Benchmarking of the Isotope Diffusive Exchange Method Using Opalinus Clay and Queenston Shale Rocks Equilibrated with Synthetic Saline Solution

NWMO TR-2014-14 **June 2014**

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ABSTRACT

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Abstract

This study aims to test recent developments for advancing the isotope diffusive exchange technique in order to adapt it to high salinity porewaters and, in a more general way, to solutions with low water activities. This report documents work performed to: 1) investigate factors that might influence the results of the isotope diffusive exchange technique for saline solutions through solution-solution experiments; and 2) benchmark the adapted diffusive exchange method using rock samples previously equilibrated with synthetic solutions of known composition (chemical and isotopic). Two different rocks have been used to perform the benchmarking tests: 1) Queenston Shale from Ontario, Canada; and 2) Opalinus Clay from the Mont Terri Underground Research Laboratory (URL), Switzerland.

Solution-solution diffusive-exchange experiments showed that perturbing factors include: 1) the water activity mismatch between the test and sample solutions; 2) the weight difference between the test and sample solutions; and 3) contrasting chemical compositions (NaCl versus $CaCl_2$) between test and sample solutions. Benchmarking of the isotope diffusive exchange method using rock samples equilibrated with synthetic solutions has tested: 1) whether or not the isotopic composition obtained by the diffusive exchange method actually corresponds to the composition of the porewater; and 2) if there are additional perturbing factors, i.e., other than those identified in the solution-solution experiments.

Equilibration of Opalinus Clay and Queenston Shale rocks (which are saturated with porewater at experiment initiation) with 0.3 and 5 molal NaCl, and 2.5 and 5 molal $CaCl_2$ synthetic solutions has been performed successfully by immersing 2 to 4 cm diameter rock pieces into air-tight PVC containers for periods of 62 and 90 days, respectively. Equilibrium was apparently attained in about 1 day for Opalinus Clay rock samples, and 4 days for the Queenston Shale rock samples. The rock samples never disaggregated during these experiments, even at 0.3 molal NaCl solution concentrations. The density of the equilibrated rocks, in all cases, is lower than that of the intact porewater-saturated rock and increases with increasing salinity of the synthetic solution. This is probably because the confining pressure in the equilibration experiments is low compared to in-situ conditions. The rock density correlates with its water content, which is higher in low salinity solutions.

Data obtained from Opalinus Clay and Queenston Shale rock experiments indicate that the diffusive exchange method gives reliable results of the isotope composition ($\delta^{18}O$ and $\delta^{2}H$) of the porewater at all salinities when the chemistries of the porewater and test waters are similar. Results for $\delta^{18}O$ values are shifted up by about 1‰ for contrasting chemistries (NaCl versus $CaCl_2$), and insignificantly for $\delta^{2}H$. The diffusive exchange technique gives reliable results for rocks with water content as low as 0.5 wt%.

For unknown reasons, the use of the diffusive exchange method for obtaining the water content of the rock gave good results at high salinities (≥2.5 molal), but overestimated values at low salinities (0.3 molal).

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1. INTRODUCTION

The difficulty associated with analyzing the water isotopic composition of brines (i.e., high salinity pore fluids) arose within the framework of a methodology study undertaken to adapt porewater analytic techniques previously developed for low permeability Jurassic clay-rich rocks from Switzerland (Opalinus Clay; e.g., Pearson et al., 2003; Gimmi and Waber, 2004) to the study of saline porewaters of Paleozoic sedimentary rocks of southern Ontario (Waber et al., 2007; Koroleva et al., 2009; Hobbs et al., 2010). The isotope diffusive exchange technique (Rogge, 1997; Rübel et al., 2002) works well for the isotopic characterization of porewaters less saline than seawater (Pearson et al., 2003; Gimmi and Waber, 2004; Gimmi et al., 2007; Altinier et al., 2006), but major changes of the protocol are needed to adapt the method to high salinity porewaters. Increasing the salinity of porewater introduces three complications: i) the water activity (a_w) of the test water has to be matched to the a_w of the sample by addition of salts to minimize water mass transfer between the test water and the sample; ii) it is impossible to directly analyze $\delta^{18}O$ and $\delta^{2}H$ for saline solutions with common routine procedures (with CO_2 equilibration in a GasBench and H_2O reduction in a H-Device, respectively) and, consequently, these samples have to be distilled first; and iii) the liquid-vapour isotope fractionation coefficient of water depends on the salinity and the type of salt (Horita et al., 1993a and 1993b).

The purpose of this work program is to evaluate and benchmark a newly adapted technique for determining stable isotopic compositions ($\delta^{18}O$, $\delta^{2}H$) of saline matrix porewaters in cores collected during site characterization activities. This report documents: i) distillation tests; ii) solution-solution (water-water) isotope diffusive exchange experiments performed using synthetic solutions of known isotopic composition (Table 1); and iii) benchmarking of the adapted diffusive exchange method using rock samples previously equilibrated with synthetic solutions of known composition (chemical and isotopic). Two different rocks have been used to perform the benchmark tests: Queenston Shale from southern Ontario, Canada, and Opalinus Clay from the Mont Terri URL, Switzerland. The Opalinus Clay bears low salinity (below seawater) porewater and has already been well characterized within the framework of the nuclear waste program of Switzerland, while the Queenston Shale is saturated with high salinity brines and has been studied within the nuclear waste program of Canada. Both lithologies are candidates being evaluated with respect to the abilities to function as host and/or barrier rocks for deep nuclear waste storage.

The adapted diffusive exchange method has first been tested with standard water solutions. The following aspects have been investigated: i) the accuracy and reproducibility of the distillation procedure applied to NaCl, $CaCl_2$ (+NaF) and NaF solutions; ii) the precision and potential salinity dependence of the isotope diffusive exchange technique; iii) the effect of water activity (salinity) mismatch between test and sample solutions; iv) the effect of changing the weight ratio between the test and sample solutions; and v) the impact of contrasting chemical compositions (NaCl versus $CaCl_2$) between test and sample solutions.

The stable isotope composition of Cambrian saline ground water from borehole DGR-3 at the Bruce Nuclear Site (OGW-10, Heagle and Pinder, 2009) in southern Ontario, Canada, has been analyzed using two methods: i) a direct procedure (NaF addition to the groundwater followed by distillation), and ii) the adapted diffusive exchange procedure using NaCl or $CaCl_2$ in the test solutions. This allows testing of the diffusive exchange method and the NaF treatment method for the distillation of complex Na-Ca-Mg-Sr-Cl brines (Cambrian groundwater) to allow comparison with data obtained by direct H_2 and CO_2 GasBench equilibration (Heagle and

Pinder, 2009). Corrections proposed by Horita et al. (1993a and 1993b), accounting for the dependence of the liquid-vapour isotope fractionation coefficients on the chemical composition of the solutions, can be compared to the results of the diffusive exchange experiments.

The isotope diffusive exchange method has been benchmarked using Opalinus Clay and Queenston Shale rocks previously equilibrated with synthetic solutions of known composition (chemical and isotopic). The following aspects have been investigated, including: 1) whether or not the isotopic composition obtained by the diffusive exchange method actually corresponds to the composition of the porewater; and 2) if there are additional factors that perturb the results of the adapted diffusive exchange method, in addition to those detected in solution-solution experiments. The method of equilibrating the rocks with synthetic solutions, as well as the diffusive exchange data, is documented in this report. The methodology development investigated in this study is discussed in detail; details of the other methods used in support of this work and method development are presented in Appendix A.

Table 1: Summary of Solution and Solution-Solution Experiments (No Rock Material)

Part	Description	Planned	Performed	δ18O and δ2H analysis of water	Distillation and δ^{18}O and δ^{2}H analysis of water	Solution-solution (water-water) diff-exchange experiments
1	**Stable isotope analysis of standard waters with a range of NaCl or $CaCl_2$ concentrations: Test potential effects of distillation and salt addition**					
1.0	Isotopic composition of the LAB, TEW, and EVIAN standard waters. 5 separate analyses of water from each standard water bottle. Average of the replicate analyzes is considered for the isotopic composition of the standard waters.	3 standard waters. LAB: 5 analyses. EVIAN: 5 analyses. TEW: 10 analyses (5 for each bottle).	As planned	20		
1.1	Test effect of distillation on pure (no salt) standard waters: Analyze stable isotope compositions of pure waters (LAB, TEW, EVIAN) after distillation.	5 distillations for each 3 standard waters.	As planned			
1.2	Test effect of adding NaCl: Add NaCl to Evian water (0.3, 1, 2.5, 5 molal), distill and analyze water isotope compositions.	4 solutions in duplicate	As planned		8	
1.3	Test effect of adding $CaCl_2$: Add $CaCl_2$ to Evian water (0.3, 1, 2.5, 5 molal), treat with NaF, distill and analyze water isotope compositions.	4 solutions in duplicate	As planned		8	
1.4	Test effect of adding NaF: Add NaF to Evian water (0.3 and 0.85 molal), distill and analyze water isotope compositions.	2 solutions in duplicate	As planned		4	
1.5	Test direct treatment of Cambrian groundwater OGW-10 (DGR3) with NaF (to remove dissolved Ca^{++} as fluorite, Mg^{++} as sellaite, and Sr^{++} as SrF_2), distill and analyze water isotope compositions.This allow comparizon of the direct NaF treatment and distillation of Cambrian water with the results obtained through the NaCl and $CaCl_2$ diffusive exchange technique (see Part 2.8).	1 sample in triplicate	As planned		3	
2	**Solution-solution (water-water) diffusive-exchange experiments (no rock material)**					
2.1	Perform diffusive exchange experiments with NaCl added to sample water and test water (0, 0.3, 1, 2.5, 5 molal). Same salinity in test and sample solutions. Distill test solutions, analyze water isotope compositions.	5 experiments	As planned. Plus analyses of sample solutions of 1 experiment (2.5 molal).	2	10	5
2.2	Perform diffusive exchange experiments with $CaCl_2$ (no NaCl) added to sample and test solutions (0.3, 1, 2.5, 5 molal). Same salinity in test and sample solutions. NaF added to test solutions after experiment, then distillation and analysis for water isotope compositions.	4 experiments	As planned. Plus analyses of sample solutions of 1 experiment (2.5 molal).		10	4
2.3	Test effect of slight mismatch (0.05 to 0.1) of water activity between test and sample solutions: Use 2.5 molal NaCl sample solution with 0.3, 1, and 5 molal NaCl test solutions. Perform diffusive exchange experiments, distill test waters, analyze water isotope compositions.	3 experiments	As planned		6	3
2.4	Test effect of important mismatch (0.15 to 0.3) of water activity between test and sample solutions: Use 2.5 molal $CaCl_2$ sample solution with 0.3, 1, and 5 molal $CaCl_2$ test solutions. Perform diffusive exchange experiments, add NaF, distill test waters, analyze water isotope compositions.	3 experiments	As planned		6	3
2.5	Test effect of test/sample water mass ratio (to simulate different water contents of rock samples): Use of 5 molal $CaCl_2$ sample and test solutions. Test water (in solution) fixed at 5 ml while sample water (in solution) is 0.5, 1, 3, or 7 ml. Treat with NaF, distill and analyze water isotope compositions of test solutions.	4 experiments	As planned		8	4
2.6	Investigate isotope fractionation between an NaCl and a $CaCl_2$ Evian solutions of similar water activity after diffusive exchange equilibration through the vapor phase. $CaCl_2$ solutions treated with NaF after experiment. Sample and test solutions distilled and analyzed for water isotope compositions.	3 experiments at 3 water activities.	As planned		6	3
2.7	Testing potential perturbations induced by contrasted chemistries between test and sample waters. The diffusive exchange technique is performed using NaCl test solutions and $CaCl_2$ sample solutions at three different water activities (initial water activities of test and sample waters are matched). $CaCl_2$ solutions treated with NaF after experiment. Sample and test solutions distilled and analyzed for water isotope compositions.	3 experiments at 3 water activities.	As planned		12	3
2.8	Diffusive exchange experiments with Cambrian groundwater OGW-10 (DGR3) as sample. Two sets of triplicate experiments, one using NaCl and the other $CaCl_2$ to match the water activity of the test solutions with the sample. This allows comparison of the NaCl and $CaCl_2$ diffusive exchange technique with the results obtained through direct NaF treatment and distillation of Cambrian water (see Part 1.5).	3 experiments with NaCl and 3 experiments with $CaCl_2$ in test water	As planned		12	6
	TOTAL			22	93	31

2. BACKGROUND INFORMATION

Water activity (a_w) of rock or liquid samples can be measured directly from the relative humidity of the air immediately surrounding the sample using a HygroPalm AW1, with a resolution of ±0.001 a_w and an accuracy of ±0.003 a_w. The water activity meter is operated in AwQuick mode. The correlation between water activity and salinity is shown in Figure 1 for the most common Cl-bearing salts encountered in porewaters: NaCl, KCl, $CaCl_2$ and $MgCl_2$. The water activity of the different salt solutions, up to saturation, can be calculated from the salt molality (x) with the following formulae, obtained from Pitzer equations:

$$a_w \text{ (NaCl molality)} = 2\text{E-}05x^4 - 0.0003x^3 - 0.0003x^2 - 0.0325x + 1 \quad (1)$$
$$a_w \text{ (KCl molality)} = 3\text{E-}05x^4 - 0.0003x^3 + 0.0009x^2 - 0.0325x + 1 \quad (2)$$
$$a_w \text{ (CaCl}_2\text{ molality)} = 2\text{E-}05x^4 + 0.0014x^3 - 0.0204x^2 - 0.0354x + 1 \quad (3)$$
$$a_w \text{ (MgCl}_2\text{ molality)} = 0.0002x^4 + 0.0002x^3 - 0.0202x^2 - 0.0386x + 1 \quad (4)$$

In this study, only NaCl and $CaCl_2$ solutions were used. The activity of pure water is 1, while water activities of brines saturated with NaCl and $CaCl_2 \cdot 6H_2O$ at 20°C are 0.75 and 0.32, respectively. Therefore, NaCl can be added to the test water to match sample water activities down to 0.75, but $CaCl_2$ has to be used if sample water activity is below 0.75. Most samples from the Paleozoic sedimentary rocks in southern Ontario have water activities between 0.55 and 0.7, thus requiring the addition of $CaCl_2$ to the test waters (Hobbs et al., 2010). In addition to dissolved species in the porewater (or osmotic effects), other factors contributing to the measured water activity of a core sample (matrix effects) include: i) surface interactions between water and the rock matrix; ii) capillary effects of porewater (e.g., Jury et al., 1991; Jarrett et al., 2004); and iii) interaction with minerals (e.g., swelling clays, anhydrite). Matching of the water activity of the test water with that of the saturated rock sample is essential to avoid water mass transfer between the test solution and rock sample.

In a closed system, mass transfer of water through the vapour phase between two reservoirs filled with water solutions of different a_w will occur until equilibrium is reached (i.e., when salinities and, therefore, a_w are equal in both reservoirs). This mass transfer does not induce errors in the results of the diffusive exchange method, if equilibrium is reached (at that point, the isotope compositions of both reservoirs are the same), but the time required for equilibrium is difficult to evaluate and might be long. It is, therefore, important to minimize disequilibrium between the water activities of the two reservoirs at the start of the experiment by adding the required amount of salt to the test solution.

The determination of the hydrogen isotope composition of saline waters using the common procedure of Cr-reduction in a Thermo Fisher (formerly Thermo Finnigan, Bremen, Germany) H-Device is not possible. Alternatively, measurements of δ^2H by H_2 equilibration (Coplen et al., 1991) and of $\delta^{18}O$ by CO_2 equilibration in a GasBench are possible, but the measured isotopic signatures will be shifted from their true values because the presence of salts changes the isotopic fractionation factor between water and vapour (Horita et al., 1993a and 1993b). Although these deviations can be corrected empirically using the brine chemical composition and the vapour-liquid equilibration temperature (Horita et al., 1993a and 1993b), the H_2 GasBench equilibration technique is not implemented in all laboratories. The alternative is to quantitatively distill the saline solutions to remove the salts before isotopic analysis, which removes potential errors associated with the empirical salt-related isotope fractionation correction.

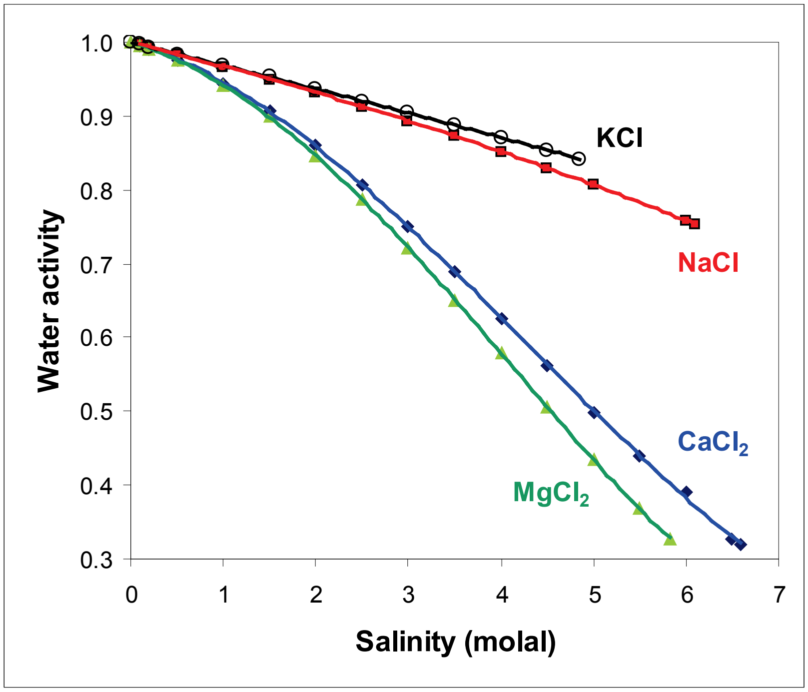


Figure 1: Water Activity versus Salinity of NaCl, KCl, $CaCl_2$, and $MgCl_2$ Solutions; Lines End at Saturation with a Solid Phase (KCl, NaCl, $CaCl_2{\bullet}6H_2O$, or $MgCl_2{\bullet}6H_2O$) and were Calculated Using Pitzer Equations and the Program Geochemist's Workbench®

Figures 2 and 3 show the $\delta^{18}O$ and $\delta^{2}H$ isotope fractionation coefficients between vapour and liquid water at 20°C with respect to water activity for NaCl, KCl, $CaCl_2$ or $MgCl_2$ (see Figure 1). At the same water activity, and considering the respective analytical errors of 0.4‰ and 1.4‰ (2σ) for $\delta^{18}O$ and $\delta^{2}H$ (see Section 4), fractionation coefficients are significantly different between NaCl and $CaCl_2$ solutions for $\delta^{18}O$ (up to 1‰ difference), but similar for $\delta^{2}H$ (maximum 3‰ difference). This implies that if a_w are matched, the effect of having different chemical compositions in the test and sample solutions is likely to be minimal for $\delta^{2}H$ (2 times the 2σ error), but would require a correction (<1‰) for $\delta^{18}O$.

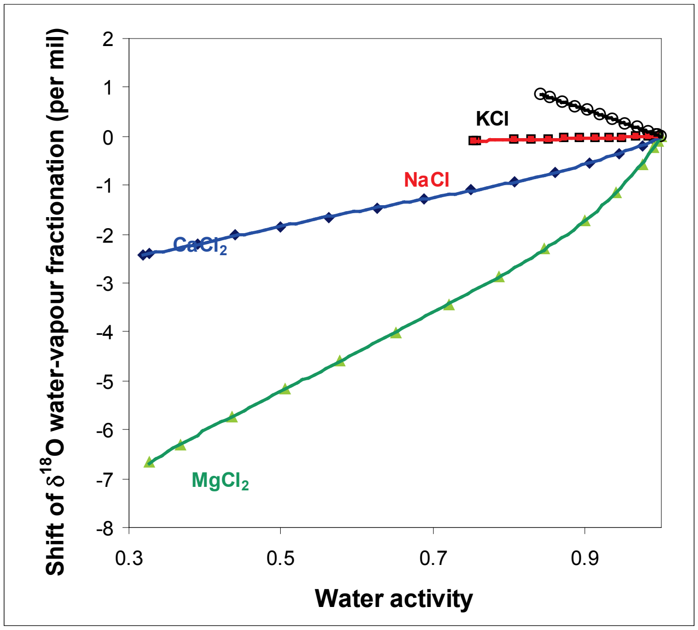


Figure 2: Calculated Shift of the δ^{18}O of Vapour at 20°C versus the NaCl, KCl, $CaCl_2$ and $MgCl_2$ Salinity, Expressed as Water Activity; Equations are Compiled from Horita et al. (1993a), and were Published for Temperatures >25°C for NaCl, KCl, and $MgCl_2$, and >50°C for $CaCl_2$; Extrapolation to 20°C has to be Considered as a Proxy, Particularly for $CaCl_2$

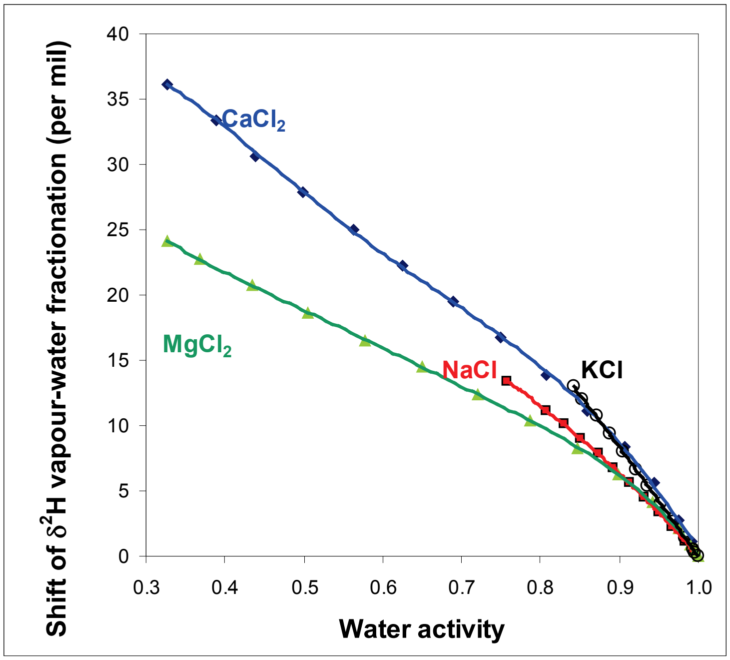


Figure 3: Calculated Shift of the δ^2H of Vapour at 20°C versus the NaCl, KCl, $CaCl_2$ and $MgCl_2$ Salinity, Expressed as Water Activity; Equations are Compiled from Horita et al. (1993a), and were Published for Temperatures >10°C for NaCl, >20°C KCl, >100°C $MgCl_2$ and >50°C for $CaCl_2$; Extrapolation to 20°C has to be Considered as a Proxy, Particularly for $MgCl_2$ and $CaCl_2$

3. STANDARD WATER SOLUTIONS

Three waters were used as standards in the experiments: LAB, TEW and EVIAN. The LAB water consists of 2 liters of tap water collected on March 25, 2009, at the University of Bern. EVIAN water consists of 3 liters of commercial mineral water that were mixed on August 26, 2009. TEW water is a light water obtained from ice cores from Greenland, prepared by the Institute of Physics, University of Bern, Switzerland, and stored in two 0.5-liter bottles. All standards waters are stored in glass bottles at ambient temperature.

