODUCTION

Several protocols were developed during the course of this study to address various aspects of the ultracentrifuge technique. They are given in detail below.

A.2 ULTRACENTRIFUGATION PROTOCOL FOR SEDIMENTARY ROCKS

Extraction of pore fluid using centrifugation methods was achieved using a Beckman model L8M/P ultra-centrifuge®. The Beckman ultra-centrifuge is capable of spinning rock samples at a rate of 16,500 rpm under thermostatically controlled conditions. The rotor spins inside a vacuum chamber, but Viton A O-rings maintain atmospheric pressure inside the buckets during the run. A titanium plate with channels leading to a central porthole separates the rock from the extracted water in the attached polyethersulfone collection tube.

A.2.1 BASIC PROTOCOL

1. Cores are unwrapped from the ProtecCore® package and the vacuum-sealed plastic wrap. Core intervals are cleaved off along the bedding plains perpendicular to the core axis using a clean hammer and chisel inside a clean rock-crushing bin lined with Para Film®.
2. Approximately 200 to 250 g of core is broken up into pieces 1 to 3 cm in diameter. A clean hammer, chisel and rock-crushing bin are used for this sample preparation.
3. Approximately equal amounts of broken core are placed in the titanium centrifuge cups and balanced to within 0.3 g of each other using core pieces. The weights of the polyethersulfone collection tubes are recorded using a 3-decimal place balance. This is done so that small volumes of extracted pore fluid can be weighed before diluting the sample with deionized water.
4. The collection tubes are then attached to the titanium rock-sample cups and the weight of the full cup assembly is recorded. Components of the tubes are shown in Figure A2-1 (reproduced with permission from Beckman).
5. Aluminium caps are screwed tightly to the titanium cups and the assemblies are placed inside three aluminium buckets.
6. The buckets are attached to the rotor and the rotor assembly is placed into the centrifuge chamber. The entire process is performed in less than 10 minutes to prevent evaporation of porewater. Samples are typically spun for a total of 6 hours at 15,000 rpm (approximately 25,000 g force). Details of the centrifugation are shown in Figure A2-2 (reproduced with permission from Beckman).
7. The pore fluid collection tubes are then removed and the weight of the extracted pore fluid, if any, is recorded. The typical extracted pore fluid sample is too small to collect so dilution of the sample with deionized water is performed directly into the collection tubes.

8. The weights of the extracted pore fluid and the added deionized water are recorded. The diluted sample is collected with a pipette and filtered using a 0.45 μm filter.
9. The centrifuged pieces are then weighed and placed in an oven for at least 48 hours at 120° C to determine the residual pore fluid volume.

A.2.2 VARYING SIZE FRACTIONS

Extraction tests were performed using different size fractions of rock. Smaller-sized rock fragments (1 cm or less) allow more sample to be loaded into the cups and shorten the distance for pore fluid to escape from the rock matrix. The chief disadvantage is that a greater surface area is created and, hence, more potential for evaporation of porewater during the 8 to 10 minute preparation time. It has been determined that smaller size fractions did not offer any advantage to pore fluid extraction and on some occasions had a lower water content than larger size fractions after centrifuging test and oven drying. The current protocol is to load the titanium cups with larger fragments (up to 3 cm) and fill in the voids with smaller fragments.

A.2.3 VARYING TEMPERATURE

Tests were performed using higher temperature settings, up to 30° C, to determine if the decrease in fluid viscosity at higher temperatures enhances pore fluid extraction. Tests have showed that there is no apparent advantage to pore fluid recovery at higher temperatures. Increasing the centrifuge chamber temperature to greater than 30°C may increase the potential for evaporation of porewater.

A.2.4 THE “QUICK LEACH” PROCEDURE

A separate protocol has been developed in which a ‘quick leach’ is performed on a sample that has been ultracentrifuged and the results compared of to a quick leach on an uncentrifuged, fresh sample. This idea is based on the possibility that salts may exist in the outer layers of the limestone pieces after 6 hours of centrifuging due to the accumulation of pore fluids that have migrated from the interior to the perimeter of the pieces. A quick leach with a known amount of deionized water would re-dissolve these salts without dissolution of the mineral grains.

