

Research Article

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

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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 Cl^- : Br^- ratios. The observed differences in Cl^- : 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 Cl^- : 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 Cl^- : Br^- ratio because each method reflects different proportions of the interlayer, diffuse double layer, and mobile fractions of porewater.

1. Introduction

The requirement for long-term geological sequestration of CO_2 [1, 2] and nuclear waste management [3–5] has prompted increased interest in low-permeability, clay-rich sedimentary rocks [6–12]. These rocks are characterized by low hydraulic conductivity ($<10^{-11}$ m/s) and, as a consequence, solute transport is dominated by diffusion [4, 13–17]. 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 [8, 10, 18–23]. Mazurek et al. [10] 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 [24]. Negatively charged clay surfaces are balanced by cation-rich water in direct contact with the surface [25, 26]. 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,

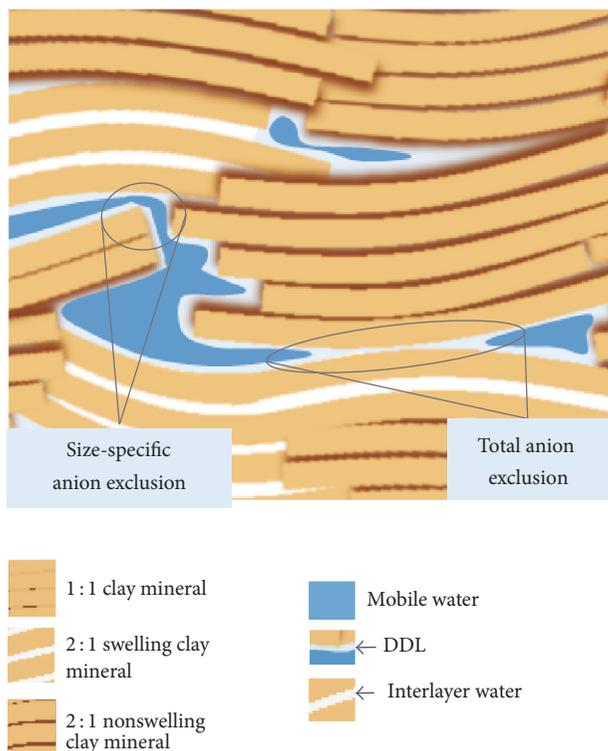


FIGURE 1: Pore-scale conceptual model for clay-rich sedimentary rock. A variety of clay minerals are depicted, including 1:1 clay minerals, such as kaolinite, 2:1 nonswelling clay minerals, such as illite, and 2:1 swelling clay minerals such as smectite. The negatively charged surfaces of these minerals 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.

extending outward into the pore spaces [27, 28]. “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 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 [39] 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 [40]. The geometry of the pores can influence the movement of solutes due to variations in the constrictivity, connectivity, and tortuosity of the pore channels [41]. In materials with narrow pore throats, DDLs can overlap, impeding the movement of anions to cause anion exclusion effects [42]. 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.

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 [29, 50], but the sampling durations are very long, on the order of months to years [51]. Indirect methods are also available, including out-diffusion [52–54], ultracentrifugation [55], high-pressure squeezing [48, 56, 57], crushing and leaching [48, 58–60], advective displacement [9], and absorption by paper [61]. These methods are susceptible to artefacts from disturbance of the equilibrium between minerals, bound water, and mobile water [62] that result in mineral dissolution [57], cation exchange [63], and changes in DDL thickness [64]. These artefacts may cause inconsistency among methods, particularly for the reactive cation species [62, 65]. In addition, effects of anion exclusion [11] 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 [10, 48, 66].

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 [48, 58–60]. The paper-absorption method is included in the comparison because it targets only the mobile water fraction.

2. Materials and Methods

2.1. 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

TABLE 1: Mineralogical and Physical properties.

	Michigan Basin			Opalinus Clay			Lorraine Group
	Queenstown	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}						
	1.1×10^{-14} – 1.0×10^{-13}			2.0×10^{-14} – 6.0×10^{-13}			N/A
	Porosity (accessible loss%) ^{f,c}						
	6–7			12–15			N/A
	Ionic strength (mol/L) ^{g,h}						
	8.2			0.4			N/A

^a[43]; ^b[44, 45]; ^cClark, Matray, and Waber: BDB-1 borehole investigation, unpublished; ^d[37]; ^e[46]; ^f[47]; ^g[30]; ^h[48, 49]; N/A = not available.