The results of repeated analyses of the isotopic composition of the LAB, EVIAN, and TEW water standards are given in Table 2 and plotted in Figures 4 and 5. In all cases, replicate measurements were identical within 2σ error, which gives confidence in the average calculated isotopic compositions (Table 3) that are used for comparison or calculations in all experiments.

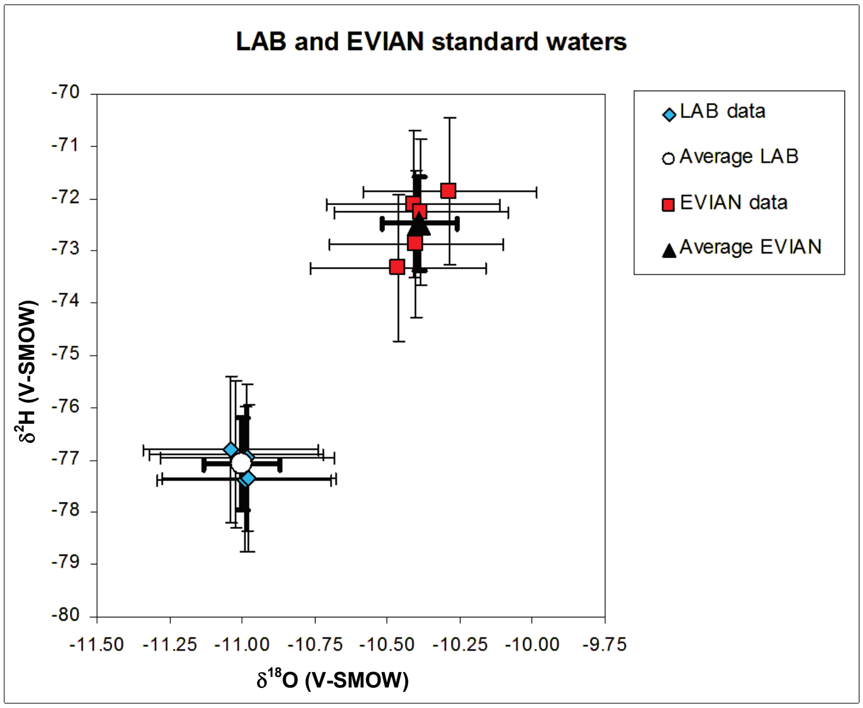


Figure 4: Isotopic Composition ($\delta^{18}O$ and $\delta^{2}H$) of Standard Waters LAB and EVIAN; All Error Bars are 2σ

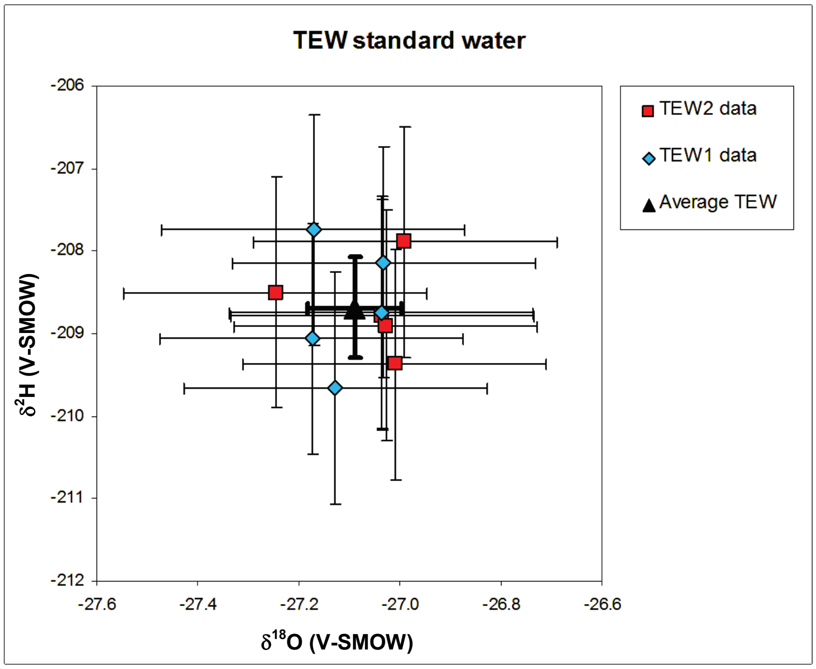


Figure 5: Isotopic Composition ($\delta^{18}O$ and $\delta^{2}H$) of Standard Water TEW; All Error Bars are 2σ

In addition to these three water standards, groundwater sampled from the Cambrian aquifer (OGW-10) in borehole DGR-3 from the Bruce Nuclear Site (Ontario, Canada) has been used in several experiments and its isotopic composition (fromHeagle and Pinder, 2009) is given in Table 3.

The required NaCl, $CaCl_2$ and NaF standard test water solutions were prepared from the LAB, TEW and EVIAN standard waters (Table 4). Salinities were obtained from the masses of water and salt added. The table gives the a_w of the solutions, calculated using Pitzer equations. Anhydrous $CaCl_2$ (product code: 1.02378; ≥98 wt% on a dry basis, $Ca(OH)_2 \leq 0.2$ wt%, loss on drying at 200°C ≤ 5.0 wt%), NaCl (product code: 1.06404; ≥99.5 wt%, for analysis) and NaF (product code: 1.06449; ≥99 wt%, for analysis) used to prepare the solutions are from Merck KGaA, 64271 Darmstadt, Germany (www.merck.de). All salts are stored in the original air-tight containers at ambient temperature. $CaCl_2$ is highly hydrophilic and Merck guarantees ≤5.0 wt% mass losses on drying at 200°C. In a previous study (Table 3 in de Haller et al., 2008), it has been shown that water released from $CaCl_2$ (no water added) at 500°C distillation has very negative $\delta^{2}H$ value (-162‰ V-SMOW), which is consistent with hydration from air humidity at ambient temperature. Because water isotope data of the previous experiments (de Haller et al., 2008) with $CaCl_2$ solutions did not show a shift towards negative $\delta^{2}H$ values, it is assumed that the amount of light water potentially added to the standard waters when preparing $CaCl_2$ standard solutions is negligible, if $CaCl_2$ is stored properly and handled rapidly to minimize contact with air.

Table 2: Measured Isotope Compositions of the EVIAN, LAB, and TEW Standard Waters (Not Distilled)

Sample ID	Date of sample preparation	Date of analysis	Standard Water	Volume of sample water	$\delta^{18}O$	2σ error	$\delta^{2}H$	2σ error
	(mo.yr)	(mo.yr)		(mL)	(‰ V-SMOW)	(‰ V-SMOW)	(‰ V-SMOW)	(‰ V-SMOW)
ND4 EVI	01.2010	03.2010	EVIAN	5	-10.46	0.3	-73.3	1.4
ND5 EVI	01.2010	03.2010	EVIAN	5	-10.41	0.3	-72.1	1.4
ND6 EVI	01.2010	03.2010	EVIAN	5	-10.29	0.3	-71.9	1.4
ND7 EVI	01.2010	03.2010	EVIAN	5	-10.38	0.3	-72.3	1.4
ND8 EVI	01.2010	03.2010	EVIAN	5	-10.40	0.3	-72.9	1.4
ND4 LAB	01.2010	03.2010	LAB	5	-11.02	0.3	-76.9	1.4
ND5 LAB	01.2010	03.2010	LAB	5	-11.04	0.3	-76.8	1.4
ND6 LAB	01.2010	03.2010	LAB	5	-10.98	0.3	-76.9	1.4
ND7 LAB	01.2010	03.2010	LAB	5	-10.99	0.3	-77.4	1.4
ND8 LAB	01.2010	03.2010	LAB	5	-10.98	0.3	-77.3	1.4
ND5 TEW1	01.2010	03.2010	TEW1	5	-27.03	0.3	-208.1	1.4
ND6 TEW1	01.2010	03.2010	TEW1	5	-27.04	0.3	-208.7	1.4
ND7 TEW1	01.2010	03.2010	TEW1	5	-27.17	0.3	-209.1	1.4
ND8 TEW1	01.2010	03.2010	TEW1	5	-27.13	0.3	-209.7	1.4
ND9 TEW1	01.2010	03.2010	TEW1	5	-27.17	0.3	-207.7	1.4
ND10 TEW2	01.2010	03.2010	TEW2	5	-27.25	0.3	-208.5	1.4
ND11 TEW2	01.2010	03.2010	TEW2	5	-27.04	0.3	-208.8	1.4
ND12 TEW2	01.2010	03.2010	TEW2	5	-27.03	0.3	-208.9	1.4
ND13 TEW2	01.2010	03.2010	TEW2	5	-27.01	0.3	-209.4	1.4
ND14 TEW2	01.2010	03.2010	TEW2	5	-26.99	0.3	-207.9	1.4

Note: TEW1 and TEW2 refer to the two standard water bottles used to prepare the standard solutions.

Table 3: Average Isotopic Compositions of Standard Waters and Available Isotope Compositions for Cambrian Ground Water

Standard water	$\delta^{18}O$ (‰ V-SMOW)	2σ error (‰ V-SMOW)	$\delta^{2}H$ (‰ V-SMOW)	2σ error (‰ V-SMOW)	Average of samples (see Table 2)	N
EVIAN	-10.39	0.13	-72.5	0.89	ND4 EVI to ND8 EVI	5
LAB	-11.00	0.13	-77.1	0.89	ND4 LAB to ND8 LAB	5
TEW1	-27.11	0.13	-208.7	0.89	ND5 TEW1 to ND9 TEW1	5
TEW2	-27.06	0.13	-208.7	0.89	ND10 TEW2 to ND14 TEW2	5
TEW(1+2)	-27.09	0.095	-208.7	0.63	ND5 TEW1 to ND14 TEW2	10
Cambrian groundwater (OGW-10 from DGR-3)[1]	-4.80	0.3	-31.8	3		

Note: TEW1 and TEW2 refer to the two standard water bottles used to prepare the standard solutions.

[1] Isotope composition of Cambrian groundwater, uncorrected for drill water contamination, is from Table 3 of Heagle and Pinder (2009) and the analytical uncertainties in these values are from I. Clark (personal communication, 2009). Isotope compositions were obtained by direct H_2 and CO_2 equilibration in a GasBench (with correction for the salt effect after Horita et al., 1993a and 1993b).

N is the number of samples.

Table 4: Standard Solutions Used in Experiments

Standard water	NaCl Standard Solutions				$CaCl_2$ Standard Solutions				NaF Standard Solutions			Prepared
	NaCl salinity (molal)	Solution (g)	H_2O in solution (g)	Calc. water activity a_w	$CaCl_2$ salinity (molal)	Solution (g)	H_2O in solution (g)	Calc. water activity a_w	NaF salinity (molal)	Solution (g)	H_2O in solution (g)	
LAB	0.301	12.226	12.015	0.9902	0.301	12.349	11.950	0.9875				Sep-09
LAB	1.003	12.680	11.978	0.9668	1.005	13.280	11.947	0.9452				Sep-09
LAB	2.501	13.746	11.993	0.9129	2.509	15.251	11.929	0.8057				Sep-09
LAB	5.017	141.782	109.639	0.8042	5.020	93.085	59.779	0.4980				Sep-09
LAB	0.270	20.280	19.965	0.9912								Oct-09
LAB	2.793	23.241	19.980	0.9016								Oct-09
LAB	5.154	26.004	19.984	0.7975								Oct-09
LAB	0.302	15.238		0.9902	1.005	16.609	14.942	0.9452				Dec-09
TEW1	0.300	12.235	12.024	0.9902	0.303	12.383	11.980	0.9874				Sep-09
TEW1	1.002	12.730	12.026	0.9669	0.994	13.260	11.942	0.9460				Sep-09
TEW1	2.504	13.733	11.980	0.9128	2.516	15.273	11.939	0.8049				Sep-09
TEW1	5.014	141.848	109.705	0.8043	5.032	92.810	59.551	0.4965				Sep-09
TEW2	0.274	15.157	14.918	0.9911								Oct-09
TEW2	2.808	17.373	14.924	0.9010								Oct-09
TEW2	5.157	19.482	14.970	0.7974								Oct-09
TEW2					0.298	15.465	14.970	0.9877				Dec-09
EVIAN	0.301	60.931	59.878	0.9902	0.301	61.812	59.816	0.9876				Sep-09
EVIAN	1.002	63.399	59.892	0.9669	1.003	66.418	59.765	0.9454				Sep-09
EVIAN	2.504	68.666	59.902	0.9128	2.513	76.389	59.730	0.8052				Sep-09
EVIAN	5.017	328.680	254.167	0.8042	5.031	247.761	158.980	0.4966				Sep-09
EVIAN	0.270	20.307	19.992	0.9912	0.181	30.536	29.936	0.9929	0.306	25.160	24.841	Oct-09
EVIAN	2.788	23.301	20.036	0.9018	1.538	34.979	29.879	0.9025	0.845	27.577	26.632	Oct-09
EVIAN	5.146	26.036	20.016	0.7979	2.584	38.454	29.884	0.7974				Oct-09

Note: No mixed solutions were prepared and each NaCl, $CaCl_2$ or NaF solutions column is independent. Water activities were calculated using Pitzer equations.

4. ANALYSIS OF OXYGEN AND HYDROGEN ISOTOPES IN SALINE WATERS

Distillation of the saline solutions and water stable isotope analyses were conducted at the Stable Isotopes Laboratory of the University of Lausanne, Switzerland (e.g., Spangenberg et al., 2007; Spangenberg and Vennemann, 2008; Spangenberg, 2012). The stable hydrogen isotope composition was measured using the H-Device hydrogen preparation system (Thermo Fisher Scientific, Bremen, Germany) connected to a Thermo Fisher Scientific Delta V Plus isotope ratio mass spectrometer. In the H-Device, H_2 gas was produced by quantitative reduction of a volume of 1.2 μL of water over hot (840°C) chromium within a quartz reactor connected to the dual inlet system of a Delta V Plus (Thermo Fisher Scientific, Bremen, Germany). Oxygen isotope analyses were carried out through equilibration of 0.5% CO_2 in He with 1.2 mL of sample water (previously loaded into an exetainer glass vial (Labco Ltd., High Wycombe, UK)) for 24 h at room temperature, followed by CO_2 extraction under continuous He flow using a GasBench II gas preparation system connected to a Delta Plus XL isotope ratio mass spectrometer (both from Thermo Fisher Scientific).

The stable hydrogen and oxygen isotope ratios (reported as $\delta^{2}H$ and $\delta^{18}O$ values; where δ-values are given in $‰=(R_{sample} – R_{standard})/R_{standard}x1000$, and $R={}^{2}H/{}^{1}H$ or ${}^{18}O/{}^{16}O$) and are reported relative to the Vienna Standard Mean Ocean Water (VSMOW). The standardization of the $\delta^{2}H$ and $\delta^{18}O$ values, relative to the international VSMOW scale, was carried out by periodic calibration of the reference gases and working standards with IAEA (Vienna, Austria) VSMOW2, SLAP2, and GISP standards. The calibration and assessment of the reproducibility of the isotopic analyses were based on replicate analyses of at least four working water standards. These included twice-glass-distilled tap water (UNIL-INH, calibration performed on 14 August 2009 gave the working values –113.1 ± 0.2‰ for $\delta^{2}H$ and –16.82 ± 0.07‰ for $\delta^{18}O$), two bottled mineral waters that were mixed in different proportions (UNIL-LIPE, working values –53.9 ± 0.4‰ $\delta^{2}H$, –8.50 ± 0.04% $\delta^{18}O$; UNIL-SCH, working values –122.0 ± 0.1‰ $\delta^{2}H$, –17.32 ± 0.05‰ $\delta^{18}O$), water from an Antarctic Lake (UNIL-ANLA, working values –146.8±0.2‰ $\delta^{2}H$, –16.22 ± 0.03‰ $\delta^{18}O$), Mediterranean ocean water (UNIL-MOW, working values 5.7 ± 0.4‰ $\delta^{2}H$, 0.47 ± 0.03‰ $\delta^{18}O$), water produced by combustion of natural gas (UNIL-TOCH, working values –141.3 ± 0.8‰ $\delta^{2}H$, 27.45 ± 0.06‰ $\delta^{18}O$), and two carefully prepared standards by mixing aliquots of 99.999995 atom% H water (CAMPRO Scientific, Berlin, Germany) with UNIL-ANLA1 (working values –197.6 ± 0.4‰ $\delta^{2}H$, –51.02 ± 0.06‰ $\delta^{18}O$) and UNIL-ANLA2 (working values –245.6 ± 0.3‰ $\delta^{2}H$, –83.99 ± 0.07‰ $\delta^{18}O$). All water samples were replicated between two and ten times. Each analytical sequence consisted of two sets of calibration standards, using three standards to test the precision and accuracy and 20 unknown samples. The reproducibility, assessed by the within-run replicate analyses of laboratory standards, was better than 0.3‰ and 0.1‰ (1σ) for $\delta^{2}H$ and $\delta^{18}O$ values, respectively. The accuracy of the analyses was checked every fourth run using the IAEA standard waters VSMOW2 (0.0 ± 0.3‰ $\delta^{2}H$, 0.0 ± 0.06‰ $\delta^{18}O$), SLAP2 (–427.5 ± 0.3‰ $\delta^{2}H$, –55.5 ± 0.03‰ $\delta^{18}O$), and GISP (–189.5 ± 0.7‰ $\delta^{2}H$, –24.8 ± 0.1‰ $\delta^{18}O$). The total analytical errors (1σ) are 0.7‰ and 0.15‰, respectively for $\delta^{2}H$ and $\delta^{18}O$.

In the current protocol, NaCl-bearing solutions are distilled to remove the salt from the solution, and the resulting water is then analyzed using the previously described standard methods. Distillation involves heating the ~5 mL solution for >4 h at 90°C, followed by 1 h at 110-130°C in a Savillex-vial connected by a screw-closed L-tube to a PTF vial cooled in ambient air (~25°C). All screw connections are sealed with Teflon tape. The condensed water is recovered and transferred into a 5 mL sealed glass bottle and stored at +4°C for isotopic analysis. This distillation procedure was originally developed at the University of Lausanne for the hydrogen and oxygen isotopic analysis of highly mineralized porewaters from mine tailings impoundments (Spangenberg et al., 2007).

Such a distillation procedure works well for NaCl solutions, but is not suitable for $CaCl_2$ solutions because it is not possible to completely dehydrate this salt at 120-130°C (de Haller et al., 2008 and 2009). This problem has been solved by converting the $CaCl_2$ solution into a NaCl solution (and solid CaF_2 (fluorite)) through the addition of NaF, following the aqueous reaction (5):

$$Ca^{+2} + 2Cl^{-} + 2Na^{+} + 2F^{-} \rightarrow CaF_2\,(\text{fluorite}) + 2Na^{+} + 2Cl^{-} \qquad (5)$$

The solubility of fluorite at the relevant temperatures and pH is low enough to limit the remaining Ca^{+2} content in the solution to amounts that are negligible in terms of the isotope salt effect ($<10^{-10}$ molal; calculated with the program Geochemist's Work Bench® using the Pitzer database). At 25°C and $CaCl_2$ molality above 3.05, equation (5) will also produce halite (NaCl) because its saturation is 6.1 molal at ambient temperature. The development of this distillation technique has been successfully tested in previous studies (de Haller et al., 2008 and 2009). In practice, 1.1 times the amount of NaF required to scavenge Ca^{+2} was added, to be sure that no Ca^{+2} was left in solution. As shown in the results below, the resulting excess NaF in solution behaves essentially as NaCl and has no impact on the distillation procedure. Errors (2σ) induced by the distillation technique in these studies were similar for NaCl solutions, $CaCl_2$ + NaF solutions and pure water, and were estimated to be <0.2‰ for $\delta^{18}O$ and <1‰ for $\delta^{2}H$. The basis for estimating the error is that all data should fit within 2σ error of the expected value.

In the present study, a new set of distillation experiments were performed with pure EVIAN water, and NaCl, $CaCl_2$ + NaF, and NaF synthetic EVIAN solutions (Table 5), with similar results (Figures 6 to 9). However, a slight tendency toward more positive values (vapour loss during distillation or sample handling?) is sometimes observed. Therefore, the estimated errors (2σ) have been increased to <0.4‰ for $\delta^{18}O$ and <1.4‰ for $\delta^{2}H$. Data obtained for one sample (sample D28EVI at 2.5 molal $CaCl_2$, Table 5 and Figure 8) is considered an outlier and is not taken into account in the error estimate. As in previous studies, there is no correlation between the salinity and the measured isotopic composition.

The NaF treatment can also be used to remove other divalent cations. For example, magnesium (Mg^{+2}) can be trapped as MgF_2 (sellaite) and Sr^{+2} as SrF_2 (no known mineral), following similar reactions as for fluorite (equation 5). The solubilities of MgF_2 and SrF_2 are low enough ($<10^{-7}$ and $<10^{-6}$ molal, respectively; calculation with the program Geochemist's Work Bench® using the Pitzer database) to minimize any significant isotope salt effect. Analysis of the stable water isotope composition of complex brines (Na-Ca-Mg-Sr-Cl) should, therefore, be possible.