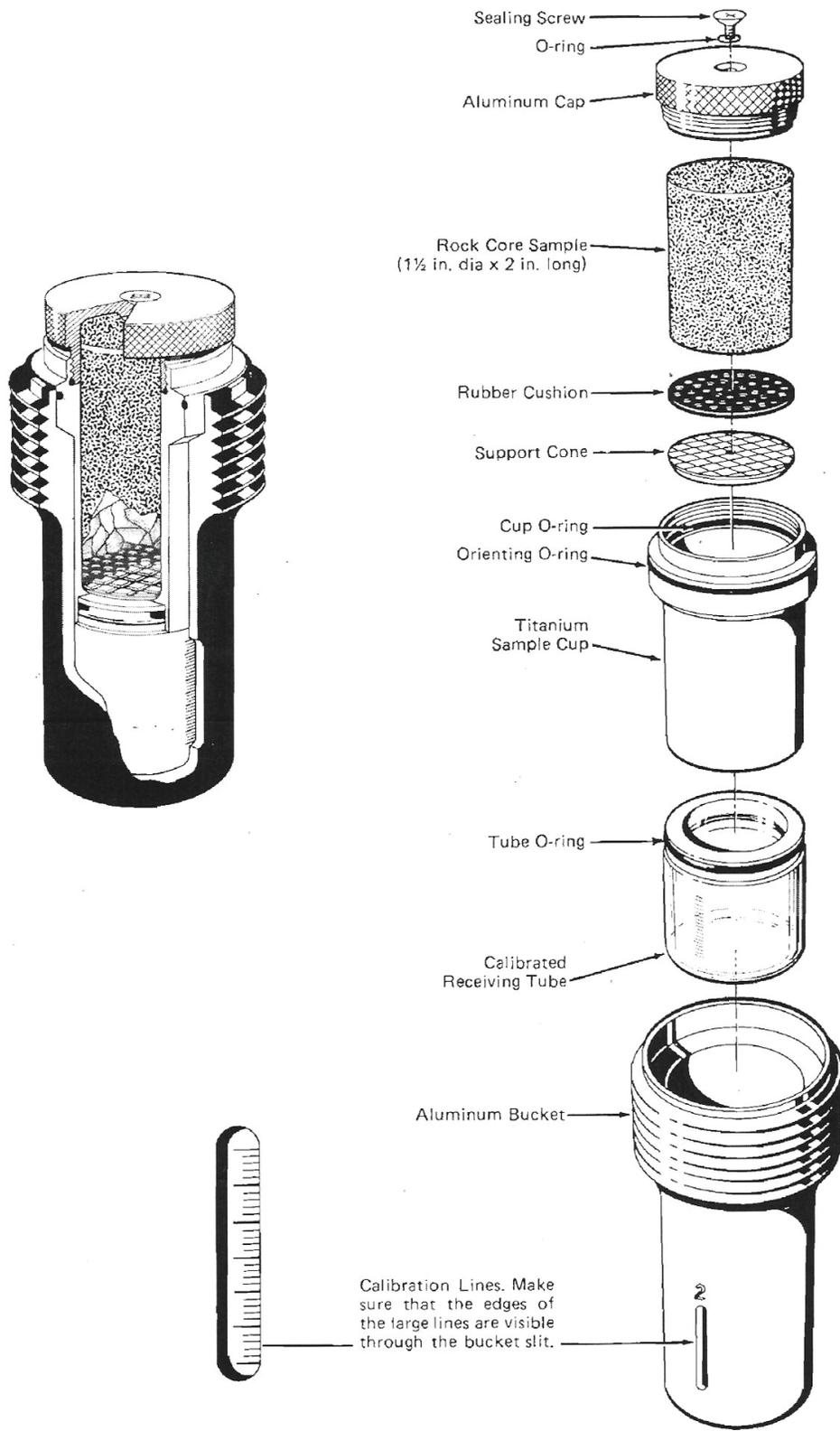
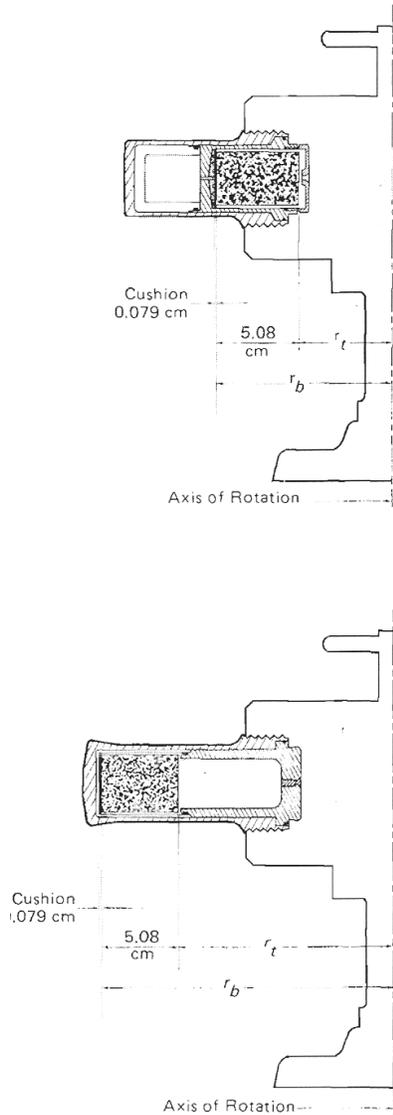