Basin at St. Édouard 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) [67]. 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 (BDB-1) 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 [68]. 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. Édouard 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 Queenstown, 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 1.

2.2. Paper Absorption. This method is based on that described by Celejewski et al. [61]. 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 [69] and Wang et al. [70] 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 [69] 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 [71]. 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 ($>18.2 \text{ M}\Omega\text{-cm}$). 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.

2.3. 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 ($<30 \text{ mm}$), 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 ($0.45 \mu\text{m}$). Concentration of Cl^- and Br^- in the leachates was quantified by ICP-MS.

3. 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 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 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 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).

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 [6], 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

TABLE 2: Masses (μg) of Cl^- and Br^- extracted by the crush-and-leach and paper-absorption methods.

Crush and leach			Paper absorption		
Sample	Cl^-	Br^-	Sample	Cl^-	Br^-
Michigan Basin					
463a	53928	630	463a	641	15
463b	63586	744	463b	1109	26
495a	45262	562	495a	5355	129
495b	49897	584	495b	4434	112
522	49783	615	522	4224	107
531	20635	261	531	4057	93
571a	70851	884	571a	5739	117
571b	80998	874	571b	4119	87
571c	79415	875	571c	3667	76
626a	53887	620	626a	5077	125
626b	54301	659	626b	5718	131
634a	53411	615	634a	1474	35
634b	55397	635	634b	1420	33
634c	54416	612	634c	1761	40
634d	59462	678	634d	4242	95
634e	55150	637	634e	3290	82
Lorraine Group Shales					
F7-1	289	2.71	F7-3	109	1.59
F7-2	295	2.75	F7-4	91	1.32
F8-1	80	0.38	F8-3	24	0.20
F8-2	78	0.39	F8-4	16	0.16
F20-1	1162	9.87	F20-3	148	2.5
F20-2	1209	10.4	F20-4	287	5.13
444-1	121	1.66	444-2	55	1.08
Opalinus Clay					
115.1	542	1.63	115	77	0.28
115.2	550	1.73			
115.3	493	1.51			
115.4	625	1.92			
119.1	1061	3.54			
119.2	984	3.32			
119.3	948	3.12			
119.4	996	3.37			
121.1	1163	3.85	128.1	85	0.33
121.2	1185	3.85	128.2	83	0.34
121.3	1239	4.14			
121.4	1131	3.72			
132.2	1454	4.74	144a	73	0.30
132.2	1554	4.90	144b	70	0.35
132.3	1576	5.00			
132.4	1467	4.47			
161.1	2899	9.39			
161.2	2832	9.00			
161.3	3049	9.70			
161.4	2539	8.02			
166.2	3418	10.84			
166.3	3367	10.73			
166.4	2886	9.21			
172.1	2469	7.86			
172.2	2581	8.36			
172.3	2517	8.11			
172.4	2519	7.94			
174.1	2702	8.42			
174.2	2857	8.97			

TABLE 2: Continued.

Crush and leach			Paper absorption		
Sample	Cl^-	Br^-	Sample	Cl^-	Br^-
174.3	2555	7.82			
174.4	2587	8.22			
179.1	1684	5.15	178a	185	0.74
179.2	1715	5.37	178b	177	0.75
179.3	1613	5.04			
179.4	1601	4.96			
190.2	1473	4.81			
190.3	1467	4.78			
190.4	1462	4.79			
192.1	3318	10.62			
192.2	3228	10.42			
192.3	3065	10.05			
192.4	3222	10.28			
203.1	3767	11.98	204a	179	0.77
203.2	3712	11.78	204b	170	0.70
203.3	3768	12.01	204c	165	0.71
203.4	3698	11.96	204d	163	0.81
209.1	4002	12.82			
209.2	3608	11.59			
209.3	3351	10.87			
209.4	3365	10.73			
220.2	2880	9.05			
220.3	2752	8.54			
220.4	2751	8.59			

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 [72], 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 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.