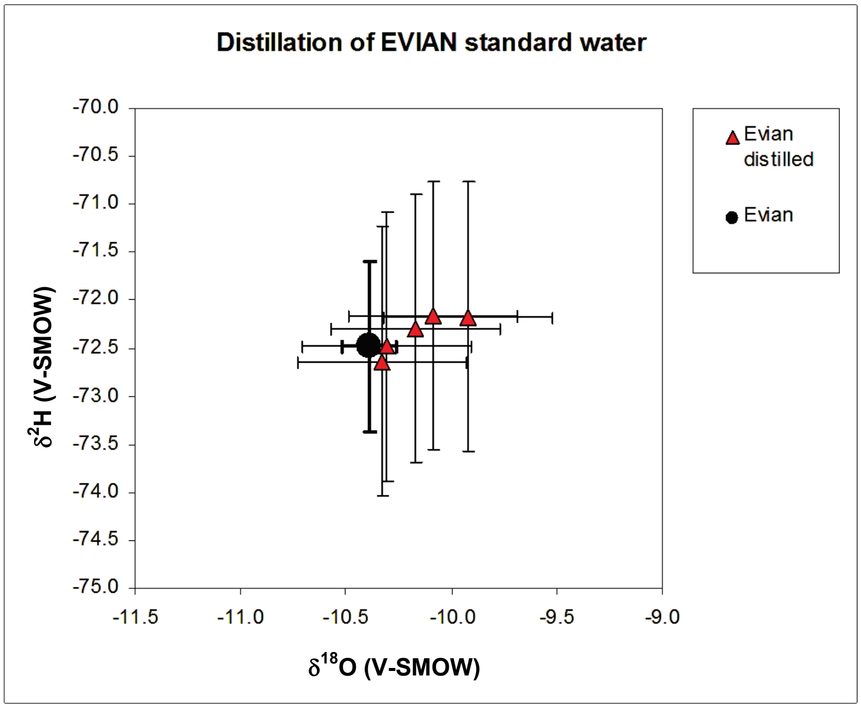


Figure 6: Isotope Composition of Five Distilled EVIAN Standard Water Aliquots (no salts added); Error Bars (2σ) are 0.4‰ and 1.4‰ for δ^{18}O and δ^{2}H, Respectively; See Table 3 for EVIAN Water Composition

The NaF treatment and distillation procedure was applied also to Cambrian groundwater taken from drillhole DGR3 (sample OGW-10), a highly saline complex brine (Table 6). The NaF treatment and distillation procedure was performed in two triplicate runs. Results for the isotopic measurements of these samples are given in Table 7 and plotted in Figure 10 for comparison with data released by the University of Ottawa (Heagle and Pinder, 2009; Table 3). One of the triplicate runs was treated with ~95% of the NaF amount required to remove all the divalent cations (Ca, Mg, Sr), while the other was treated with ~110% of this amount. The isotopic results for the 110% NaF-treatment fit with data released by Heagle and Pinder (2009) within 2σ error. In contrast, data obtained with 95% NaF-treatment are slightly shifted (0.5‰) toward more negative δ^{18}O values. In this case, the small amount of remaining divalent cations that were not removed from the solution as fluoride is apparently sufficient to induce some salt-related isotopic effect. It is, therefore, important to add excess NaF to avoid this problem.

The NaF treatment and distillation procedure provides an alternative to the H_2 and CO_2 GasBench equilibration method, where the obtained results require a correction for the effect of salinity (Horita et al., 1993a and 1993b). The coincidence of the results measured using both methods yields confidence that the obtained isotope values are representative.

Table 5: Water Isotope Composition of Distilled Pure EVIAN Water and NaCl, NaF and $CaCl_2$+NaF EVIAN Solutions

Sample ID	NaCl salinity (molal)	NaF salinity (molal)	$CaCl_2$ salinity (molal)	Wt. of EVIAN sample solution (g)	Calculated wt. of water in sample solution (g)	Theoretical amount of NaF required[1] (g)	Actual amount of NaF added[1] (g)	$\delta^{18}O$ (‰ V-SMOW)	2σ (‰ V-SMOW)	$\delta^{2}H$ (‰ V-SMOW)	2σ (‰ V-SMOW)
D23EVI	--	--	--	4.957	4.957	--	--	-9.9	0.4	-72.2	1.4
D24EVI	--	--	--	4.466	4.466	--	--	-10.1	0.4	-72.2	1.4
D25EVI	--	--	--	4.957	4.957	--	--	-10.3	0.4	-72.5	1.4
D26EVI	--	--	--	4.832	4.832	--	--	-10.3	0.4	-72.6	1.4
D27EVI	--	--	--	4.955	4.955	--	--	-10.2	0.4	-72.3	1.4
D3 EVI	0.301	--	--	5.153	5.064	--	--	-10.62	0.4	-71.9	1.4
D4 EVI	0.301	--	--	5.173	5.084	--	--	-10.81	0.4	-72.7	1.4
D5 EVI	1.002	--	--	5.445	5.144	--	--	-10.49	0.4	-72.3	1.4
D6 EVI	1.002	--	--	5.488	5.184	--	--	-10.32	0.4	-71.8	1.4
D7 EVI	2.504	--	--	6.207	5.414	--	--	-10.28	0.4	-71.8	1.4
D8 EVI	2.504	--	--	6.154	5.369	--	--	-10.24	0.4	-72.7	1.4
D9 EVI	5.017	--	--	7.376	5.704	--	--	-10.57	0.4	-72.7	1.4
D10 EVI	5.017	--	--	7.365	5.696	--	--	-10.41	0.4	-72.7	1.4
D19 EVI	--	0.306	--	5 mL of sol.	--	--	--	-10.04	0.4	-72.0	1.4
D20 EVI	--	0.306	--	5 mL of sol.	--	--	--	-10.40	0.4	-72.7	1.4
D21 EVI	--	0.845	--	5 mL of sol.	--	--	--	-10.37	0.4	-72.7	1.4
D22 EVI	--	0.845	--	5 mL of sol.	--	--	--	-10.35	0.4	-72.8	1.4
D28EVI	--	--	0.301	5.098	4.933	0.137	0.146	-9.6	0.4	-72.2	1.4
D29EVI	--	--	0.301	5.092	4.928	0.137	0.142	-10.2	0.4	-72.3	1.4
D30EVI	--	--	1.003	5.346	4.810	0.446	0.445	-10.2	0.4	-71.9	1.4
D31EVI	--	--	1.003	5.376	4.837	0.448	0.453	-10.1	0.4	-72.2	1.4
D32EVI	--	--	2.513	5.905	4.617	1.072	1.075	-10.1	0.4	-72.3	1.4
D33EVI	--	--	2.513	5.851	4.575	1.062	1.062	-10.1	0.4	-72.2	1.4
D34EVI	--	--	5.031	6.599	4.234	1.968	1.966	-10.0	0.4	-72.2	1.4
D35EVI	--	--	5.031	6.395	4.103	1.907	1.909	-10.0	0.4	-72.1	1.4

[1] The objective was to add 10% more NaF than required to the $CaCl_2$ solutions, to ensure that all Ca^{+2} was converted into CaF_2 (fluorite) before distillation.

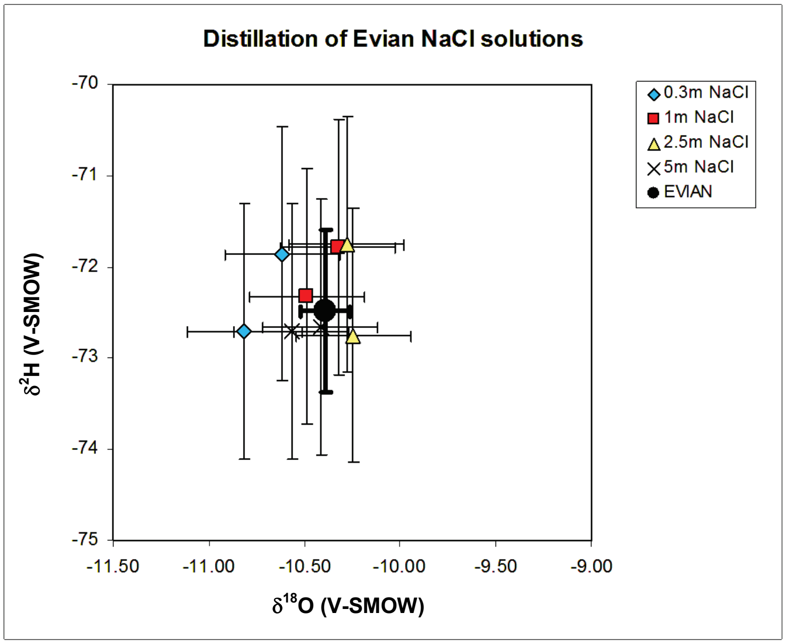


Figure 7: Duplicate Distillations of 0.3, 1, 2.5 and 5 Molal NaCl EVIAN Solutions; Error Bars (2σ) are 0.4‰ and 1.4‰ for δ^{18}O and δ^2H, Respectively; See Table 3 for EVIAN Water Composition

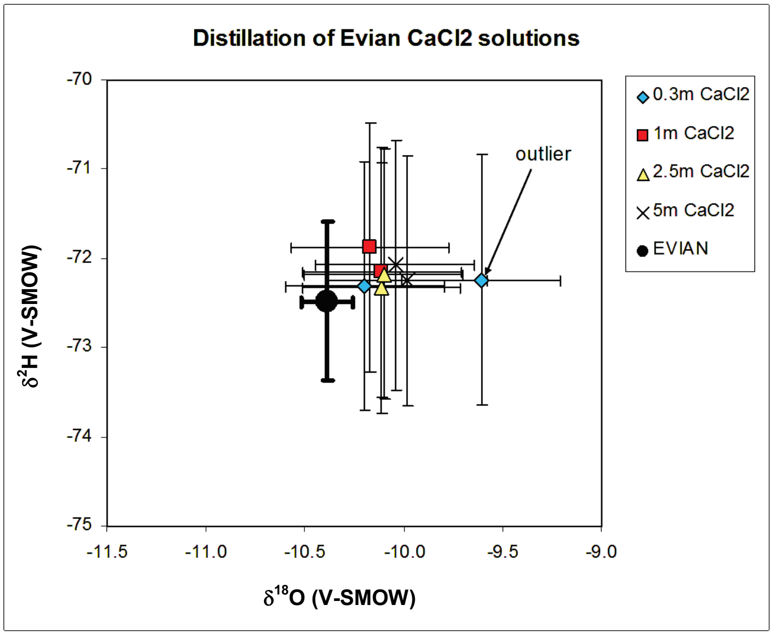


Figure 8: Duplicate Distillations of 0.3, 1, 2.5 and 5 Molal $CaCl_2$ EVIAN Solutions; Error Bars (2σ) are 0.4‰ and 1.4‰ for δ^{18}O and δ^2H, Respectively; See Table 3 for EVIAN Water Composition; One of the Data Points is Out of the Estimated 2σ Error for δ^{18}O and is Considered to be an Outlier (likely resulting from a problem during distillation or sample handling)

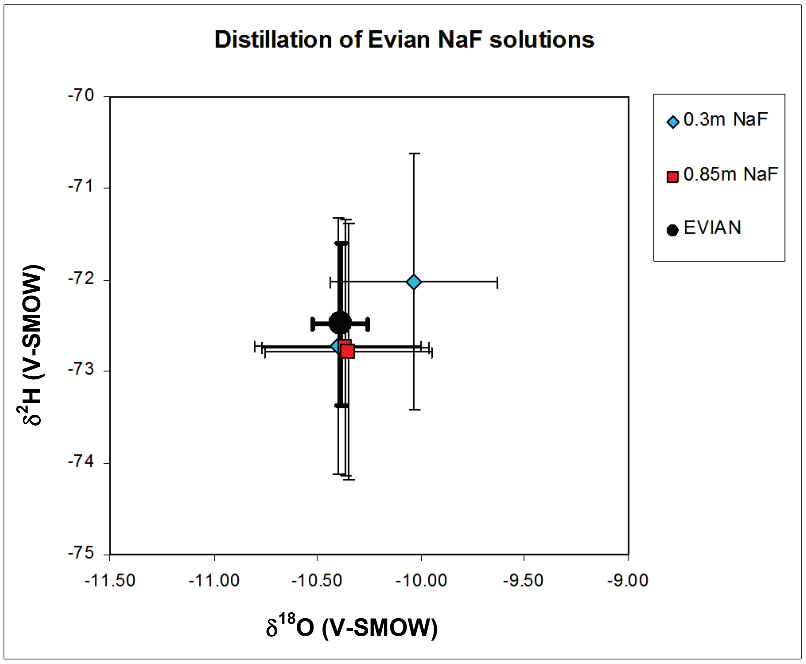


Figure 9: Duplicate Distillations of 0.3 and 0.85 Molal NaF EVIAN Solutions; Error Bars (2σ) are 0.4‰ and 1.4‰ for δ^{18}O and δ^{2}H, Respectively; See Table 3 for EVIAN Water Composition

Table 6: Chemistry of Cambrian Groundwater (OGW-10) and NaF Treatment

Element	Concentration (mg/kg solution)	Concentration (mole/kg solution)	Equiv. NaF (mg/kg solution)
Na	28174	1.225	
Ca	31478	0.785	65954
Mg	5122	0.211	17691
K	799	0.020	
Sr	822	0.009	788
Total		2.251	84433
Cl	126957	3.581	
Br	1391	0.017	
SO_4	304	0.003	
Total		3.602	

Note: concentrations are those uncorrected for drilling fluid contamination (Heagle and Pinder, 2009). The indicated amounts of NaF are those required to remove the corresponding divalent cations.

In summary, the distillation procedure has been tested with pure EVIAN water, NaCl and NaF EVIAN solutions, and NaF-treated $CaCl_2$ EVIAN solutions, with satisfactory results. In some cases, a slight shift toward higher isotopic compositions was observed, which was significant for $\delta^{18}O$, but within the analytical 2σ error for $\delta^{2}H$ (1.4‰). Consequently, the estimated 2σ error of distilled samples has been increased to 0.4‰ for $\delta^{18}O$, slightly higher than the 0.3‰ 2σ analytical error. This tendency toward higher $\delta^{18}O$ and $\delta^{2}H$ values, compared to undistilled aliquots, is not related to the type of salt or to the salinity, and probably results from minor vapour losses during the distillation procedure or sample handling.

Table 7: Water Isotope Composition of Distilled Cambrian Groundwater OGW-10 from DGR-3 Treated with NaF

Sample ID	Date of sample preparation (mo.yr)	Date of analysis (mo.yr)	Molarity of divalent cations (Ca+Mg+Sr) in solution (mole/kg)	Weight of Cambrian ground water sample (g)	Calculated weight of water in sample solution (from TDS) (g)	Actual amount of NaF added[1] (g)	% of NaF required to remove all divalent cations[1] (%)	$\delta^{18}O$ (‰ V-SMOW)	2σ (‰ V-SMOW)	$\delta^{2}H$ (‰ V-SMOW)	2σ (‰ V-SMOW)
D23GW1	01.2010	03.2010	2.011	6.875	5.333	0.553	95.3	-5.10	0.4	-31.5	1.4
D24GW1	01.2010	03.2010	2.011	6.884	5.340	0.552	95.0	-5.18	0.4	-31.7	1.4
D25GW1	01.2010	03.2010	2.011	6.928	5.374	0.569	97.3	-5.41	0.4	-31.6	1.4
D26GW1	12.2010	01.2011	2.011	5.767	4.473	0.552	113.4	-4.96	0.4	-33.1	1.4
D27GW1	12.2010	01.2011	2.011	5.713	4.431	0.535	110.9	-4.95	0.4	-32.4	1.4
D28GW1	12.2010	01.2011	2.011	5.726	4.441	0.536	110.9	-4.88	0.4	-32.1	1.4

[1] The actual amounts of NaF added are about 95% (D23GWI to D25GWI) and 110% (D26GWI to D28GWI) of what is required to completely remove the divalent cations (Ca^{+2}, Mg^{+2}, and Sr^{+2}) from the groundwater, as insoluble CaF_2 (fluorite), MgF_2 (sellaite) and SrF_2 before distillation.

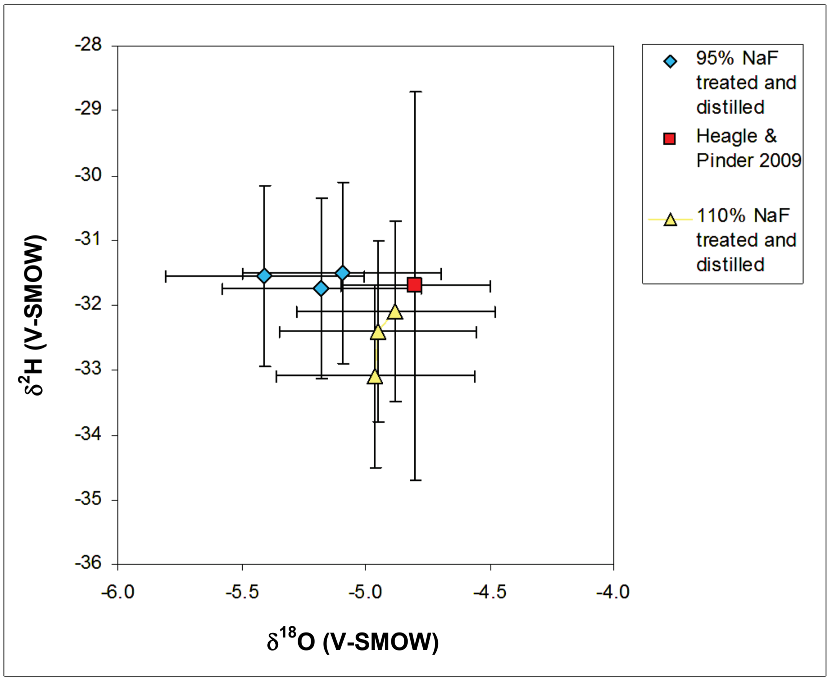


Figure 10: Triplicate Distillations of Cambrian Ground Water from DGR3 Borehole (OGW-10) Treated with ~95 and ~110% of the Required Amount of NaF to Remove All Divalent Cations (Ca, Mg, Sr); Error Bars (2σ) are 0.4‰ and 1.4‰ for $\delta^{18}O$ and $\delta^{2}H$, Respectively; the Isotopic Composition in Heagle and Pinder (2009; Table 3) is Shown in Red

5. TESTING OF THE DIFFUSIVE-ISOTOPE EXCHANGE TECHNIQUE ADAPTED FOR SALINE SOLUTIONS

For the methodology study, saline solutions were used as samples instead of porewater-saturated rock samples. Two small crystallization dishes, each containing a known mass of water solution (~5 mL) of known isotopic composition, were placed in a vapour-tight container at ambient temperature and equilibrated for 30 days, which was considered to be conservative considering that the typical equilibration time for the Opalinus Clay ranges between about 2.5 and 20 days (Rübel et al., 2002; Hobbs and Waber, 2002). Experiments were performed in duplicate, with the same sample solution (in most cases EVIAN water) and two different test solutions (LAB and TEW waters).

The test solution, sample solution and the container were weighed before and after the equilibration experiment, to provide a control on possible mass transfer between the test and sample solutions, and to check the tightness of the container, respectively. After reaching equilibrium, the test and sample water were removed from the crystallization dishes and stored in small vapour-tight PE-bottles for stable water isotope ($\delta^{18}O$ and $\delta^{2}H$) analysis.

All data from the solution-solution diffusive exchange experiments are presented in Tables 8 through 12.

5.1 DIFFUSIVE EXCHANGE SOLUTION-SOLUTION EXPERIMENTS: NO SALT, NaCl AND $CaCl_2$ SOLUTIONS

Diffusive exchange experiments were performed with pure water and 0.3, 1, 2.5 and 5 molal NaCl and $CaCl_2$ solutions, with the same salt and salinity in the sample and test solutions (Tables 8 to 12). As shown in Figures 11 and 12, the calculated isotopic compositions ($\delta^{18}O$ and $\delta^{2}H$) of the sample EVIAN water solutions (Table 11) are consistent with the value obtained by direct analysis of pure EVIAN water (Table 3) in all cases (within 2σ error), except one, though there is a tendency toward slightly higher values than those obtained by direct analysis. For unknown reasons, the 2.5 m $CaCl_2$ experiment gave a $\delta^{18}O$ result slightly above the expected value within 2σ error. Results are independent of the salinity of the solutions.

Test and sample solutions at 2.5 molal NaCl and 2.5 molal $CaCl_2$ show that isotopic compositions are similar, within error, at the end of the experiment, which indicates full equilibration has been attained (Table 11).

Because the weight of sample used in the calculation is the weight of the water in the sample solution (not the weight of the solution), the calculated water content should be 100 wt% (estimated 2σ error is <5 wt%). The measured water content results (Figures 13 and 14) fit within 2σ error for both $\delta^{18}O$ and $\delta^{2}H$, whereas the absolute errors derived from $\delta^{18}O$ data (around ± 16 wt%) are more than two times higher than those for the $\delta^{2}H$ data (around ± 6.5 wt%). For unknown reasons, the calculated water contents tend to be slightly overestimated.

These results show that the adapted diffusive exchange technique works well when test and sample solutions have similar chemical compositions and water activities.