Figure A2-1 Components of the centrifuging system (with permission from Beckman).

INSTRUCTIONS FOR USING THE TYPE PIR 16.5 ROTOR
In the Beckman Model L8M/P and L5-50P Ultracentrifuges



SPECIFICATIONS

Standard Buckets

Maximum speed	16 500 rpm
Relative centrifugal force* at maximum speed	
At r_b (core bottom) 9.13 cm	27 800 x g
At r_t (core top) 4.05 cm (nominal) [†]	12 400 x g
Nominal dimensions of rock core	1½ in. dia x 2 in. long
Max. dimensions of rock core	1.555 in. dia x 2.050 in. long
Maximum density of rock core	2.82 g/mL
Number of buckets	3
Volume of receiving tubes	see Table 1
Tube material	polyethersulfone
Rotor material	aluminum
Maximum imbalance of buckets	0.3 gram
Weight of empty rotor	4.7 kg (10.4 lbs)
Conditions requiring speed reductions	see Rotor Speeds

Inverted Buckets

Maximum speed	15 000 rpm
Relative centrifugal force* at maximum speed	
At r_b (core bottom) 16.63 cm	41 900 x g
At r_t (core top) 11.55 cm (nominal) [†]	29 100 x g
Nominal dimensions of rock core	1½ in. dia x 2 in. long
Max. dimensions of rock core	1.555 in. dia x 2.050 in. long
Maximum density of rock core	2.82 g/mL
Number of buckets	3
Volume of receiving tubes	see Table 1
Tube material	polyethersulfone
Rotor material	aluminum
Maximum imbalance of buckets	0.3 gram
Weight of empty rotor	4.7 kg (10.4 lbs)
Conditions requiring speed reductions	see Rotor Speeds

*Calculated for a rock of nominal dimensions using the equation
 $g' = 1.12 \times 10^{-5} \text{ RPM}^2 r.$

[†]Operator must measure the core to be centrifuged and determine r_t .

Figure A2-2. Details of the centrifuging equipment (with permission from Beckman).

A.3 VACUUM DISTILLATION METHOD

The USGS Geochemistry Team uses distillation methods for extracting water from unsaturated zone core samples for isotopic analysis and for measuring water contents. During vacuum distillation, a sample is heated in a closed system under vacuum, and the water is condensed and frozen in a cold trap. The volume of water is measured gravimetrically and transferred to glass vials. The water can be used for analyzing tritium, oxygen 18/16, and deuterium/hydrogen.

A.3.1 VACUUM DISTILLATION APPARATUS

1. U-tube glassware with stopcock
2. Glass sample chamber with lid and stopcock
3. Glass water collection bulb

All glass components of the distillation apparatus are thoroughly washed with DI water and oven dried for at least 4 hours. Isopropyl alcohol may be used to remove stopcock grease prior to washing with DI water.

A.3.2 VACUUM DISTILLATION PROCEDURE:

1. A vacuum is applied to the distillation apparatus for one hour to check for vacuum leaks.
2. The core sample is weighed inside the sample chamber and the sample chamber is attached to the distillation apparatus and a vacuum is applied.
3. A heating mantle is wrapped around the sample chamber and heating tape around the U-tube.
4. The sample chamber is heated to $\sim 180^{\circ}\text{C}$ resulting in a core temperature of $\sim 130^{\circ}\text{C}$.
5. The core water vapor is expelled and condensed in the collection bulb that immersed in a dry ice/alcohol mixture at a temperature of $\sim -80^{\circ}\text{C}$.
6. The total volume of water recovered is weighed and transferred to a glass vial.
7. The distilled core is weighed in the sample chamber before being removed and placed inside and oven at $\sim 130^{\circ}\text{C}$ for at least 72 hours to check for further water loss.
8. For most core samples, the total distillation time takes 6 hours to ensure complete extraction of porewater.