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. [29] are presented in Figure 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

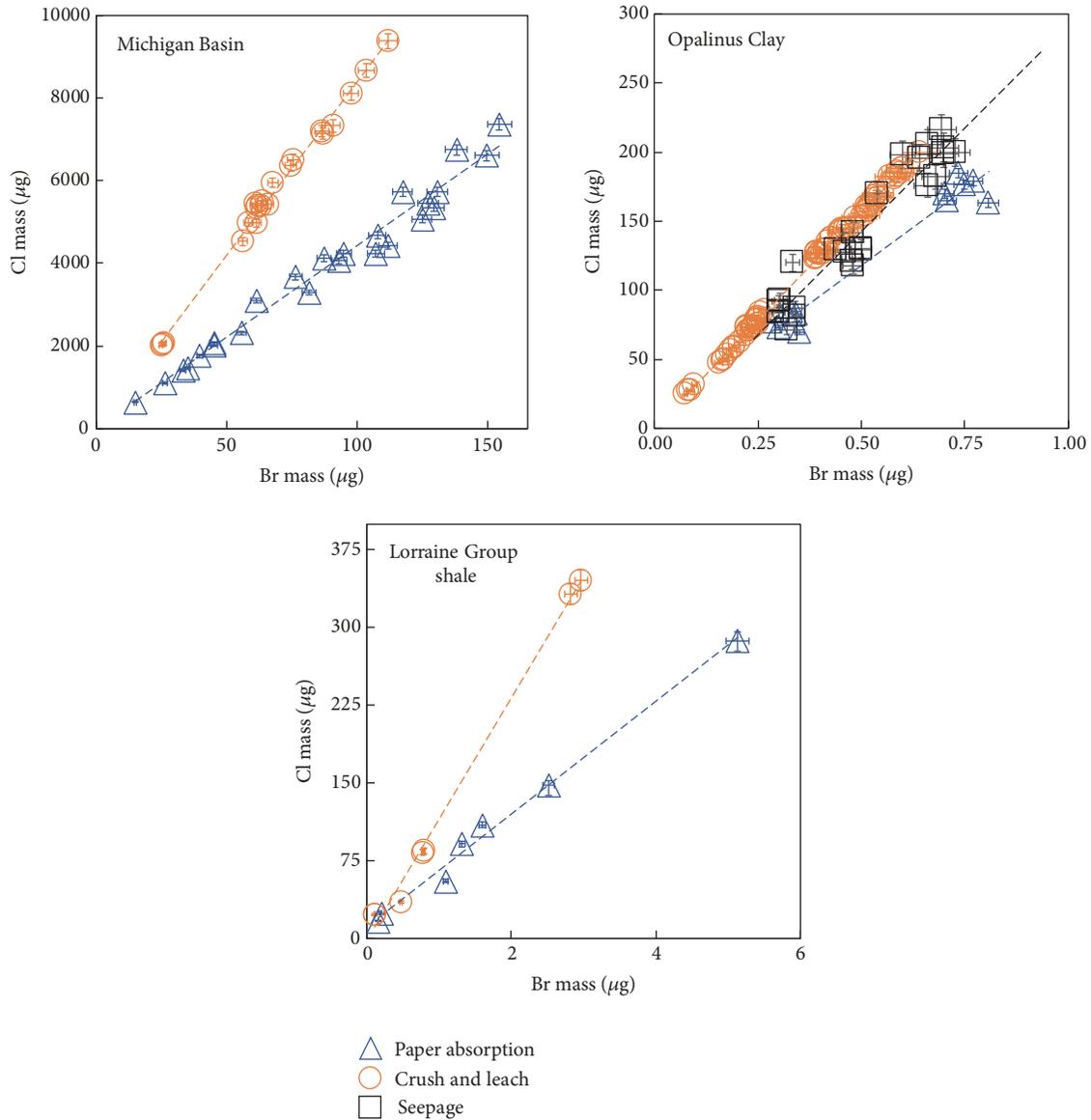


FIGURE 2: Cl^- versus Br^- mass extracted using the paper-absorption and crush-and-leach methods for rock cores from the Michigan Basin, Opalinus Clay, and the Lorraine Group. Scaling factors of 10, 20, and 3.5, respectively, were applied to the masses extracted by crush and leach to allow for direct comparison between methods. 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. [29]. Error bars represent the instrumental error on solute analysis.

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 [73].