Table 8: Weights of Test and Sample Solutions during LAB and EVIAN Experiments

Exp	Start of exp (d.m.y)	End of exp (d.m.y)	Initial wt.of LAB / EVIAN test sol.[1] (g)	Initial wt. of test water (no salt)[1,2] (g)	Final wt. of LAB / EVIAN test sol.[1] (g)	Final wt. of test water (no salt)[1,2] (g)	Delta wt. LAB / EVIAN test sol. (end-ini.) (g)	Initial wt. of sample solution[3] (g)	Initial wt. of sample water (no salt)[2,3] (g)	Final wt. of sample sol.[3] (g)	Final wt. of sample water (no salt)[2,3] (g)	Delta wt. sample sol. (end-ini.) (g)	Initial mass of system[4] (g)	Final mass of system[4] (g)	Delta mass (end-ini.) (g)
Diffusive exchange with NaCl solutions															
1	08.10.09	09.11.09	4.987	4.987	4.762	4.762	-0.225	4.989	4.989	4.618	4.618	-0.371	631.958	631.938	-0.020
2b	16.12.09	18.01.10	4.997	4.910	4.989	4.902	-0.008	5.033	4.946	4.924	4.837	-0.109	633.919	633.864	-0.055
3	08.10.09	09.11.09	5.670	5.356	5.680	5.366	0.010	5.643	5.331	5.581	5.269	-0.062	627.094	627.072	-0.022
4	08.10.09	09.11.09	6.711	5.855	6.691	5.835	-0.020	6.706	5.850	6.689	5.833	-0.017	641.048	641.036	-0.012
5	08.10.09	09.11.09	8.616	6.663	8.622	6.669	0.006	8.614	6.661	8.579	6.626	-0.035	635.315	635.301	-0.014
Diffusive exchange with $CaCl_2$ solutions															
7	08.10.09	09.11.09	5.169	5.002	5.154	4.987	-0.015	5.193	5.025	5.148	4.980	-0.045	634.719	634.695	-0.024
8b	16.12.09	18.01.10	5.659	5.091	5.615	5.047	-0.044	5.712	5.140	5.691	5.119	-0.021	637.976	637.943	-0.033
9b	15.10.10	17.11.10	5.867	4.589	5.856	4.578	-0.011	5.937	4.642	5.897	4.602	-0.040	634.416	634.376	-0.040
10	08.10.09	09.11.09	8.356	5.366	8.344	5.354	-0.012	8.381	5.378	8.389	5.386	0.008	644.872	644.863	-0.009
Effect of slight water activity mismatch (0.05 to 0.1) between test and sample NaCl solutions															
11	27.11.09	28.12.09	5.009	4.923	3.405	3.319	-1.604	5.431	4.738	6.968	6.275	1.537	632.657	632.632	-0.025
12	27.11.09	28.12.09	5.264	4.973	4.416	4.125	-0.848	5.417	4.726	6.207	5.516	0.790	639.383	639.354	-0.029
13	27.11.09	28.12.09	5.795	4.481	7.048	5.734	1.253	5.399	4.710	4.097	3.408	-1.302	635.888	635.874	-0.014
Effect of significant water activity mismatch (0.15 to 0.3) between test and sample $CaCl_2$ solutions															
15	27.11.09	28.12.09	5.067	4.903	2.625	2.461	-2.442	5.872	4.591	8.264	6.983	2.392	640.270	640.256	-0.014
16	27.11.09	28.12.09	5.343	4.807	3.765	3.229	-1.578	5.860	4.582	7.390	6.112	1.530	633.784	633.768	-0.016
18	27.11.09	28.12.09	6.597	4.236	8.053	5.692	1.456	5.894	4.609	4.411	3.126	-1.483	638.095	638.085	-0.010
Effect of changing the sample/test water mass ratio															
19b	17.12.09	18.01.10	6.599	5.103	6.556	5.060	-0.043	0.667	0.516	0.668	0.517	0.001	630.142	630.112	-0.030
20	08.10.09	9.11.09	6.576	5.085	6.552	5.061	-0.024	1.231	0.952	1.225	0.946	-0.006	634.079	634.061	-0.018
21	08.10.09	9.11.09	6.638	5.133	6.621	5.116	-0.017	3.923	3.034	3.913	3.024	-0.010	632.847	632.835	-0.012
22	08.10.09	9.11.09	6.624	5.122	6.624	5.122	0.000	9.143	7.070	9.116	7.043	-0.027	639.975	639.959	-0.016
Isotope fractionation between $CaCl_2$ and NaCl solutions at same water activity equilibrated through the vapour phase [1]															
28	27.11.09	28.12.09	5.032	4.933	4.877	4.799	-0.125	5.002	4.924	5.071	4.972	0.039	635.386	635.345	-0.041
29	27.11.09	28.12.09	6.163	5.264	6.024	5.183	0.021	6.003	5.162	6.091	5.192	-0.072	633.694	633.678	-0.016
30	27.11.09	28.12.09	7.180	5.580	7.098	5.470	0.055	7.043	5.415	7.084	5.484	-0.096	643.686	643.674	-0.012
Diffusive exchange with NaCl test solutions and $CaCl_2$ sample solutions at three different water activities (0.99, 0.9, and 0.8)															
31b	29.10.10	01.12.10	4.987	4.910	4.970	4.893	-0.017	5.120	5.019	5.046	4.945	-0.074	636.700	636.697	-0.003
32b	29.10.10	01.12.10	5.450	4.685	5.501	4.736	0.051	5.631	4.810	5.531	4.710	-0.100	642.643	642.623	-0.020
33b	29.10.10	01.12.10	5.766	4.431	5.807	4.472	0.041	5.985	4.651	5.908	4.574	-0.077	639.116	639.122	0.006
Triplicate diffusive exchange with NaCl and $CaCl_2$ test waters and Cambrian groundwater sample (OGW-10)															
34	04.02.10	07.03.10	6.994	5.409	7.259	5.679	0.289	6.906	5.355	6.527	4.979	-0.366	635.337	635.270	-0.067

Exp	Start of exp	End of exp	Initial wt.of LAB / EVIAN test sol.[1]	Initial wt. of test water (no salt)[1,2]	Final wt. of LAB / EVIAN test sol.[1]	Final wt. of test water (no salt)[1,2]	Delta wt. LAB / EVIAN test sol. (end-ini.)	Initial wt. of sample solution [3]	Initial wt. of sample water (no salt)[2,3]	Final wt. of sample sol.[3]	Final wt. of sample water (no salt)[2,3]	Delta wt. sample sol. (end-ini.)	Initial mass of system[4]	Final mass of system[4]	Delta mass (end-ini.)
	(d.m.y)	(d.m.y)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)
Triplicate diffusive exchange with NaCl and $CaCl_2$ test waters and Cambrian groundwater sample (OGW-10) *cont'd*															
35	04.02.10	07.03.10	6.888	5.327	7.221	5.644	0.266	6.865	5.324	6.521	4.975	-0.365	633.614	633.524	-0.090
36	04.02.10	07.03.10	6.945	5.371	7.226	5.653	0.288	6.880	5.335	6.547	5.002	-0.336	635.773	635.758	-0.015
37	04.02.10	07.03.10	7.035	5.502	7.224	5.694	0.199	6.873	5.330	6.675	5.122	-0.244	636.934	636.919	-0.015
38	04.02.10	07.03.10	7.053	5.516	7.197	5.666	0.168	6.867	5.325	6.574	5.032	-0.296	631.213	631.096	-0.117
39	04.02.10	07.03.10	7.125	5.572	7.322	5.771	0.202	6.880	5.335	6.630	5.084	-0.254	638.089	638.057	-0.032

[1] Test waters are always LAB, except in Experiments 28 to 30 where both test and sample waters are EVIAN (EVIAN-EVIAN experiments). [2] Calculated from the salinity (see Table 10). [3] All sample solutions were prepared with EVIAN water, except for Experiments 34 to 39 where the sample solution was Cambrian groundwater from borehole DGR3 (sample OGW-10 in Heagle and Pinder, 2009). [4] System = container + sample solution + test solution + Petri dishes

Table 9: Weights of Test and Sample Solutions during TEW Experiments

Exp	Start of exp	End of exp	Initial wt. TEW test sol.	Initial wt. TEW test water (no salt)[1]	Final wt. TEW test sol.	Final wt. TEW test water (no salt)[1]	Delta wt. TEW test sol. (end-ini.)	Initial wt. sample sol.	Initial wt. sample water (no salt)[1]	Final wt. sample sol.	Final wt. sample water (no salt)[1]	Delta wt. sample sol. (end-ini.)	Initial mass of system[2]	Final mass of system[2]	Delta mass (end-ini.)
	(d.m.y)	(d.m.y)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)
Diffusive exchange with NaCl solutions															
1	08.10.09	09.11.09	4.980	4.980	4.812	4.812	-0.168	4.996	4.996	4.679	4.679	-0.317	635.208	635.186	-0.022
2	08.10.09	09.11.09	5.130	5.042	5.124	5.036	-0.006	5.112	5.024	5.042	4.954	-0.070	635.149	635.118	-0.031
3	08.10.09	09.11.09	5.669	5.356	5.667	5.354	-0.002	5.665	5.352	5.615	5.302	-0.050	630.231	630.210	-0.021
4b	16.12.09	18.01.10	5.697	4.970	5.698	4.971	0.001	5.762	5.027	5.702	4.967	-0.060	640.933	640.958	0.025
5	08.10.09	09.11.09	8.595	6.647	8.585	6.637	-0.010	8.597	6.648	8.580	6.631	-0.017	633.644	633.629	-0.015
Diffusive exchange with $CaCl_2$ solutions															
7b	16.12.09	18.01.10	5.173	5.007	5.134	4.968	-0.039	5.234	5.065	5.087	4.918	-0.147	629.637	629.478	-0.159
8	08.10.09	09.11.09	5.674	5.110	5.656	5.092	-0.018	5.686	5.116	5.660	5.090	-0.026	639.042	639.029	-0.013
9	08.10.09	09.11.09	6.607	5.165	6.603	5.161	-0.004	6.597	5.158	6.572	5.133	-0.025	634.836	634.817	-0.019
10	08.10.09	09.11.09	8.346	5.355	8.334	5.343	-0.012	8.340	5.351	8.348	5.359	0.008	640.318	640.307	-0.011
Effect of slight water activity mismatch (0.05 to 0.1) between test and sample NaCl solutions															
11	27.11.09	28.12.09	5.005	4.919	3.548	3.462	-1.457	5.367	4.682	6.765	6.080	1.398	637.475	637.462	-0.013
12	27.11.09	28.12.09	5.127	4.843	4.166	3.882	-0.961	5.420	4.728	6.323	5.631	0.903	632.958	632.940	-0.018
13	27.11.09	28.12.09	5.782	4.472	6.943	5.633	1.161	5.405	4.715	4.149	3.459	-1.256	632.216	632.136	-0.080
Effect of significant water activity mismatch (0.15 to 0.3) between test and sample $CaCl_2$ solutions															
15	27.11.09	28.12.09	5.080	4.915	2.627	2.462	-2.453	5.909	4.620	8.324	7.035	2.415	634.037	634.023	-0.014
16	27.11.09	28.12.09	5.353	4.821	3.838	3.306	-1.515	5.885	4.602	7.352	6.069	1.467	629.17	629.155	-0.015
18	27.11.09	28.12.09	6.611	4.242	8.064	5.695	1.453	5.906	4.618	4.426	3.138	-1.480	630.214	630.203	-0.011
Effect of changing the sample/test water mass ratio															
19b	17.12.09	18.01.10	6.602	5.106	6.558	5.062	-0.044	0.665	0.514	0.673	0.522	0.008	632.658	632.63	-0.028
20	08.10.09	9.11.09	6.637	5.133	6.614	5.110	-0.023	1.257	0.972	1.253	0.968	-0.004	634.01	633.996	-0.014
21	08.10.09	9.11.09	6.628	5.126	6.589	5.087	-0.039	3.893	3.010	3.869	2.986	-0.024	631.411	631.341	-0.070
22	08.10.09	9.11.09	6.616	5.117	6.602	5.103	-0.014	9.082	7.023	9.072	7.013	-0.010	640.997	640.983	-0.014
Isotope fractionation between $CaCl_2$ and NaCl solutions at same water activity equilibrated through the vapour phase[1]															
28															
29	No TEW experiment, see Table 8														
30															
Diffusive exchange with NaCl test solutions and $CaCl_2$ sample solutions at three different water activities (0.99, 0.9, and 0.8)															
31b	29.10.10	01.12.10	5.002	4.923	4.958	4.879	-0.044	5.103	5.003	5.052	4.952	-0.051	635.318	635.290	-0.028
32b	29.10.10	01.12.10	5.449	4.681	5.499	4.731	0.050	5.627	4.807	5.531	4.711	-0.096	632.839	632.842	0.003
33b	29.10.10	01.12.10	5.808	4.463	5.856	4.511	0.048	5.981	4.648	5.892	4.559	-0.089	629.377	629.368	-0.009
Triplicate diffusive exchange with NaCl and $CaCl_2$ test waters and Cambrian groundwater sample (OGW-10)															
34	04.02.10	07.03.10	6.994	5.409	7.289	5.704	0.295	6.906	5.355	6.564	5.013	-0.342	638.148	638.127	-0.021
35b	15.10.10	17.11.10	5.765	4.459	6.020	4.714	0.255	5.848	4.535	5.546	4.233	-0.302	635.306	635.273	-0.033
36	04.02.10	07.03.10	6.945	5.371	7.228	5.654	0.283	6.880	5.335	6.553	5.008	-0.327	642.281	642.267	-0.014
37	04.02.10	07.03.10	7.035	5.502	7.233	5.700	0.198	6.873	5.330	6.629	5.086	-0.244	643.466	643.448	-0.018
38	04.02.10	07.03.10	7.053	5.516	7.258	5.721	0.205	6.867	5.325	6.613	5.071	-0.254	636.974	636.953	-0.021
39	04.02.10	07.03.10	7.125	5.572	7.328	5.775	0.203	6.880	5.335	6.626	5.081	-0.254	644.238	644.216	-0.022

[1] Calculated from salinity (see Table 10). [2] System = container + sample solution + test solution + Petri dishes

Table 10: Calculated Salinities of Test and Sample Solutions at Start and End of Experiments

	LAB test solution (molal) (EVIAN in Exp. 28 to 30)[1]				TEW test solution (molal)				EVIAN sample solution (molal)					
Expt.	NaCl in test water (t=0)	NaCl in test water (end)	$CaCl_2$ in test water (t=0)	$CaCl_2$ in test water (end)	NaCl in test water (t=0)	NaCl in test water (end)	$CaCl_2$ in test water (t=0)	$CaCl_2$ in test water (end)	NaCl in sample water (t=0)	NaCl in sample water (end LAB / EVIAN)[1]	NaCl in sample water (end TEW)	$CaCl_2$ in sample water (t=0)	$CaCl_2$ in sample water (end LAB / EVIAN)[1]	$CaCl_2$ in sample water (end TEW)
Diffusive exchange with NaCl solutions														
1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
2bLAB/2TEW	0.302	0.302	0	0	0.300	0.301	0	0	0.301	0.307	0.305	0	0	0
3	1.003	1.001	0	0	1.002	1.002	0	0	1.002	1.014	1.011	0	0	0
4LAB/4bTEW	2.501	2.510	0	0	2.504	2.503	0	0	2.503	2.511	2.534	0	0	0
5	5.016	5.012	0	0	5.013	5.021	0	0	5.016	5.043	5.029	0	0	0
Diffusive exchange with $CaCl_2$ solutions														
7LAB/7bTEW	0	0	0.301	0.302	0	0	0.298	0.300	0	0	0	0.301	0.303	0.310
8bLAB/8TEW	0	0	1.004	1.013	0	0	0.994	0.998	0	0	0	1.003	1.007	1.008
9bLAB/9TEW	0	0	2.509	2.515	0	0	2.516	2.518	0	0	0	2.513	2.535	2.525
10	0	0	5.020	5.032	0	0	5.032	5.044	0	0	0	5.032	5.025	5.025
Effect of slight water activity mismatch (0.05 to 0.1) between test and sample NaCl solutions														
11	0.300	0.446	0	0	0.300	0.427	0	0	2.503	1.890	1.928	0	0	0
12	1.003	1.209	0	0	1.002	1.250	0	0	2.503	2.145	2.102	0	0	0
13	5.016	3.920	0	0	5.013	3.980	0	0	2.503	3.460	3.412	0	0	0
Effect of significant water activity mismatch (0.15 to 0.3) between test and sample $CaCl_2$ solutions														
15	0	0	0.301	0.599	0	0	0.303	0.605	0	0	0	2.513	1.652	1.650
16	0	0	1.005	1.497	0	0	0.994	1.450	0	0	0	2.513	1.884	1.906
18	0	0	5.020	3.736	0	0	5.032	3.749	0	0	0	2.513	3.706	3.699
Effect of changing the sample/test water mass ratio														
19b	5.016	5.059	0	0	5.013	5.057	0	0	5.016	5.006	4.939	0	0	0
20	5.016	5.040	0	0	5.013	5.036	0	0	5.016	5.048	5.037	0	0	0
21	5.016	5.033	0	0	5.013	5.052	0	0	5.016	5.033	5.056	0	0	0
22	5.016	5.016	0	0	5.013	5.027	0	0	5.016	5.035	5.023	0	0	0
Isotope fractionation between $CaCl_2$ and NaCl solutions at same water activity equilibrated through the vapour phase[1]														
28	0.270	0.277	0	0					0	0		0.181	0.179	
29	2.788	2.777	0	0					0	0		1.538	1.559	
30	5.146	5.094	0	0					0	0		2.584	2.629	
Diffusive exchange with NaCl test solutions and $CaCl_2$ sample solutions at three different water activities (0.99, 0.9, and 0.8)														
31b	0.270	0.271	0	0	0.274	0.277	0	0	0	0	0	0.181	0.183	0.182
32b	2.793	2.763	0	0	2.808	2.778	0	0	0	0	0	1.538	1.571	1.569
33b	5.154	5.107	0	0	5.157	5.102	0	0	0	0	0	2.584	2.628	2.635
Triplicate diffusive exchange with NaCl and $CaCl_2$ test waters and Cambrian groundwater sample (OGW-10)														
34	5.016	4.761	0	0	5.013	4.754	0	0	Sample solution is Cambrian groundwater (complex brine) from DGR-3 borehole (sample OGW-10 in Heagle & Pinder, 2009), not EVIAN					
35	5.016	4.780	0	0	5.013	5.068	0	0						
36	5.016	4.761	0	0	5.013	4.762	0	0						
37	0	0	2.509	2.422	0	0	2.511	2.424						
38	0	0	2.509	2.435	0	0	2.511	2.421						
39	0	0	2.509	2.422	0	0	2.511	2.423						

[1] Experiments 28 to 30 were performed with EVIAN water as test and sample solutions.

Table 11: Sample Water Composition Calculated from Diffusive Exchange Experiment Data

Experiment	Test solution “LAB” (tap water)				Test solution “TEW” (glacial meltwater)				Sample solution LAB experiments[3]		Sample solution TEW experiments[3]		Calculated sample water isotopic composition[3]			
	Initial $\delta^{18}O$ test solution[1]	Final $\delta^{18}O$ test solution[2]	Initial $\delta^{2}H$ test solution[1]	Final $\delta^{2}H$ test solution[2]	Initial $\delta^{18}O$ test solution[1]	Final $\delta^{18}O$ test solution[2]	Initial $\delta^{2}H$ test solution[1]	Final $\delta^{2}H$ test solution[2]	Final $\delta^{18}O$ sample solution[2]	Final $\delta^{2}H$ sample solution[2]	Final $\delta^{18}O$ sample solution[2]	Final $\delta^{2}H$ sample solution[2]	$\delta^{18}O$	2σ	$\delta^{2}H$	2σ
	(‰ V-SMOW)	(‰ V-SMOW)	(‰ V-SMOW)	(‰ V-SMOW)	(‰ V-SMOW)	(‰ V-SMOW)	(‰ V-SMOW)	(‰ V-SMOW)	(‰ V-SMOW)	(‰ V-SMOW)	(‰ V-SMOW)	(‰ V-SMOW)	(‰ V-SMOW)	(‰)	(‰ V-SMOW)	(‰)
Diffusive exchange with NaCl solutions																
1	-11.00	-10.67	-77.07	-73.7	-27.09	-18.72	-208.68	-139.7					-10.3	0.8	-70.2	3.1
2bLAB/2TEW	-11.00	-10.46	-77.07	-73.5	-27.09	-18.32	-208.68	-137.6					-10.0	0.8	-70.1	3.0
3	-11.00	-10.49	-77.07	-73.8	-27.09	-18.37	-208.68	-139.5					-10.0	0.8	-70.5	3.1
4LAB/4bTEW	-11.00	-10.53	-77.07	-74.1	-27.09	-18.24	-208.68	-138.9	-10.6	-74.5	-18.9	-139.5	-10.1	0.8	-71.2	3.0
5	-11.00	-10.58	-77.07	-74.6	-27.09	-18.67	-208.68	-140.4					-10.2	0.9	-72.1	3.1
Diffusive exchange with $CaCl_2$ solutions																
7LAB/7bTEW	-11.00	-10.40	-77.07	-75.1	-27.09	-17.83	-208.68	-138.1					-9.9	0.8	-73.2	2.9
8bLAB/8TEW	-11.00	-10.34	-77.07	-74.3	-27.09	-18.14	-208.68	-138.4					-9.7	0.8	-71.7	3.0
9bLAB/9TEW	-11.00	-10.19	-77.07	-73.7	-27.09	-18.39	-208.68	-139.1	-10.29	-73.9	-18.6	-139.3	-9.4	0.9	-70.4	3.0
10	-11.00	-10.72	-77.07	-75.0	-27.09	-18.78	-208.68	-139.7					-10.4	0.8	-73.1	3.0
Effect of slight water activity mismatch (0.05 to 0.1) between test and sample NaCl solutions																
11	-11.00	-9.2	-77.07	-68.2	-27.09	-17.6	-208.68	-135.5					-7.3	1.0	-59.4	3.3
12	-11.00	-10.1	-77.07	-71.3	-27.09	-18.3	-208.68	-138.2					-9.3	0.9	-65.6	3.2
13	-11.00	-11.3	-77.07	-75.8	-27.09	-18.9	-208.68	-140.7					-11.7	0.8	-74.5	3.0
Effect of significant water activity mismatch (0.15 to 0.3) between test and sample $CaCl_2$ solutions																
15	-11.00	-8.8	-77.07	-64.2	-27.09	-16.8	-208.68	-130.0					-6.5	1.1	-51.3	3.6
16	-11.00	-9.7	-77.07	-70.6	-27.09	-17.7	-208.68	-135.5					-8.5	0.9	-64.4	3.2
18	-11.00	-10.4	-77.07	-74.5	-27.09	-18.3	-208.68	-136.9					-9.7	0.9	-72.2	2.9
Effect of changing the sample/test water mass ratio																
19b	-11.00	-11.0	-77.07	-76.6	-27.09	-25.5	-208.68	-195.5					-10.7	4.2	-72.4	17.3
20	-11.00	-10.7	-77.07	-74.9	-27.09	-24.2	-208.68	-187.7					-9.3	2.9	-62.0	12.6
21	-11.00	-10.8	-77.07	-74.4	-27.09	-20.9	-208.68	-156.9					-10.6	1.1	-69.9	4.2
22	-11.00	-10.7	-77.07	-73.6	-27.09	-17.6	-208.68	-129.6					-10.5	0.7	-71.1	2.6
Isotope fractionation between $CaCl_2$ and NaCl solutions at same water activity equilibrated through the vapour phase																
28	-10.39	-10.4	-72.48	-71.4	-10.39	-10.5	-72.48	-71.8	*In Part 2.6, test and sample solutions are EVIAN water (EVIAN-EVIAN experiments)*							
29	-10.39	-10.9	-72.48	-70.6	-10.39	-10.0	-72.48	-73.4								
30	-10.39	-11.0	-72.48	-69.8	-10.39	-9.4	-72.48	-72.6								
Diffusive exchange with NaCl test solutions and $CaCl_2$ sample solutions at three different water activities (0.99, 0.9, and 0.8)																
31b	-11.00	-9.9	-77.07	-73.0	-27.09	-18.2	-208.68	-137.9	-10.13	-73.4	-18.95	-140.8	-8.6	1.0	-69.1	3.1
32b	-11.00	-10.7	-77.07	-72.5	-27.09	-18.5	-208.68	-136.2	-9.68	-74.6	-19.22	-141.3	-10.4	0.8	-68.2	3.0
33b	-11.00	-11.0	-77.07	-72.5	-27.09	-18.7	-208.68	-135.2	-9.94	-75.8	-19.15	-140.6	-11.1	0.8	-68.4	3.0
Triplicate diffusive exchange with NaCl and $CaCl_2$ test waters and Cambrian groundwater sample (OGW-10)																
34	-11.00	-8.7	-77.07	-53.5	-27.09	-16.6	-208.68	-120.1					-6.5	1.0	-29.4	4.2
35	-11.00	-8.1	-77.07	-52.9	-27.09	-16.1	-208.68	-117.1					-5.2	1.1	-29.1	4.1
36	-11.00	-8.6	-77.07	-52.9	-27.09	-16.7	-208.68	-119.1					-6.2	1.1	-28.6	4.2
37	-11.00	-8.0	-77.07	-55.2	-27.09	-16.3	-208.68	-121.7					-4.9	1.2	-33.1	4.1
38	-11.00	-7.8	-77.07	-54.8	-27.09	-16.4	-208.68	-122.1					-4.1	1.3	-31.5	4.2
39	-11.00	-7.9	-77.07	-56.1	-27.09	-16.8	-208.68	-123.1					-4.2	1.3	-34.4	4.1

[1] Initial $\delta^{18}O$ and $\delta^{2}H$ values of LAB and TEW standard waters, as well as the measured isotopic composition of the EVIAN water, are given in Table 3.
[2] The estimated errors (2σ) in the final $\delta^{18}O$ and $\delta^{2}H$ values of the distilled solutions are <0.4‰ and <1.4‰, respectively.
[3] All sample solutions were prepared with EVIAN water, except for experiments 34 to 39 where the sample solution was Cambrian groundwater from DGR3 (sample OGW-10 in Heagle and Pinder, 2009).
[4] In Experiments 28 to 30 (highlighted), test and sample solutions are EVIAN water (EVIAN-EVIAN experiments). Values reported in the LAB and TEW test water solutions columns are for test and sample EVIAN water solutions, respectively.

Table 12: Calculated Water Contents

Experiment	WC $_{\delta 18O}$ (wt%)	2σ (wt%)	WC$_{\delta 2H}$ (wt%)	2σ (wt%)
Diffusive exchange with NaCl solutions				
1	100.2	13.6	99.9	5.9
2	105.1	14.9	105.6	6.6
3	104.4	14.8	100.2	6.3
4b	107.6	15.3	102.0	6.4
5	99.0	14.1	100.0	6.2
Diffusive exchange with $CaCl_2$ solutions				
7b	115.2	16.5	107.6	6.7
8	106.3	15.1	105.3	6.6
9bLAB/9TEW	96.5	13.7	101.5	6.3
10	99.7	14.2	103.6	6.5
Effect of slight water activity mismatch (0.05 to 0.1) between test and sample NaCl solutions				
11	96.9	13.6	101.1	6.2
12	99.8	14.1	99.3	6.2
13	107.0	15.4	97.5	6.2
Effect of significant water activity mismatch (0.15 to 0.3) between test and sample $CaCl_2$ solutions				
15	107.4	15.3	106.2	6.6
16	108.2	15.4	107.9	6.7
18	95.0	13.5	101.8	6.4
Effect of changing the sample/test water mass ratio				
19b	110.1	46.1	105.9	23.0
20	102.8	27.7	88.0	12.5
21	102.0	15.5	101.5	6.9
22	98.2	14.2	98.4	6.2
Isotope fractionation between $CaCl_2$ and NaCl solutions at same water activity equilibrated through the vapour phase				
28				
29	No data			
30				
Diffusive exchange with NaCl test solutions and $CaCl_2$ sample solutions at three different water activities (0.99, 0.9, and 0.8)				
31b	90.8	12.9	101.2	6.3
32b	104.0	14.8	103.8	6.5
33b	104.4	14.8	105.6	6.6
Triplicate diffusive exchange with NaCl and $CaCl_2$ test waters and Cambrian groundwater sample (OGW-10)				
34	104.7	7.5	98.6	4.4
35	99.8	7.2	102.3	6.5
36	99.5	7.2	99.6	4.4
37	97.4	7.0	101.3	4.5
38	90.0	6.5	98.9	4.4
39	85.3	6.3	100.9	4.5

Note: Real water content (WC) is always 100 wt%.

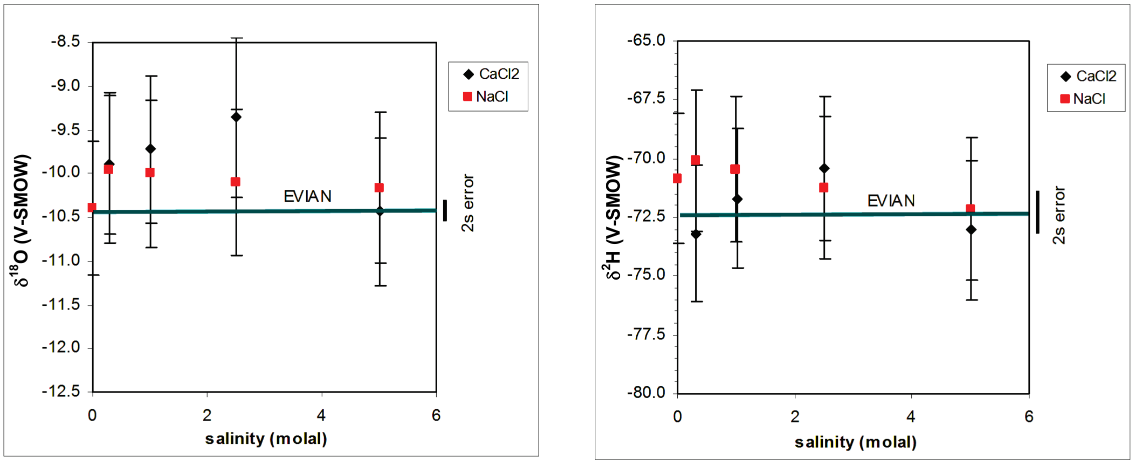


Figure 11: Calculated Isotopic Composition ($\delta^{18}O$ and $\delta^{2}H$) of Sample EVIAN Water Solutions at Different NaCl and $CaCl_2$ Salinities; the Horizontal Line Represents the Value for Pure EVIAN Water and the Vertical Line to the Right of the Diagram Represents the Associated Error (see Table 3)

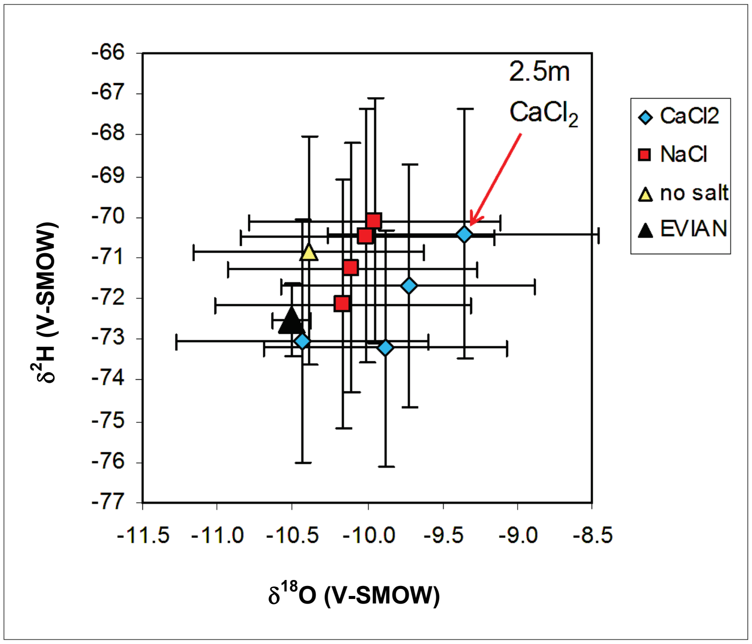


Figure 12: Calculated $\delta^{2}H$ versus $\delta^{18}O$ Values of EVIAN Sample Solutions at Various NaCl and $CaCl_2$ Salinities Compared to EVIAN Standard Water Isotope Composition (see Table 3)

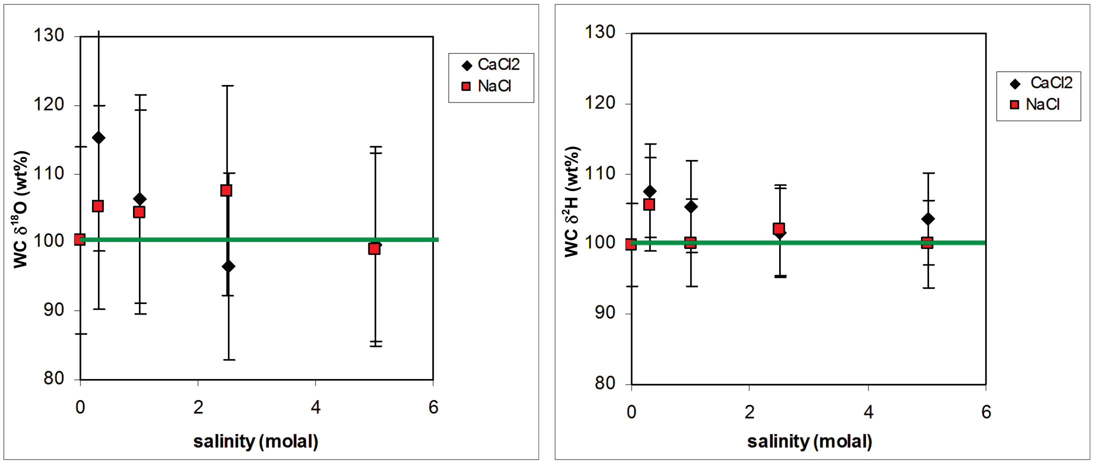


Figure 13: Calculated Water Content (WC) from the δ^{18}O ($WC_{\delta 18O}$) and δ^{2}H ($WC_{\delta 2H}$) Data versus NaCl and $CaCl_2$ Salinities; Real WC of the Sample is 100 ± 5 wt%

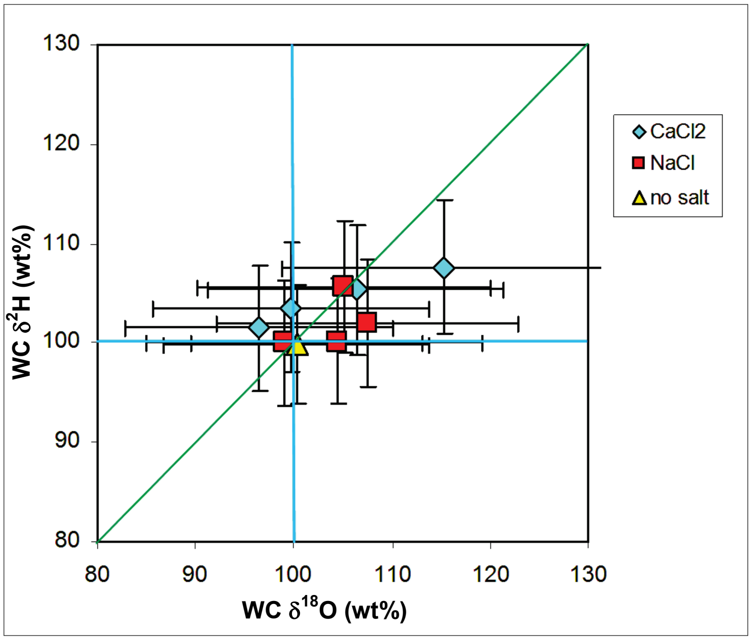


Figure 14: Comparison of the Sample Water Content Calculated with the δ^{2}H Data ($WC_{\delta 2H}$) and with the δ^{18}O Data ($WC_{\delta 18O}$); Real Water Content is 100 ± 5 wt%

5.2 DIFFUSIVE EXCHANGE SOLUTION-SOLUTION EXPERIMENTS: EFFECT OF SLIGHT MISMATCH (0.05 TO 0.1) OF WATER ACTIVITY BETWEEN TEST AND SAMPLE NACL SOLUTIONS

For the salinity mismatch testing, all diffusive exchange experiments were performed using NaCl test and sample solutions. The salinity of the sample solution was the same for all experiments (2.5 molal), while the salinities of the test solutions were 0.3, 1 and 5 molal. This corresponds to initial water activity differences between test and sample solutions ranging from 0.055 to 0.107 (see Tables 4 and 10). Equilibration time at ambient temperature was 30 days for all experiments.

Figure 15 shows that initial water activity disequilibrium does not affect significantly the calculated water content of the sample (Table 12), which could suggest equilibrium was reached during the 30 day experiment time. However, when plotted (Figures 16 through 20), the calculated isotopic compositions, test and sample solutions salinities, and water activities indicate that this was not the case.

When the initial water activities are different in test and sample solutions, the system must equilibrate not only for isotopes but also for salinities (and therefore water activities). If salinities are different in the two reservoirs, water is slowly transferred from the low salinity reservoir to the higher salinity reservoir until both have similar salinities, so that at equilibrium:

$$\text{SaltA} / (\text{waterA} + x) = \text{SaltB} / (\text{waterB} - x) \tag{6}$$

and, therefore,

$$x = (\text{SaltA} * \text{waterB} - \text{SaltB} * \text{waterA}) / (\text{SaltA} + \text{SaltB}), \tag{7}$$

where A is test solution, B is sample solution (same salt in both test and sample solutions), SaltA (or B) is the amount of salt in grams in reservoir A (or B), waterA (or B) is the amount of water in reservoir A (or B), and x is the amount of water transferred from one reservoir to the other through the vapour phase.

Although results from the first series of NaCl-NaCl and $CaCl_2$-$CaCl_2$ diffusive exchange experiments (see Section 5.1) showed that 30 days is sufficient to equilibrate the test and sample water isotopic compositions, this amount of time might not be enough to equilibrate them when the salinities (i.e., water activities) of the porewater (sample water) and test water are not well matched. At equilibrium, isotope compositions of test and sample solutions are the same. Disequilibrium in the water activities of both reservoirs induces isotopic disequilibrium, and the resultant shift of the calculated isotopic composition of the sample water can be significant (Figure 16). As shown in Figures 17 and 18, this shift is directly correlated to the amount of salinity-water activity disequilibrium at the end of the experiment. Figures 19 and 20 show that only about 40% equilibrium is reached when using test solutions at 0.3 and 1 molal NaCl, but more than 80% equilibrium is reached when 5 molal NaCl test solution is equilibrated with the 2.5 molal sample solution. This indicates that the time of water activity equilibration is shorter at higher salinities.

Results show that for 30-day long experiments, water activities must be carefully matched with an initial $\Delta a_w < 0.05$. Because equilibration time is shorter at higher salinities, it is better to have a test solution with an initial water activity that is lower than that of the sample.

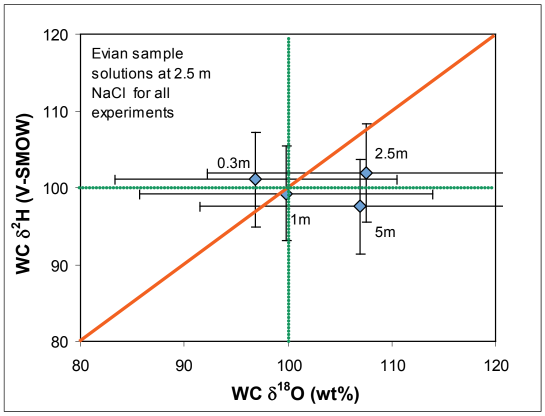


Figure 15: Calculated Water Contents (WC) Using Oxygen and Hydrogen Isotope Data; Correct Water Content Should be 100 wt%; Salinity (molal NaCl) of the Test Solution is Indicated Near Each Data Point; 2.5 Molal Test Solution Data are from Experiment Number 4 (Tables 8 through 12)

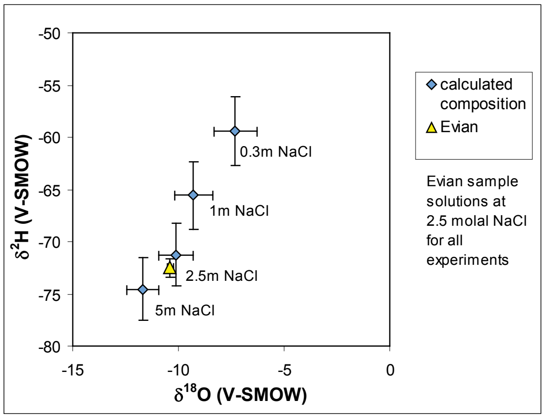


Figure 16: Calculated δ^{18}O and δ^{2}H Values of EVIAN Sample Water; Salinity of the Test Solution is Indicated Near Each Data Point; 2.5 Molal Test Solution Data are from Experiment Number 4 (Tables 8 through 12)

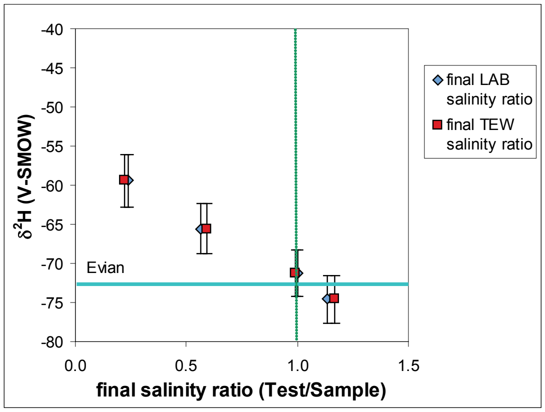


Figure 17: Calculated δ^{2}H Value of EVIAN Sample Water versus the Test to Sample Solution Salinity Ratio at the End of the Experiment; Experiment Reached Equilibrium if the Salinity Ratio = 1; the Point Plotting at the Final Salinity Ratio of 1 Corresponds to the 2.5 Molal Test Solution Data from Experiment Number 4 (see Tables 8 through 12); A Similar Plot Can be Obtained for δ^{18}O Values

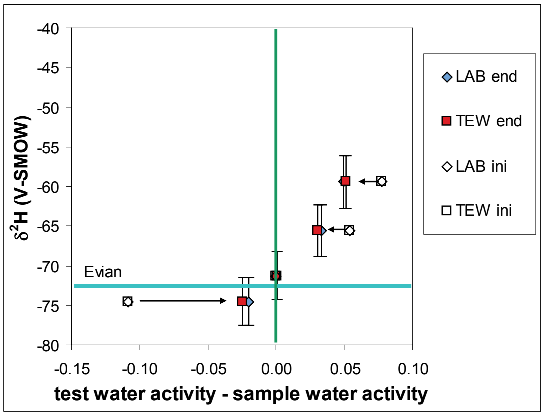


Figure 18: Calculated δ^{2}H Value of EVIAN Sample Water versus the Water Activity Difference Between Test and Sample Solution at the Start and End of the Experiment; Experiment Reached Equilibrium if this Difference is 0; the Point Plotting at $\Delta a_w = 0$ Corresponds to the 2.5 Molal Test Solution Data from Experiment Number 4 (Tables 8 through 12); A Similar Plot Can be Obtained for δ^{18}O Values

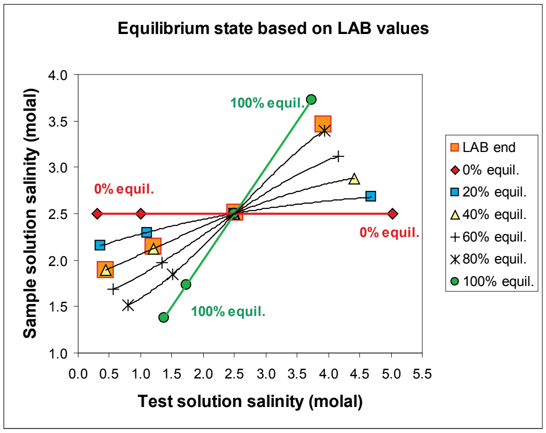


Figure 19: Diagram Showing the Sample versus LAB Test Solution Salinities at the Start and End of the Experiment; Calculated Salinities at Various Rates of Equilibration are Shown; the Point Plotting at 100% Equilibrium Corresponds to the 2.5 Molal NaCl Experiment Number 4 (Tables 8 through 12)

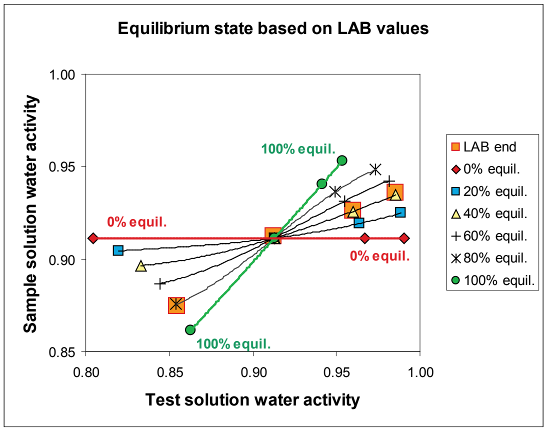


Figure 20: Diagram Showing the Sample versus LAB Test Solution Water Activities at the Start and End of the Experiment; Calculated Salinities at Various Rates of Equilibration are Shown; the Point Plotting at 100% Equilibrium Corresponds to the 2.5 Molal NaCl Experiment Number 4 (Tables 8 through 12)

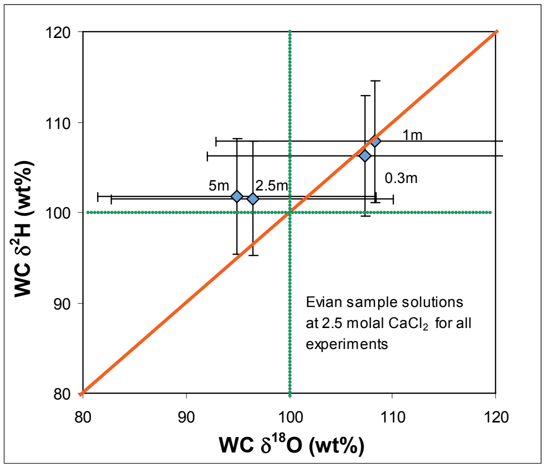
5.3 DIFFUSIVE EXCHANGE SOLUTION-SOLUTION EXPERIMENTS: EFFECT OF SIGNIFICANT MISMATCH (0.15 TO 0.3) OF WATER ACTIVITY BETWEEN TEST AND SAMPLE $CaCl_2$ SOLUTIONS

These significant salinity mismatch experiments are similar to those described in Section 5.2, but $CaCl_2$ was used in test and sample solutions instead of NaCl. As in the NaCl experiments, the salinity of the sample solution was the same for all experiments (2.5 molal), while the salinities of the test solutions were 0.3, 1 and 5 molal. This corresponds to initial water activity differences between test and sample solutions ranging from 0.13 to 0.29, which is much higher than in the experiments using NaCl solutions. Equilibration time at ambient temperature was 30 days for all experiments. Results are plotted in Figures 21 through 26.