3.1. Porewater Model. A commonly used conceptual model for porewater occurrence in low-permeability clay-rich sedimentary rock is depicted in Figure 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 (1); [63, 74]]:

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

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

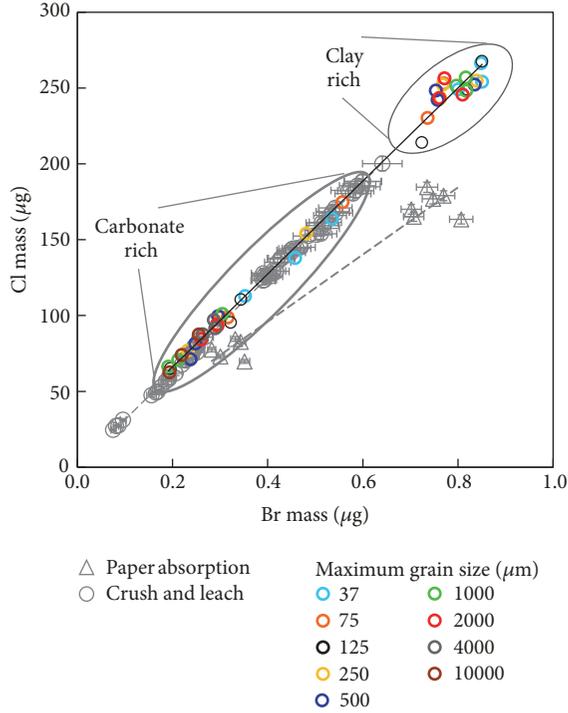


FIGURE 3: Anion masses extracted by crush and leach from Opalinus Clay samples crushed to a range of grain sizes (<37, 37–75, 75–125, 125–250, 250–500, 500–1000, 1000–2000, 2000–4000, and 4000–10000 μm).

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 [48, 56, 58–60], while the paper-absorption method relies on capillary-pressure gradients to draw water from the mobile water fraction. Hodgson and Berg [75] 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. [76] 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 [75] to calculate the capillary pressure (P_c) of water in the fibres with the Young-Laplace relationship,

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

yield a value of 14 MPa. Intera [37] reports air-entry pressures for the shales in the Michigan Basin ranging from 9 to 29 MPa, and Marschall et al. [38] 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 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)

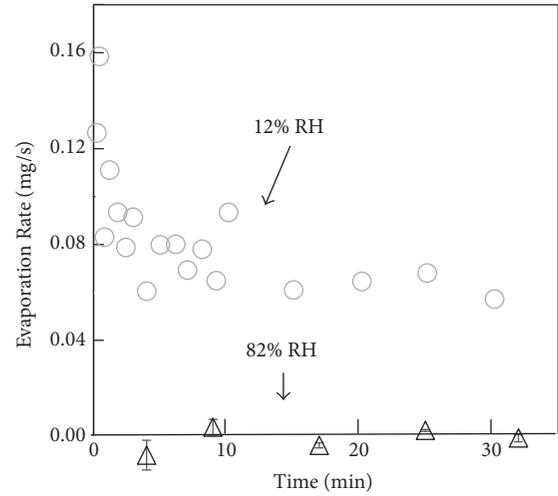


FIGURE 4: Evaporation rates of synthetic porewater [30] under open lab conditions (12% RH) and in a humidity chamber (82% RH).

the mobile water porosity is equal to the anion-accessible porosity, (2) the anion-accessible porosity represents 50% of the total porosity [48], (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:

$$\text{Depth} = \frac{V_{\text{H}_2\text{O}} / (n \cdot 0.5)}{2SA}, \quad (3)$$

where $V_{\text{H}_2\text{O}}$ is the volume of porewater extracted, n is the anion-accessible porosity, and SA is the area of the absorbing paper.

The distribution of dissolved anions is limited, predominantly, to the mobile fraction [39, 77–80], 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 [81–83] and that not all anions are affected equally [12, 24, 84, 85]. Appelo et al. [24] 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 (4); [86]]:

$$G_f = \frac{\tau^2}{\delta}, \quad (4)$$

where τ is tortuosity and δ is constrictivity. Appelo et al. [24] 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 [87] 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