The underlying mechanisms are the same as the NaCl water activity matching experiments. The effect of water activity mismatching on the calculated water content of the $CaCl_2$ sample might be slightly higher than NaCl experiments, although it is still very close to the estimated 2σ error (Figure 21). As shown in Figures 22 through 26, water activity mismatching can lead to important shifts in the calculated sample solution isotopic composition when using 30 days equilibration time. The shift of the calculated isotopic composition of the sample water is proportional to the magnitude of the salinity-water activity disequilibrium at end of experiment (Figures 23 and 24).

Figures 25 and 26 show that the isotopic composition of the test solutions were between 60 and 80% of the equilibrium value for test solutions with 0.3 and 1 molal $CaCl_2$, but 100% equilibrium is reached when 5 molal $CaCl_2$ test solution is equilibrated with the 2.5 molal sample solution.

This indicates that the equilibration time is shorter at high salinities (as observed in the experiments with NaCl) and shorter with $CaCl_2$ than with NaCl solutions.



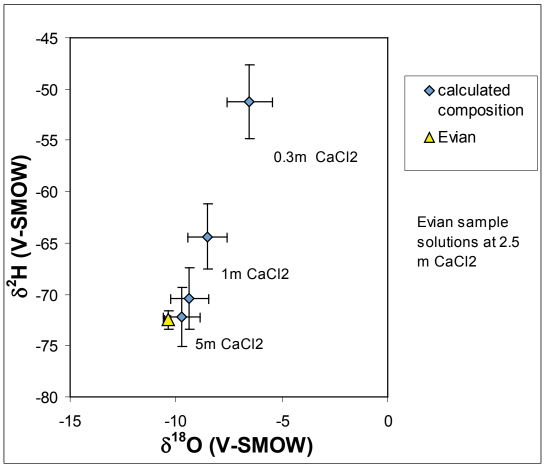


Figure 21: Calculated Water Contents Using Oxygen and Hydrogen Isotope Data; Correct Water Content is 100 wt%; Salinity (molal $CaCl_2$) of the Test Solution is Indicated Near Each Data Point; 2.5 Molal Test Solution Data are from Experiment Number 9 (Tables 8 through 12)

Figure 22: Calculated $\delta^{18}O$ and $\delta^{2}H$ Values of the EVIAN Sample Water; Salinity of the Test Solution is Indicated Near Each Data Point; 2.5 Molal Test Solution Data are from Experiment Number 9 (Tables 8 through 12)

The results of these experiments, which investigated the importance of water activity mismatch between test and sample $CaCl_2$ solutions, indicate that, for the same experiment time, the accuracy of the water activity matching between the test and sample solution is less critical for $CaCl_2$ solutions than for NaCl solutions because the equilibration of the salinities and water activities is faster for $CaCl_2$ solutions. As observed for the NaCl system, it is better to have the initial water activity of the test solution lower than that of the sample solution.

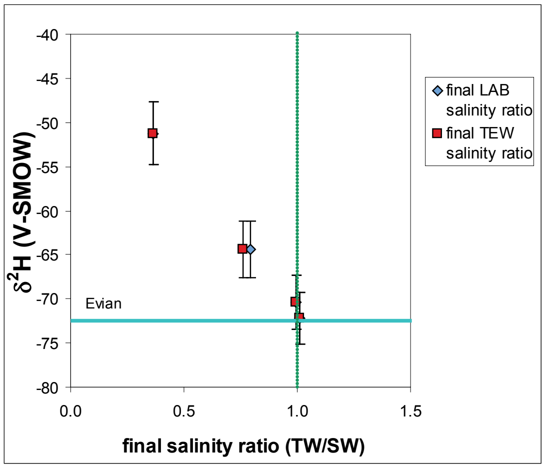


Figure 23: Calculated δ^2H Value of EVIAN Sample Water versus the Test to Sample Solution Salinity Ratio at the End of the Experiment; Experiment Reached Equilibrium if the Salinity Ratio = 1; the Point Plotting at the Final Salinity Ratio of 1 Corresponds to the 2.5 Molal Test Solution Data from Experiment Number 9 (Tables 8 through 12); A Similar Plot is Obtained for $\delta^{18}O$ Values

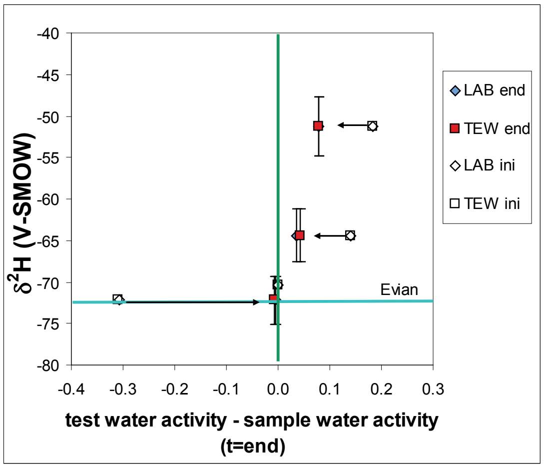


Figure 24: Calculated δ^2H Value of EVIAN Sample Water versus the Water Activity Difference Between Test and Sample Solution at the Start and End of the Experiment; Experiment Reached Equilibrium if this Difference is 0; the point Plotting at $\Delta a_w = 0$ Corresponds to the 2.5 Molal Test Solution Data from Experiment Number 9 (Tables 8 through 12); A similar Plot is Obtained for $\delta^{18}O$ Values

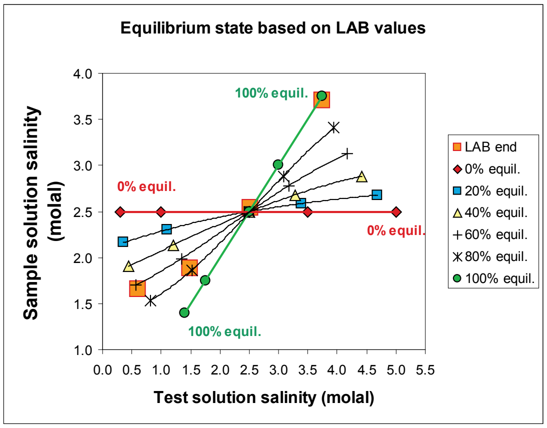


Figure 25: Diagram Showing the Sample versus LAB Test Solution Salinities at the Start and End of the Experiment; Calculated Salinities at Various Rates of Equilibration are Shown; the Point Plotting at 100% Equilibrium Corresponds to the 2.5 Molal $CaCl_2$ Experiment Number 9 (Tables 8 through 12)

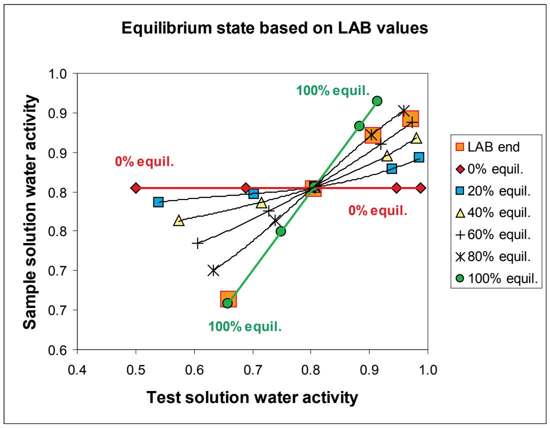


Figure 26: Diagram Showing the Sample versus LAB Test Solution Water Activities at the Start and End of the Experiment; Calculated Salinities at Various Rates of Equilibration are Shown; the Point Plotting at 100% Equilibrium Corresponds to the 2.5 Molal $CaCl_2$ Experiment Number 9 (Tables 8 through 12)

5.4 DIFFUSIVE EXCHANGE SOLUTION-SOLUTION EXPERIMENTS: EFFECT OF TEST / SAMPLE WATER MASS RATIO

The effect of sample water:test water (SW/TW) mass ratio was investigated using approximately 5 mL of test solution (LAB or TEW) and varying the sample (EVIAN) size to span a SW/TW mass ratio range of 0.1 to 1.4. All test and sample solutions were 5 molal NaCl. Figures 27 and 28 show that all results are consistent, within 2σ error. As shown in Figures 29 and 30, the errors on the calculated $\delta^{18}O$ and $\delta^{2}H$ values increase significantly when the SW/TW mass ratio decreases.

These results demonstrate that changing the SW/TW mass ratio does not perturb the diffusive exchange experiment, even at 5 molal NaCl. Because of the steep increase of errors with decreasing SW/TW mass ratio, it is recommended to have the SW/TW mass ratio ≥0.5. This means that the lowest rock water content (pore-connected) that can be analyzed using the isotope diffusive exchange technique is about 0.5 wt%, when equilibrating 3 mL of test water with about 300 grams of rock (respective practical minima and maxima for the volume of test water and mass of rock). High SW/TW mass ratios were not investigated because rocks with very low porosity and water content are the main challenge when applying the diffusive exchange technique.

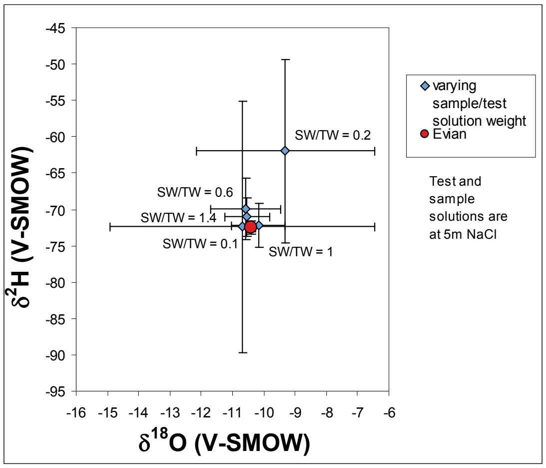


Figure 27: Plot of Calculated $\delta^{2}H$ versus $\delta^{18}O$ of Sample Water; SW/TW Refers to the Sample Water to Test Water Mass Ratio at the Start of the Experiment; Initial Isotopic Composition of All Sample Solutions is EVIAN

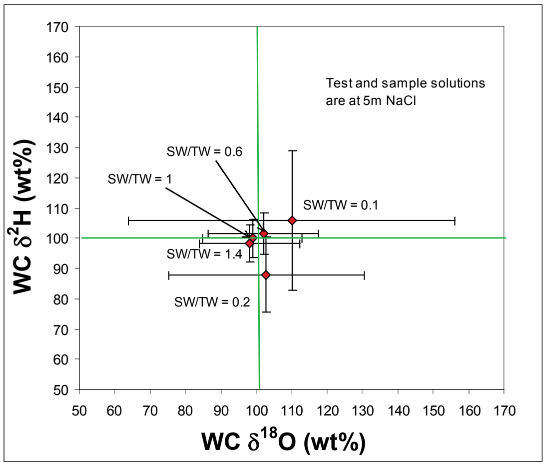
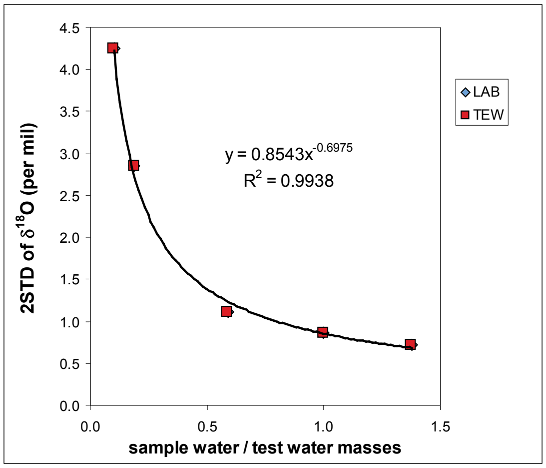


Figure 28: Comparison of the Sample Water Content Calculated with the $\delta^{2}H$ Data ($WC_{\delta 2H}$) and with the $\delta^{18}O$ Data ($WC_{\delta 18O}$); Actual Water Content is 100 ± 5 wt%; SW/TW Refers to the Sample Water to Test Water Mass Ratio at the Start of the Experiment



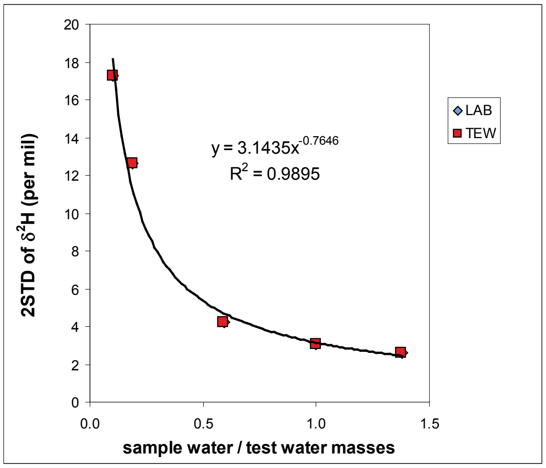


Figure 29: Variation of the 2σ Error of the δ^{18}O Value versus the Sample to Test Water Mass Ratio (SW/TW); SW/TW with LAB or TEW Test Waters are Practically Identical

Figure 30: Variation of the 2σ Error of the δ^{2}H Value versus the Sample to Test Water Mass Ratio (SW/TW); SW/TW with LAB or TEW Test Waters are Practically Identical

5.5 DIFFUSIVE EXCHANGE SOLUTION-SOLUTION EXPERIMENTS: ISOTOPE FRACTIONATION BETWEEN NaCl AND $CaCl_2$ SOLUTIONS OF SIMILAR WATER ACTIVITY

The effect of salt addition on the liquid-vapour isotope fractionation coefficient of water (Horita et al., 1993a and 1993b) is not an issue when the same salt is dissolved in test and sample solutions, because both sides (test and sample water) fractionate to the same extent. However, results obtained by the diffusive exchange technique might be perturbed if test and sample solutions have different chemical compositions. This has been investigated by equilibrating a series of $CaCl_2$ and NaCl EVIAN test and sample solution pairs, matched to have the same water activity. Results are given in Tables 8, 10 and 11. Figures 31 and 32 show the fractionation of δ^{18}O and of δ^{2}H in $CaCl_2$ versus NaCl solutions with matched water activity. The initial masses of water in the test and sample solutions are similar and are conserved throughout the experiment. The fractionation effect is broadly proportional to the water activity of the solutions and is up to about 1‰ for δ^{18}O and 2‰ for δ^{2}H. These values are close to the estimated 1.4‰ 2σ error for δ^{2}H, but are significantly higher than the 0.4‰ 2σ error for δ^{18}O. Figures 33 and 34 compare the calculated δ^{18}O and δ^{2}H values with respect to salinity (NaCl or $CaCl_2$). Given the limited data available (4 points), and the magnitude of the errors, linear regression has been used as a broad approximation of the isotope fractionation trend. The formulae and the plot of these equations are given in Figures 33 and 34. These are compared with the equations proposed by Horita et al. (1993a). The water activity-salinity dependence was calculated using the Pitzer database (using Geochemist's Workbench®).

The δ^{2}H value of $CaCl_2$ EVIAN solution ($\delta^{2}H_{CaCl2sol.}$) equilibrated with NaCl solution at 20°C relates to isotopic fractionation coefficients, as follows:

$$\delta^{2}H_{CaCl2sol.} = \delta^{2}H_{EVIAN} + \Delta^{2}H_{NaClsol\text{-}vapour} - \Delta^{2}H_{CaCl2sol.\text{-}vapour}$$

$= \delta^2H_{EVIAN} + NaCl[molal] * \{-2.89 + [1503.1 / (273.15 + 20)]\} - CaCl_2[molal] * \{-2.34 + [2318 / (273.15 + 20)]\}$ (8)

where the δ^2H_{EVIAN} is the isotope composition of pure EVIAN water, $\Delta^2H_{NaClsol\text{-}vapour}$ and $\Delta^2H_{CaCl2sol.\text{-}vapour}$ are the equations of Horita et al. (1993a) for the salt-induced isotope fractionation for NaCl and $CaCl_2$ solutions, and NaCl [molal] and $CaCl_2$ [molal] are the molality of the NaCl and $CaCl_2$ EVIAN solutions at isotopic equilibrium.

Similarly, the $\delta^{18}O$ of $CaCl_2$ EVIAN solution ($\delta^{18}O_{CaCl2sol.}$) equilibrated with NaCl solution at 20°C relates to isotopic fractionation coefficients as follows:

$$\delta^{18}O_{CaCl2sol.} = \delta^{18}O_{EVIAN} + \Delta^{18}O_{NaClsol\text{-}vapour} - \Delta^{18}O_{CaCl2sol.\text{-}vapour}$$

$= \delta^{18}O_{EVIAN} + NaCl[molal] * (-0.015) - CaCl_2[molal] * (-0.368)$ (9)

The δ^2H and $\delta^{18}O$ values of NaCl EVIAN solutions ($\delta^2H_{NaClsol.}$ and $\delta^{18}O_{NaClsol.}$) equilibrated with $CaCl_2$ solutions at 20°C correspond to the following formulae, with the sign of the last two members of the equation being inverted compared to equations (8) and (9):

$$\delta^2H_{NaClsol.} = \delta^2H_{EVIAN} - \Delta^2H_{NaClsol\text{-}vapour} + \Delta^2H_{CaCl2sol.\text{-}vapour} \quad (10)$$

$$\delta^{18}O_{NaClsol.} = \delta^{18}O_{EVIAN} - \Delta^{18}O_{NaClsol\text{-}vapour} + \Delta^{18}O_{CaCl2sol.\text{-}vapour} \quad (11)$$

The polynomial approximation of the salinity-water activity (a_w) relationship, used to build the diagrams shown in Figure 33 and 34, is given by the following equations (r^2 >0.9995):

$$NaCl\ [molal] = -55.1a_w^4 + 155.23a_w^3 - 177.17a_w^2 + 77.027a_w \quad (12)$$
$$KCl\ [molal] = 728.19a_w^4 - 2649.1a_w^3 + 3599.1a_w^2 - 2194.9a_w + 516.67 \quad (13)$$
$$CaCl_2\ [molal] = 70.789a_w^5 - 276.11a_w^4 + 393.7a_w^3 - 259.97a_w^2 + 71.643a_w \quad (14)$$
$$MgCl_2\ [molal] = 47.002a_w^5 - 201.35a_w^4 + 304.45a_w^3 - 210.51a_w^2 + 60.452a_w \quad (15)$$

Figure 33 shows that the $\delta^{18}O$ values closely match with what is expected from the Horita et al. (1993a) equations. As observed in Figure 34, a poorer match is obtained for δ^2H values, but, in that case, salt-induced fractionation is weak – close to the 1.4‰ 2σ error.

These experiments show that isotope compositions obtained from equilibrated NaCl and $CaCl_2$ solutions can be shifted by up to about 1‰ for $\delta^{18}O$ and 2‰ for δ^2H, compared to the initial isotope composition. Therefore, the effect of differing chemical compositions in the test and sample waters in diffusive exchange experiments can be significant for $\delta^{18}O$ but minor for δ^2H, considering the respective analytical errors. These results are consistent with the Horita et al. (1993a and 1993b) water activity-isotope fractionation coefficient relationships shown in Figures 2 and 3, where the difference of fractionation coefficients between NaCl and $CaCl_2$ solutions at the same water activity is significant for $\delta^{18}O$ (up to 1‰) but minimal for δ^2H (up to 3‰), considering the respective analytical errors for $\delta^{18}O$ and δ^2H. These values might be higher if $MgCl_2$ or KCl are dominant species (see Figures 2 and 3). Therefore, when dealing with rocks, an understanding of the chemical composition of the porewater is necessary to estimate the maximum isotopic fractionation between the test solution and the sample solution.