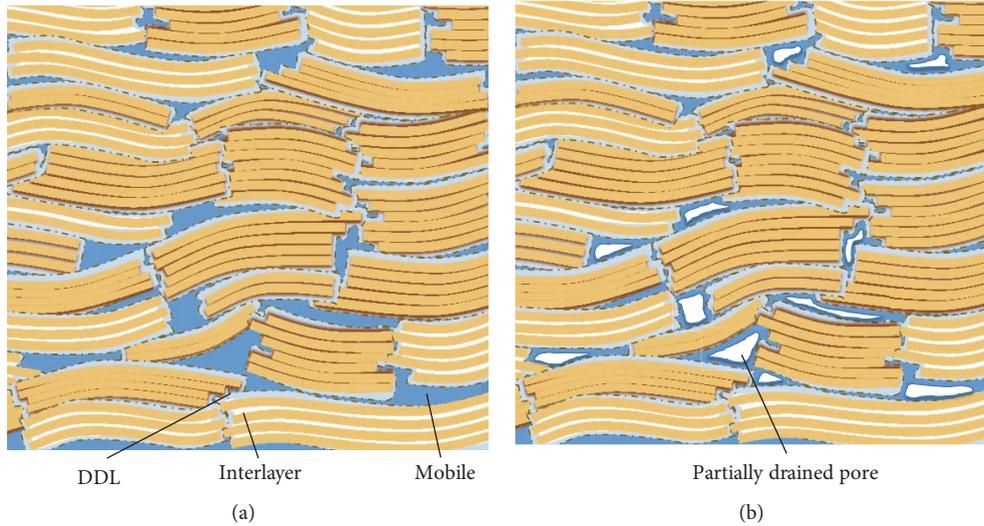


FIGURE 5: (a) A pore-scale conceptual model of the different porewater fractions found in a low-permeability clay-rich sedimentary rock. (b) The paper-absorption method extracts porewater from the largest interconnected pores. In this example, partially drained pore spaces are assumed to be connected in the third dimension.

(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. [11] 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.

3.2. Ion Pairing and Clustering. Ion pairing refers to a short-lived association between oppositely charged ions in aqueous solutions [88–90]. 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 [32, 87, 91–94]. 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. [93] 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 [95, 96].

Chen and Pappu [32] 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 [32] 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 [87] 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 [31]. This is a reasonable proxy because porewaters in the Michigan Basin [97, 98] and the Opalinus Clay [29] 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 6. The fraction of Cl^- in positively charged and neutral species is 2% to 7% higher than for Br^- , and, consistent with electrolyte theory [99],

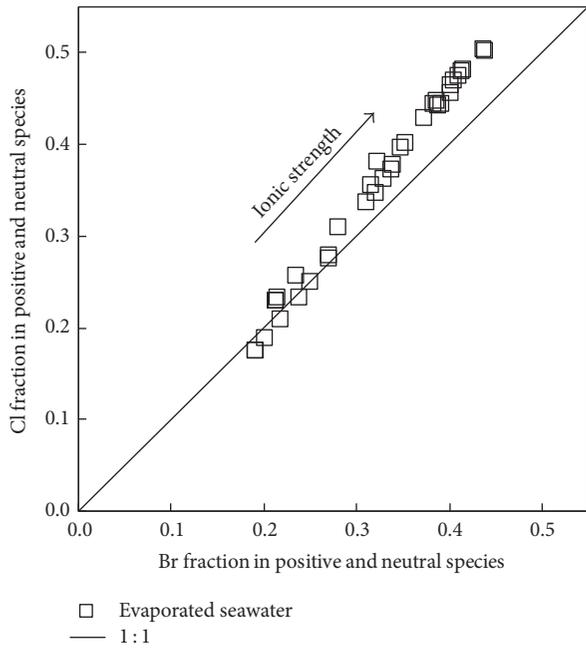


FIGURE 6: Fraction of Cl^- and Br^- occurring in the form of positively charged and neutral ion pairs and clusters. Calculations are for seawater, evaporated to variable degrees [31], using K_{assoc} values from Chen and Pappu [32].

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.

3.3. 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 [10, 19, 24, 56]. 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 [24, 39].

Based on physical principles it can be expected that size-specific anion exclusion (Figure 1) will occur in highly compacted, clay-rich rocks [100]. Size-specific anion exclusion should result in fractionation of anions of differing size/charge and a nonuniform anionic distribution in the pore spaces. Hydrated anion radii are compared in Figure 7, demonstrating that there is a systematic increase in radii with increasing atomic number among the halides. Based on (1) and synthetic porewater compositions (Table 1), an estimated

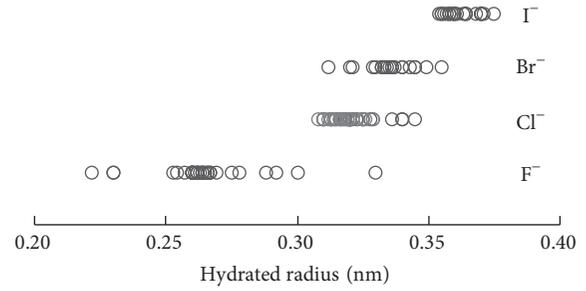


FIGURE 7: Compilation of hydrated anion radii reported in the literature [33, 34].

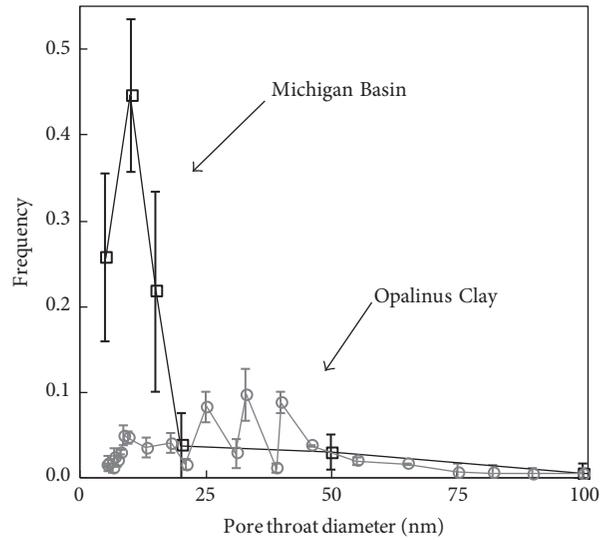


FIGURE 8: Pore throat diameters quantified by MIP. Opalinus clay data (adapted from [35]) from a pair of samples from the Mont Terri Rock Laboratory (borehole BCS-2, gallery 98). Data for the Michigan Basin (adapted from [36]) are from the Queenston, Georgian Bay, and Blue Mountain formation shales. The error bars represent standard deviation.

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 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 [35] and values on the order of 9 nm are reported for shales from the Michigan Basin [36]. The ionic-strength effect on the respective DDL thicknesses is small

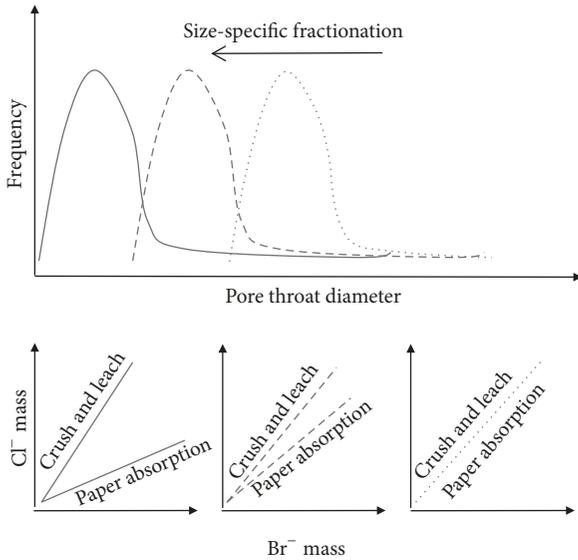


FIGURE 9: Conceptual model depicting the fractionation of Br^- from Cl^- due to size-specific anion exclusion and the relationship to pore throat diameter.

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 9.

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 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 10. There are only two points so it

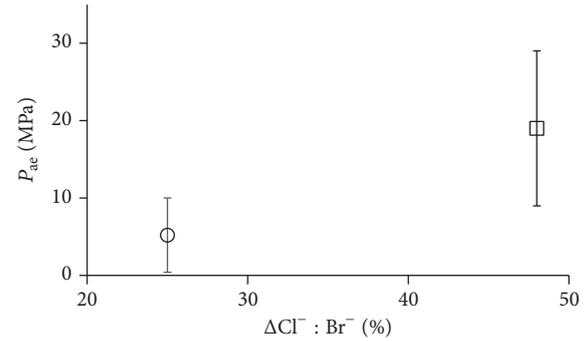


FIGURE 10: Relationship between air-entry pressure (P_{ae}) and the difference in $\text{Cl}^- : \text{Br}^-$ ratios ($\Delta\text{Cl}^- : \text{Br}^-$) measured by the crush-and-leach versus the paper-absorption method for the Opalinus Clay (circles) and the Michigan Basin (squares). The error bars represent the range of air-entry pressures reported by Intera [37] for Ordovician shales in the Michigan Basin and by Marschall et al. [38] for the Opalinus Clay.

remains for future work to determine the strength and nature of such a relationship.

4. 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.

Conflicts of Interest

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

Acknowledgments

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