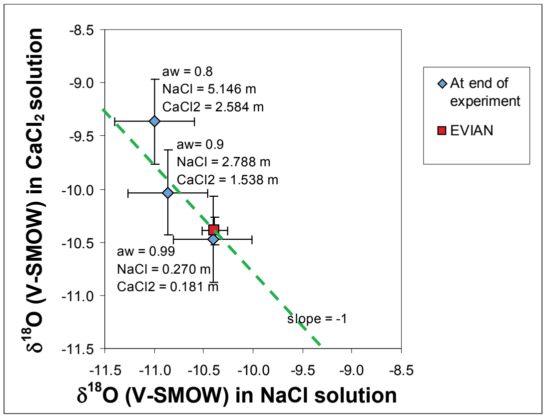


Figure 31: Plot of the $\delta^{18}O$ Values Obtained from the NaCl and $CaCl_2$ EVIAN Solutions After 30 Days of Equilibration at Ambient Temperature Through the Vapour Phase; Isotopic Composition of the EVIAN Water (not equilibrated) is Plotted; Water Activity (aw) and the NaCl and $CaCl_2$ Molalities of Each Pair of Solutions are Shown Near Each Plotted Data Point; Green Dotted Line with a -1 Slope Passes Through the EVIAN Water Composition; Because the Masses of Each of the Reservoirs are Similar and Constant (same initial a_w), Any Deviation from the EVIAN Water Value Should Sit on This Line

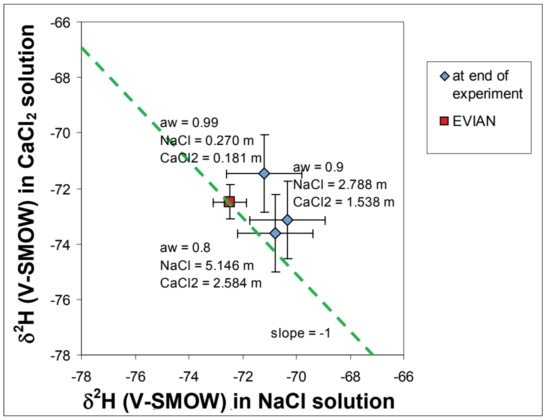


Figure 32: Plot of the $\delta^{2}H$ Values Obtained from the NaCl and $CaCl_2$ EVIAN Solutions After 30 Days of Equilibration at Ambient Temperature Through the Vapour Phase; Isotopic Composition of the EVIAN Water (not equilibrated) is Plotted; Water Activity (aw) and the NaCl and $CaCl_2$ Molalities of Each Pair of Solutions are Shown Near Each Plotted Data Point; Green Dotted Line with a -1 Slope Passes Through the EVIAN Water Composition; Because the Masses of Each of the Reservoirs are Similar and Constant (same initial a_w), Any Deviation from the EVIAN Water Value Should Sit on This Line

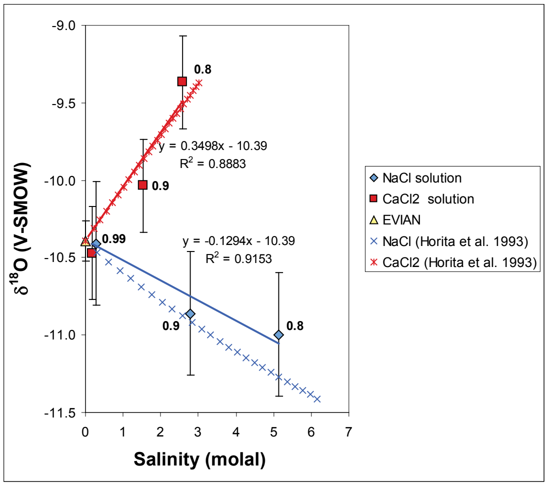


Figure 33: $\delta^{18}O$ Value of Equilibrated NaCl and $CaCl_2$ EVIAN Solutions; Linear Regression Lines are Shown with Equation for Both NaCl and $CaCl_2$ Solutions; Dotted Lines Correspond to the Fractionation Coefficients Calculated from Horita et al. (1993a) Using Water Activity-Salinity Dependence Calculated Using Pitzer (1987) Equations; Bold Numbers Near Data Points are Water Activity

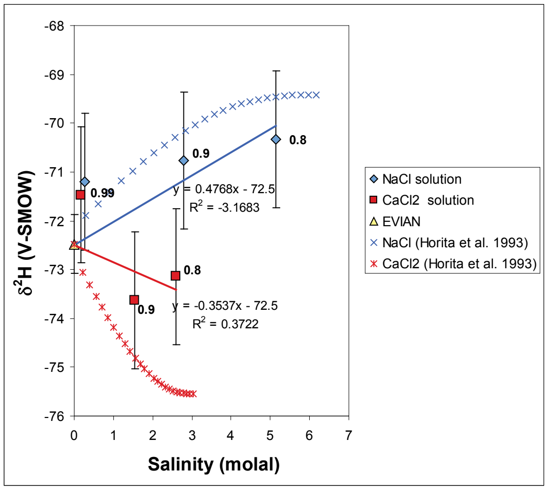


Figure 34: $\delta^{2}H$ Value of Equilibrated NaCl and $CaCl_2$ EVIAN Solutions; Linear Regression Lines are Shown with Equation for both NaCl and $CaCl_2$ Solutions; Dotted Lines Correspond to the Fractionation Coefficients Calculated from Horita et al. (1993a) Using Water Activity-Salinity Dependence Calculated Using Pitzer (1987) Equations; Bold Numbers Near Data Points are Water Activity

5.6 DIFFUSIVE EXCHANGE SOLUTION-SOLUTION EXPERIMENTS: EFFECT OF DIFFERING CHEMICAL COMPOSITIONS IN TEST AND SAMPLE SOLUTIONS

Three diffusive exchange experiments were performed using NaCl in the test solutions (LAB and TEW) and $CaCl_2$ in the sample solutions (EVIAN) to explore the magnitude of the perturbing effect of having different chemical compositions in the test and sample solutions. The experiments were performed at water activities of 0.99, 0.9 and 0.8, with NaCl and $CaCl_2$ salinities of test and sample solutions adjusted accordingly (see Tables 4 and 10). Results are given in Tables 8 through 12 and shown in Figures 35 through 37.

Figures 35 and 36 show that the calculated $\delta^{18}O$ values for the EVIAN samples vary significantly based on the water activity of the experiment. In contrast, the $\delta^{2}H$ values are consistently shifted toward higher values compared to the pure EVIAN water composition – the obtained $\delta^{2}H$ values appear to be only slightly dependent on water activity. Such behavior has already been documented in the previous experiment (see Section 5.5; Figure 32), where $\delta^{2}H$ values obtained from NaCl solutions are shifted slightly toward higher values when compared to the pure EVIAN water. Calculated water contents fit the expected 100 wt% value in all cases, within 2σ error.

As expected from the previous experiment (Section 5.5), the deviation of the calculated $\delta^{2}H$ values due to the different chemical composition of test and sample solutions is small, close to the 2σ error. In contrast, the deviation of the calculated $\delta^{18}O$ values can be significant, up to about 2‰. Strangely, the highest water activity experiment (lowest salinities) shows the highest deviation compared to the EVIAN water composition, and all data are shifted toward higher values than expected. There is no explanation for this behavior at the moment.

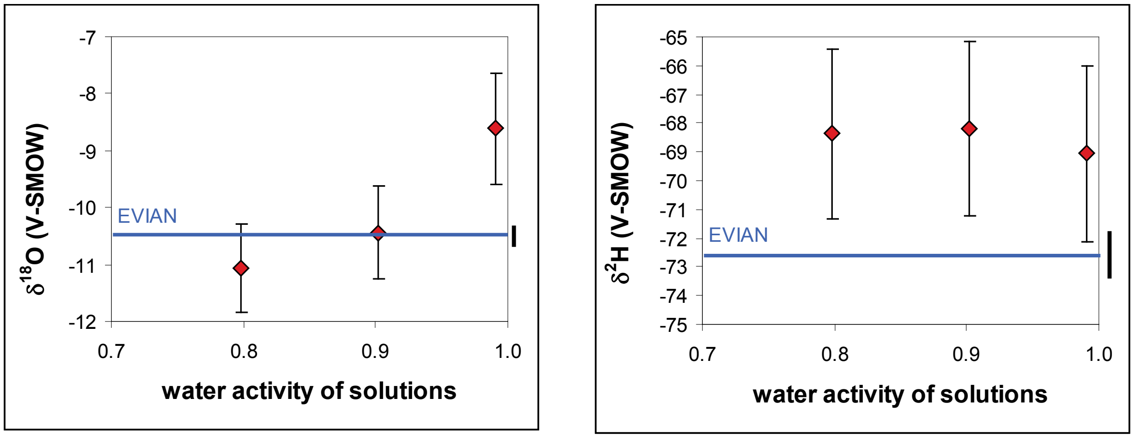
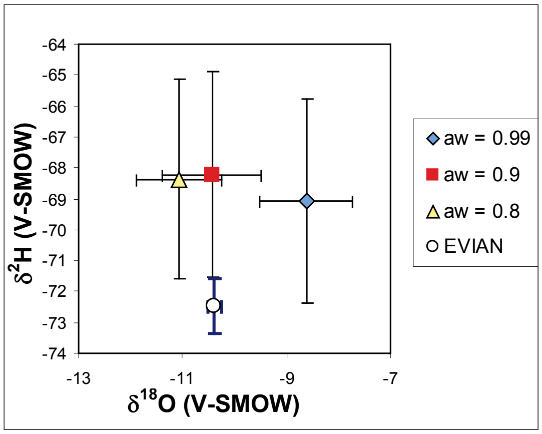


Figure 35: Calculated Isotopic Composition of the EVIAN Sample $CaCl_2$ Solution from Data Measured for NaCl test Solutions; Experiments were Performed at Different Water Activities (matched sample and test solutions); Horizontal Line Represents the Isotopic Composition of Pure EVIAN Water and the Vertical Line to the Right of the Diagrams Represents the Associated 2σ Error (see Table 3)

The implications are that even with completely different chemical compositions between test and sample solutions, the water composition of the sample solution can be obtained with <5‰ deviation for $\delta^{2}H$, provided the water activities on both sides of the experiment are carefully matched. Results for $\delta^{18}O$ show a significant deviation that is dependent on the water activity; the fact that major deviations are observed at the lowest salinities (highest water activity) is confusing (see Section 5.5). The $\delta^{18}O$ data are, therefore, more ambiguous (or prone to perturbation), and should be treated cautiously when chemical compositions are different in the test and sample waters.

The calculated water content is not significantly sensitive to the contrast in chemical composition between test and sample waters.



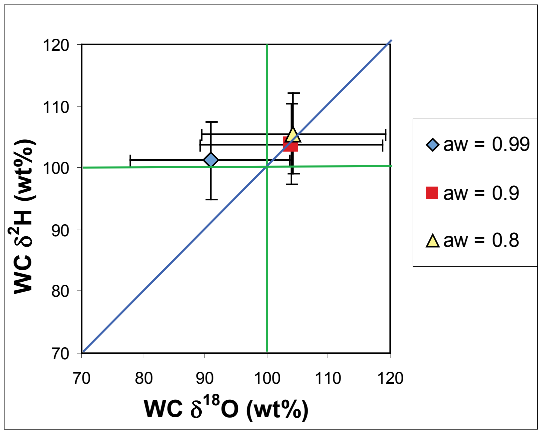


Figure 36: Calculated δ^2H versus $\delta^{18}O$ Values of EVIAN Sample Solutions at Various Water Activities Compared to EVIAN Standard Water Isotope Compositions (see Table 3)

Figure 37: Comparison of the Sample Water Content Calculated with the δ^2H Data ($WC_{\delta 2H}$) and with the $\delta^{18}O$ Data ($WC_{\delta 18O}$); Real Water Content is 100 ± 5 wt%

5.7 DIFFUSIVE EXCHANGE SOLUTION-SOLUTION EXPERIMENTS: APPLICATION TO CAMBRIAN GROUNDWATER WITH NaCl AND $CaCl_2$ TEST SOLUTIONS

Cambrian groundwater from borehole DGR3 (sample OGW-10 in Heagle and Pinder, 2009) is a highly saline complex brine (Na-Ca-Mg-K-Cl; see Table 6) and, therefore, is well suited for testing the adapted diffusive exchange technique. This groundwater has been analyzed for water isotopes using direct H_2 and CO_2 equilibration in a GasBench and applying the correction factors recommended by Horita et al. (1993a). Comparison can, thus, be made among the diffusive exchange results, the values obtained by the direct distillation of NaF treated groundwater (Section 4), and the data presented in Heagle and Pinder (2009).

Diffusive exchange experiments were performed in triplicate with either NaCl or $CaCl_2$ test solutions. Results show that data obtained using NaCl and $CaCl_2$ test solutions are shifted in opposite ways (Figure 38). This deviation is small for δ^2H (about 1.5‰, which is within the 2σ error), but higher for $\delta^{18}O$ (about 1‰), which is significant but still within, or close to, the 2σ error.

An approximate correction can be applied using equations derived from the best fit linear regression obtained by equilibrating NaCl and $CaCl_2$ solutions (see Section 5.5). These equations consider sample solution with mixed NaCl and $CaCl_2$, but do not take into account the minor amounts of $MgCl_2$ and KCl present in the Cambrian groundwater. They consider the effect of mixing NaCl and $CaCl_2$ as linear, in agreement with observations by Horita et al. (1993b).

When test solution is prepared with NaCl, the correction of the isotopic values uses the following equations:

$$\delta^{18}O_{corrected} = [CaCl_{2[sample]} / (NaCl_{[sample]} + CaCl_{2[sample]})] * 0.1294 * NaCl_{[test]} + \delta^{18}O_{[test]} \qquad (16)$$

$$\delta^{2}H_{corrected} = -[CaCl_{2[sample]} / (NaCl_{[sample]} + CaCl_{2[sample]})] * 0.4768 * NaCl_{[test]} + \delta^{2}H_{[test]} \qquad (17)$$

When test solution is prepared with $CaCl_2$, the correction of the isotopic values uses the following equations:

$$\delta^{18}O_{corrected} = [NaCl_{[sample]} / (NaCl_{[sample]} + CaCl_{2[sample]})] * 0.3498 * CaCl_{2[test]} + \delta^{18}O_{[test]} \qquad (18)$$

$$\delta^{2}H_{corrected} = -[NaCl_{[sample]} / (NaCl_{[sample]} + CaCl_{2[sample]})] * 0.3537 * CaCl_{2[test]} + \delta^{2}H_{[test]} \qquad (19)$$

where "$salt_{[sample]}$" and "$salt_{[test]}$" refer to the molal salinity of the sample and test solutions, "$\delta^{18}O_{[test]}$" and "$\delta^{2}H_{[test]}$" are the measured isotopic ratios of the test water, and $\delta^{18}O_{corrected}$ and $\delta^{2}H_{corrected}$ are the corrected values for equilibrated test water to be used in the calculation of the sample isotopic composition and water content.

Results corrected with these equations are plotted in Figure 39 and fit within 2σ error with the data obtained by direct NaF treatment and distillation (see Section 4) or those reported by Heagle and Pinder (2009) (H_2 and CO_2 equilibration in a GasBench). The practical implications are that complex brines can be measured with the diffusive exchange method, and that deviation from the real isotopic composition – due to differing chemical composition between test solution and sample – Is negligible for $\delta^{2}H$ and very close to the 2σ error for $\delta^{18}O$.

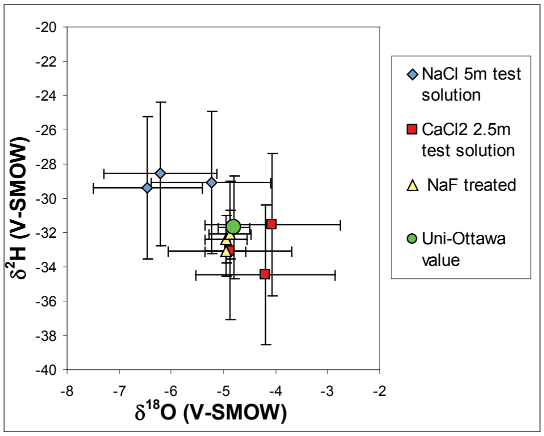


Figure 38: Plot of the Isotopic Composition of Cambrian Groundwater (OGW-10) Obtained by Diffusive Exchange with 5 Molal NaCl Test Water or 2.5 Molal $CaCl_2$ Test Water; Results are Compared with Data Obtained Through Direct NaF Treatment and Distillation (see Section 4) and Data Presented in Heagle and Pinder (2009)

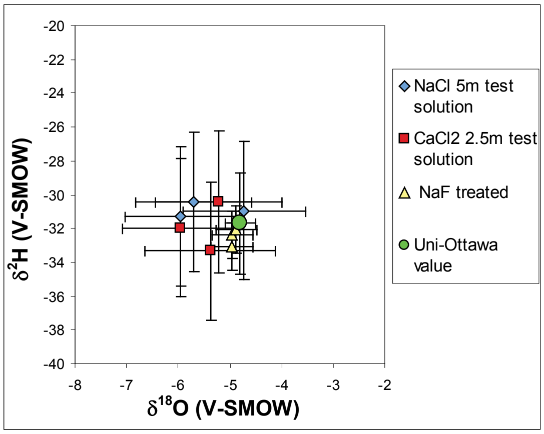


Figure 39: Same Plot as Figure 37 but Diffusive Exchange Results are Corrected for the Difference in Liquid-Vapour Isotope Fractionation as a Result of the Different Chemical Compositions in Test and Sample Solutions (Section 4); Correction Only Considers $CaCl_2$ and NaCl – Minor $MgCl_2$ and KCl Present in Cambrian Ground Water are Neglected; Corrections Assume Water Masses are Equal (test and sample solution)

6. EQUILIBRATION OF ROCK MATERIAL WITH SYNTHETIC SOLUTIONS: METHODOLOGY, PROCEDURES AND RESULTS

6.1 SELECTED ROCK MATERIALS

Equilibration experiments were conducted using two different rock materials:

- Opalinus Clay (shaly facies) from the Mont Terri URL, Switzerland. Sample DR-17 (9.35 to 9.50 m).
- Queenston Formation (red shale), Bruce Nuclear Site, Ontario, Canada. Core samples DGR4-451.08 and DGR4-453.11.

Rock sample selection included the following criteria:

- Relevance of the formations to the Canadian and Swiss nuclear waste management organizations (NWMO and Nagra, respectively);
- Availability of sufficient homogeneous porewater-saturated material (complete porewater saturation is favourable, because the presence of a separate gas phase would hinder re-saturation with synthetic solution);
- Water content as high as possible to minimize errors during the diffusive exchange experiments;
- Avoid rocks that might contain solid salts (e.g., halite) or sulphate minerals (gypsum or anhydrite); and
- Inclusion of two clay-rich rocks with very different physical properties (e.g., water content, ratio of swelling clay minerals).

6.2 MECHANICAL STABILITY OF THE ROCK

Although change of some physical properties of rock samples (e.g., density, water content, porosity, etc.) will not compromise the experimental results and the interpretation, the integrity of the rock has to be preserved during the equilibration with synthetic solutions (i.e., disaggregation must be avoided because the mechanical instability would significantly complicate the set up of the equilibration procedure). Compared to the Queenston Shale, the Opalinus Clay (shaly facies) has a lower mechanical stability due to its very high clay content (58-76 wt%), of which a significant proportion consists of swelling clays (5-20 wt%; Pearson et al., 2003). Due to the high swelling clay content, the Opalinus Clay has higher risk of disaggregation compared with the illite-chlorite shale of the Queenston Formation. Therefore, the Opalinus Clay has been selected to test the mechanical stability during long-term (months) immersion in synthetic solutions of different NaCl or $CaCl_2$ salinities. Rock pieces from core sample OPA DR-17 (9.35-9.50 m along hole; shaly facies), which were stored vacuum-sealed and refrigerated, were used for these experiments.

Experimental Set-Up

- NaCl and $CaCl_2$ salt solutions were prepared, each with concentrations of 0.3, 1, 2.5 and 5 molal.

- Porewater-saturated rock core from the Opalinus Clay, Mont Terri URL, Switzerland was used in the experiments.
- Porewater of the Opalinus Clay from the DR-17 borehole has a salinity (Cl^-) of approximately 0.17 molal, $\delta^{18}O$ around -7.74‰ VSMOW and δ^2H around -54.7‰ VSMOW (T. Gimmi – personal communication, 2012; Pearson and Waber, 2006).
- The aluminum-PE sealing material in which core sample DR-17 was preserved was opened and rock material was removed from the core with a hammer.
- Three small rock pieces (23.3 to 24.8 g) were taken for replicate measurements of the bulk wet density of the original core material.
- 270 and 300 g of material were placed in two pre-labelled, pre-weighed glass dishes for duplicate gravimetric water content measurements.
- For the mechanical stability experiments, small rock pieces (≈ 2-3 cm^3) were placed in plastic containers and photographed.
- Saline solution was added and the samples were photographed again, before the containers were sealed. The sealed containers were placed inside glass mason jars to minimize evaporation of the saline solutions.
- At intervals of 4 to 35 days, the plastic containers were opened and the rock pieces submerged in the saline solutions were photographed. This was done 4 times during the 63 day duration of the experiment.

Results

The experiments showed that the mechanical stability of Opalinus Clay is preserved at all salinities considered, for both NaCl and $CaCl_2$ solutions. It was observed that the samples immersed in 0.3 molal solutions were softer than those immersed in higher salinity solutions, but did not disaggregate. No significant change can be seen between pictures taken at the start and at the end of the experiments (Figure 40). The main observed difference is that for $CaCl_2$ solutions, an iron oxide-rich deposit formed at the bottom of the container.

In all of the experiments, the bulk wet density of the rock pieces determined after the 63-day immersion period was lower when compared to that of the intact porewater-saturated rock (Table 13). A good correlation between the bulk wet density and the salinity of the solution was observed (Figure 41), which is consistent with the fact that swelling capacity is lowered at high salinity. It is a well-known feature that shales, in general, and Opalinus Clay, in particular, swell and reach water contents well above the original in-situ values when immersed under unconfined atmospheric conditions (see Nagra, 2002 – Section 5.7), even if the salinity of the solution is equal to or higher than that of the in-situ porewater (here around 0.17 molal Cl^-). Swelling alone cannot explain the fact that rock density, after immersed in saline solutions, is lower than the in-situ rock density, because equilibration with very high salinity solutions (i.e., 5 molal) should significantly limit the swelling effect. Stress release, due to a lower confining pressure than in-situ conditions, most likely increases the rock porosity and, therefore, lowers the rock density.

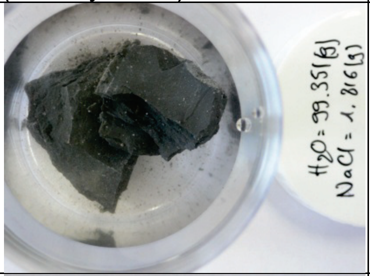
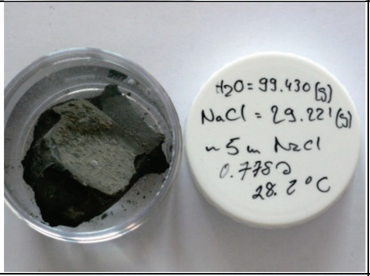
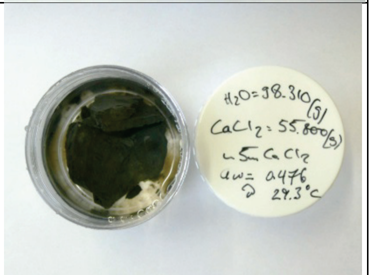
Type of solution	Before immersion	Start of experiment (16 July 2010)	End of experiment (17 September 2011)
0.3 m NaCl			
5 m NaCl			
0.3 m $CaCl_2$			
5 m $CaCl_2$			

Figure 40: Selected Examples of Mechanical Stability Experiments Performed with Opalinus Clay Rock Pieces and Synthetic Solutions at Various Salinities

Table 13: Bulk Wet Density of Opalinus Clay Before and After Equilibration with Saline Solutions

Solution	Average measured bulk wet density (n=2)
None (fresh porewater-saturated core pieces)	2.52*
0.3 m NaCl	2.32
1.0 m NaCl	2.35
2.5 m NaCl	2.39
5.0 m NaCl	2.42
0.3 m $CaCl_2$	2.32
1.0 m $CaCl_2$	2.32
2.5 m $CaCl_2$	2.38
5.0 m $CaCl_2$	2.42

*average of 3 replicate measurements (n = 3)

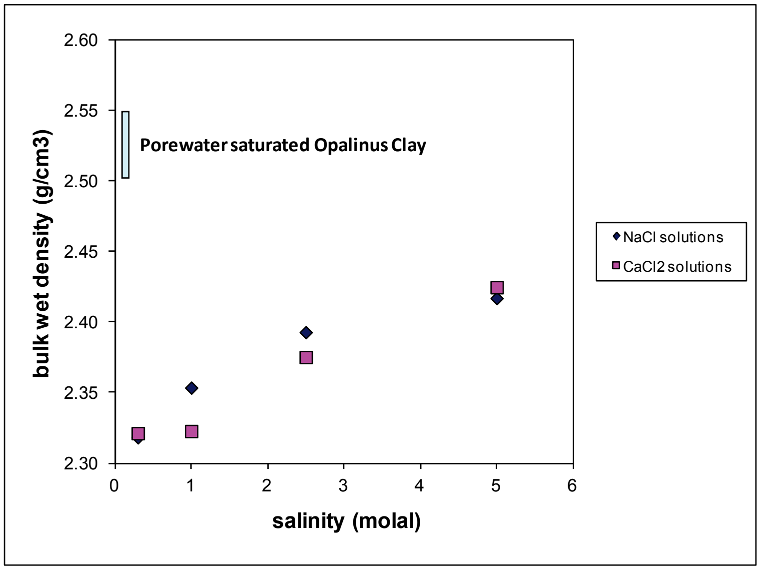


Figure 41: Bulk Wet Density of Opalinus Clay After Equilibration with Saline NaCl and $CaCl_2$ Solutions; the Range of Bulk Wet Density and Salinity of the Original Porewater-Saturated Opalinus Clay is Higher (blue box)

6.3 SCOPING CALCULATIONS

As a first step in developing a pre-conditioning procedure, scoping calculations were conducted to investigate two different experimental techniques for replacing in-situ porewater in rock materials with a synthetic porewater of known composition. The time required to replace in-situ porewater in saturated, intact rock samples using the in/out diffusion technique and the advective displacement technique was estimated. Scoping calculations were conducted for three different formations relevant to the Canadian and Swiss nuclear waste management programs:

- Queenston Formation from southwestern Ontario, Canada;
- Cobourg Formation from southwestern Ontario, Canada; and
- Opalinus Clay Formation, Switzerland.

The tracers considered in the scoping calculations include chloride (Cl^-) and stable water isotopes (δ^2H, $\delta^{18}O$).

The details of the considered parameters and scoping calculation results are given in Appendix B. The scoping calculations reveal that replacement of the porewater by advective displacement is not practical for rocks with a very low hydraulic conductivity (ca. 10^{-14} m/s), such as those from the three formations examined here, as it would take far too much time (minimum of 8 months to displace one pore volume within a core piece of 20 cm length). In/out diffusion is faster and has, therefore, been used to equilibrate rock materials (Queenston Formation and Opalinus Clay) with synthetic porewater. Scoping calculations (Appendix B) showed that in/out diffusion equilibration times for intact 20 cm long core pieces of Queenston Formation are ~60 days for water isotope composition and ~130 days for chloride content. In the case of the Opalinus Clay, these numbers are respectively ~15 days and ~44 days. Equilibrating the chloride content is important to avoid non-homogeneous salt-related fractionation effects. To decrease the time required for full chemical and isotopic equilibration, smaller rock pieces (2-4 cm size) have been used rather than intact core, as originally considered in the scoping calculations.

6.4 STANDARD SOLUTIONS

Standard solutions used in the experiments include LAB (tap water from the University of Bern), TEW (light water prepared with melted Greenland ice) and Vittel mineral water (French mineral water having relatively high $\delta^{18}O$ and δ^2H). The Vittel mineral water was used to prepare the synthetic solutions equilibrated with the saturated rock (Opalinus Clay and Queenston Shale). The isotopic composition of this mineral water was analysed for 4 aliquots, and the average value is used in the calculations. The LAB and TEW standard waters were used to prepare the test solutions for the diffusive exchange experiments. Their isotopic compositions (average from 5 or 10 measurements) are presented in Table 14, together with the values for Vittel water. The exact salinities of the synthetic solutions used in the experiments are given in Table 15.

Table 14: Isotopic Composition of the Standard Waters

Standard Water	$\delta^{18}O$ (‰ V-SMOW)	2σ error (‰ V-SMOW)	$\delta^{2}H$ (‰ V-SMOW)	2σ error (‰ V-SMOW)	N
LAB (aver. value[1])	-11.00	0.13	-77.07	0.89	5
TEW (aver. value[1])	-27.09	0.095	-208.68	0.63	10
Vittel water					
ND20VIT	-8.6	0.3	-55.4	1.4	
ND23VIT	-8.6	0.3	-55.4	1.4	
ND22VIT	-8.6	0.3	-55.6	1.4	
ND23VIT	-8.5	0.3	-55.8	1.4	
VITTEL (aver. value)	-8.57	0.15	-55.56	0.70	4

[1] LAB and TEW average values are from Table 3

Table 15: Standard Solutions Used in the Experiments

Standard Water	Expt.[1]	NaCl Standard Solutions			$CaCl_2$ Standard Solutions		
		NaCl salinity (molal)	Solution (g)	H_2O in solution (g)	$CaCl_2$ salinity (molal)	Solution (g)	H_2O in solution (g)
LAB	OPA/CAN	0.301	12.226	12.015	2.509	15.251	11.929
LAB	OPA/CAN	5.017	141.782	109.639	5.020	93.085	59.779
TEW1	OPA/CAN	0.300	12.235	12.024	2.516	15.273	11.939
TEW1	OPA/CAN	5.014	141.848	109.705	5.032	92.810	59.551
VITTEL	OPA	0.299	1525.4	1499.2	2.499	1919.8	1503.0
VITTEL	OPA	4.980	1944.6	1506.2	4.991	2333.9	1501.9
VITTEL	CAN	0.298	1530.0	1503.8	2.495	1921.9	1505.1
VITTEL	CAN	4.995	1939.7	1501.4	5.002	2336.3	1502.3

[1] OPA = experiments with Opalinus Clay; CAN = experiments with Queenston shale.

6.5 EQUILIBRATION PROCEDURE

Protocol for equilibration of rock materials

- Four equilibration experiments were conducted on each rock material using four standard solutions: two using NaCl (0.3 or 5.0 molal) and two using $CaCl_2$ (2.5 or 5.0 molal).
- The four standard solutions were prepared using Vittel® mineral water. Vittel water is, isotopically, the heaviest mineral water available, and it was chosen as a standard because its isotopic composition is significantly different from the LAB and TEW standards (Table 14). For each standard solution (i.e., each salinity and salt type), two 1.5 L bottles of Vittel mineral water were mixed to homogenize the isotopic composition of the water. One 20 mL aliquot of each of these 3 L batches of mixed water was taken for stable isotope analysis (δ^2H, $\delta^{18}O$). Mineral water used in all experiments was bottled on the same date at the source, as indicated by the date on the bottles.
- Rock material was equilibrated with the four different solution compositions/salinities in 4 pairs of PVC containers with threaded PVC lids, sealed with an o-ring. The volume of each cell is approximately 150 cm^3. Each pair of cells included one cell with two sampling ports in the lid and one cell without sampling ports; one pair of cells was used for each standard solution.
- The cells and all equipment were pre-labeled and weighed prior to starting the equilibration experiments.

Preparation of core

- Rock core sealed in aluminum with PE liner was opened and 5 cm^3 rock pieces were broken off using a hammer.
- Two or three small pieces (between 10 and 37 g) were taken for bulk wet density and measured immediately.
- Two aliquots of rock material (90 to 300 g) for gravimetric water content measurements were placed in pre-labeled, pre-weighed glass dishes, and the weight of the dishes plus wet rock were recorded immediately; later they were placed in oven at 105°C for drying. To improve the drying of $CaCl_2$-saturated samples, drying at 150°C was performed subsequently on most series.

6.6 SAMPLING PROCEDURE

6.6.1 Monitoring Equilibration: Time-Series Sub-Sampling

For each salt and salinity, one of the two containers was equipped with a sampling port. Sampling of 0.5 mL was performed using a syringe at increasing time intervals. After connection to the sampling port, the syringe was slowly filled and emptied three times (solution goes in and out of the cell) to ensure that the sample taken is representative of the solution in the cell, and not simply the solution that is present in the capillary tube. The 0.5 mL samples were filtered and stored in sealed 1 mL bottles for further chemical analysis.

6.6.2 Sampling Protocol for Equilibrated Rock Materials

Procedure

- Weight of entire cell was recorded.
- Cell was opened and the solution was decanted into a pre-labelled bottle.
- The solid material was quickly transferred from the cell onto layers of paper toweling and spread out; free solution on the surfaces of the rock material was removed by gently patting the surfaces dry using fresh paper towelling (latex gloves were worn at all times while handling samples).
- A small aliquot of the solid was broken into smaller pieces for measurement of water activity, which was measured using the AwQuick mode on the activity meter.
- Approximately 100 grams of the rock material were then placed in each of two pre-labelled, pre-weighed glass jars for the diffusive exchange experiments.
- Separate aliquots (between 95 and 150 g) were taken for gravimetric water content and placed in pre-weighed, pre-labelled glass dishes, and the weight of the dish and rock material was recorded.
- An additional aliquot (between 110 and 200 g) was taken for aqueous extraction. This solid was placed in a container and immediately placed into a desiccator, which was sealed under a light vacuum. The desiccator was then transferred into a glove box (N_2 atmosphere) and a dish with phosphorus pentoxide was placed in the bottom of the dessicator to dry the samples. The desiccant was replaced at intervals until the rock samples were dry (usually 6 to 8 weeks).
- Two pieces of rock with masses of between 12 and 25 g were taken for bulk wet density measurements immediately.

Solutions

- Immediately after sampling was complete, water activity was measured for aliquots of the unfiltered, decanted solution.
- Aliquots of the unfiltered solutions were weighed into pre-labelled, pre-weighed 15 mL bottles for stable isotopic (δ^2H, $\delta^{18}O$) analyses. For NaCl solutions, where no NaF addition was required, the 15 mL bottles were filled. For $CaCl_2$ solutions, only ~10 mL of solution was added, to allow sufficient volume for NaF addition.
- Separate aliquots were taken for cation and anion analyses, which were filtered through 0.45 µm syringe filters into pre-labelled bottles. An additional aliquot was taken as a reserve sample (in case the analyses needed to be performed again).
- Aliquots for cation analyses were acidified by adding several drops (2 to 5) of 1:1 HNO_3.

6.7 OPALINUS CLAY RESULTS

6.7.1 Physical and Mineralogical Properties Before and After Equilibration

6.7.1.1 Bulk Density

The bulk wet density of one intact porewater-saturated Opalinus Clay rock sample is given in Table 16, while bulk wet densities of the same rock equilibrated with synthetic solutions are given in Table 17. The data plotted in Figure 42 show that the bulk wet density of intact rock is higher than that of rock equilibrated with synthetic solutions, and that density increases with the salinity of the synthetic solution. Similar behaviour was observed in the rock mechanical stability experiments (Section 6.2).

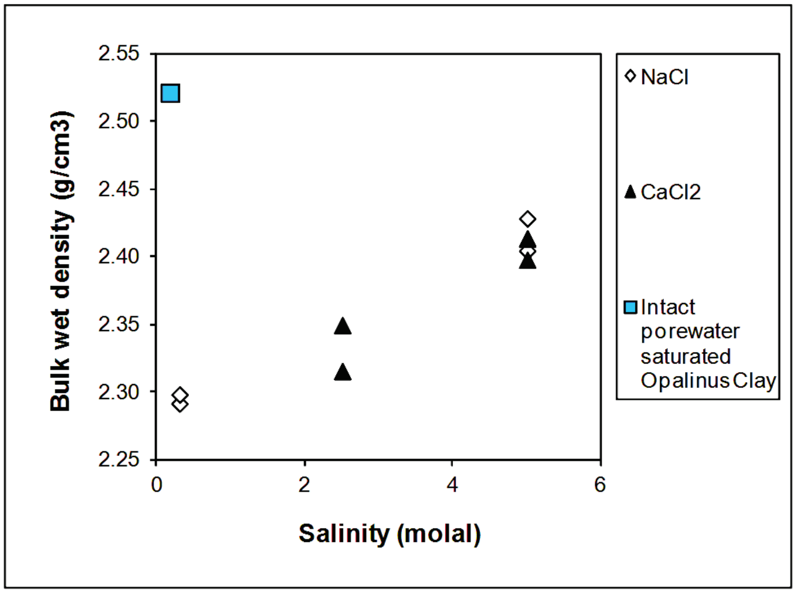


Figure 42: Bulk Wet Density of Opalinus Clay Rock Equilibrated with Synthetic Solutions of Various Salinities; Density and Porewater Salinity Values for Intact Porewater-Saturated Opalinus Clay are Shown for Comparison

6.7.1.2 Grain Density

Grain density of the Opalinus Clay equilibrated with synthetic saline solutions was measured for two replicate samples by kerosene pycnometry. Data are given in Table 18 and plotted in Figure 43. Although samples equilibrated with $CaCl_2$ solutions gave lower grain density than those equilibrated with NaCl solutions, all results overlap within 1σ error, which means there is no significant effect of the salinity and type of salt on the grain density measurement. The water content of samples dried in the N_2 glove box are smaller than those obtained by drying at 105°C and 150°C, which suggests drying was not complete in the glove box. This might affect the grain density value, because part of the measured weight corresponds to remnants of porewater resulting in a lower measured density. This effect might explain the lower measured densities of samples saturated with $CaCl_2$ solution, which are more difficult to dehydrate than those saturated with NaCl solution.

After drying, the rock material includes salts precipitated from the porewater, which might lower the measured density. However, Hobbs et al. (2011) showed that correction for the presence of salts would be negligible compared to the error in the measurement.

The average grain density of all measurements is 2.821 ± 0.032 (g/cm^3), 2σ error. However, considering the problems discussed above, the obtained grain density values are to be considered of poor reliability.

Table 16: Bulk Wet Density of Porewater-Saturated Opalinus Clay before Equilibration with Synthetic Solution

Sample ID	Density of Paraffin (g/cm^3)	Replicate A			Replicate B			Replicate C			Average Calculated Bulk density (g/cm^3)
		Wt. of rock in air (g)	Wt. of rock in paraffin (g)	Calculated Bulk density (g/cm^3)	Wt. of rock in air (g)	Wt. of rock in paraffin (g)	Calculated Bulk density (g/cm^3)	Wt. of rock in air (g)	Wt. of rock in paraffin (g)	Calculated Bulk density (g/cm^3)	
OPA DR-17 (9.35-9.50)	0.86	23.3246	15.4508	2.55	24.1764	15.8986	2.5117	37.7131	24.7582	2.5036	2.52

Table 17: Bulk Wet Density of Opalinus Clay Samples after Equilibration with Synthetic Solutions

Expt.	Solution salinity	Type	PWC container ID	Density of Paraffin (g/cm^3)	Replicate A			Replicate B			Average Calculated Bulk density (g/cm^3)
					Wt. of rock in air (g)	Wt. of rock in paraffin (g)	Calculated Bulk density (g/cm^3)	Wt. of rock in air (g)	Wt. of rock in paraffin (g)	Calculated Bulk density (g/cm^3)	
40	0.3	NaCl	OPA1	0.861	12.3815	7.6700	2.263	14.6248	9.1980	2.320	2.29
41	0.3	NaCl	OPA1A	0.861	22.9547	14.3568	2.299	19.1437	11.9699	2.298	2.30
42	5	NaCl	OPA2	0.861	14.6315	9.5042	2.457	20.6635	13.2488	2.399	2.43
43	5	NaCl	OPA2A	0.861	19.2232	12.2817	2.384	13.2675	8.5557	2.424	2.40
44	2.5	$CaCl_2$	OPA3	0.861	22.0510	14.0672	2.378	15.7545	9.9096	2.321	2.35
45	2.5	$CaCl_2$	OPA3A	0.861	12.5195	7.8262	2.297	25.4238	16.0456	2.334	2.32
46	5	$CaCl_2$	OPA4	0.861	16.1152	10.3791	2.419	23.7647	15.2672	2.408	2.41
47	5	$CaCl_2$	OPA4A	0.861	16.5982	10.6446	2.400	19.2846	12.3514	2.395	2.40

Table 18: Grain Density of Opalinus Clay Samples after Equilibration with Synthetic Solutions

Sample ID	Type of solution	Average of replicates (g/cm^3)	STD (n=2) (g/cm^3)
S40VIT	0.3m NaCl	2.820	0.029
S41VIT	0.3m NaCl	2.794	0.048
S42VIT	5m NaCl	2.821	0.002
S43VIT	5m NaCl	2.849	0.030
S44VIT	2.5m $CaCl_2$	2.752	0.043
S45VIT	2.5m $CaCl_2$	2.767	0.026
S46VIT	5m $CaCl_2$	2.760	0.069
S47VIT	5m $CaCl_2$	2.768	0.043

Note: All samples were dried in N_2 glove box before milling and measurement.

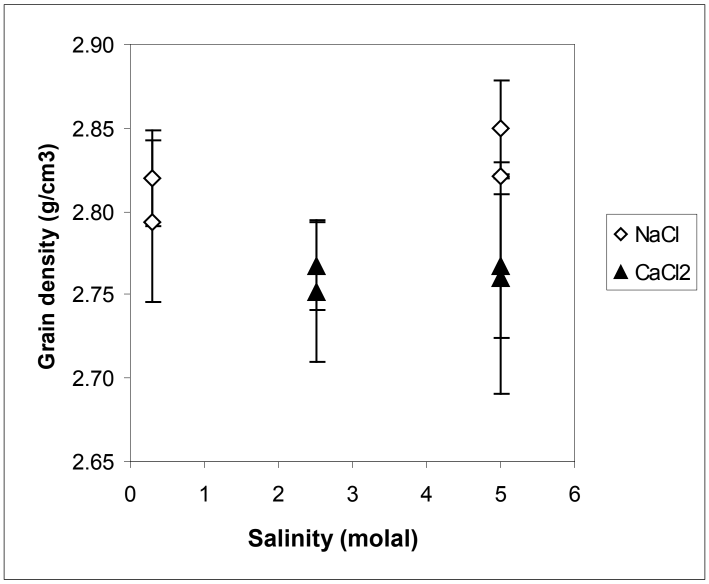


Figure 43: Plot of Grain Density of Equilibrated Opalinus Clay versus the Salinity of the Synthetic Saline Solution; Errors Bars are 1σ

6.7.1.3 Water Content

Water content (WC) was measured by drying the rock samples at 105°C until the samples reach constant weight. The minimum weight reached has been used to calculate the WC. Water content data for intact Opalinus Clay (OPA) rocks, and of samples equilibrated with synthetic solutions, are presented in Table 19 and plotted in Figure 44. The WC corresponds to the pure water contained in the porewater, which does not account for the mass of dissolved salts.

The WC of OPA rock samples, after isotope diffusive exchange experiments, are given in Table 20 and plotted in Figure 45. Drying was performed first at 105°C, and then at 150°C, in order to dry the $CaCl_2$-saturated samples more completely ($CaCl_2$ is likely not completely dry at 105°C, and may not be completely dehydrated at 150°C).

Figures 44 and 45 show that the WC of rock samples equilibrated with synthetic solutions is similar before and after isotope diffusive exchange experiments. As expected, samples equilibrated with $CaCl_2$ solutions are more thoroughly dried at 150°C than at 105°C, and the WC obtained at 150°C is therefore slightly higher than at 105°C, with a difference of <10% of the WC at 105°C.

There is a clear, inverse correlation between the salinity of the solution and the WC, which is apparently not related to the chlorinity, but instead is related to the molality of the cations (Ca^{+2} or Na^{+}). The WC of equilibrated samples is higher than that of the intact OPA rock, especially at low salinity. This is probably related to the stress release at atmospheric pressure compared to in-situ pressure conditions, which allows greater swelling of the clays.

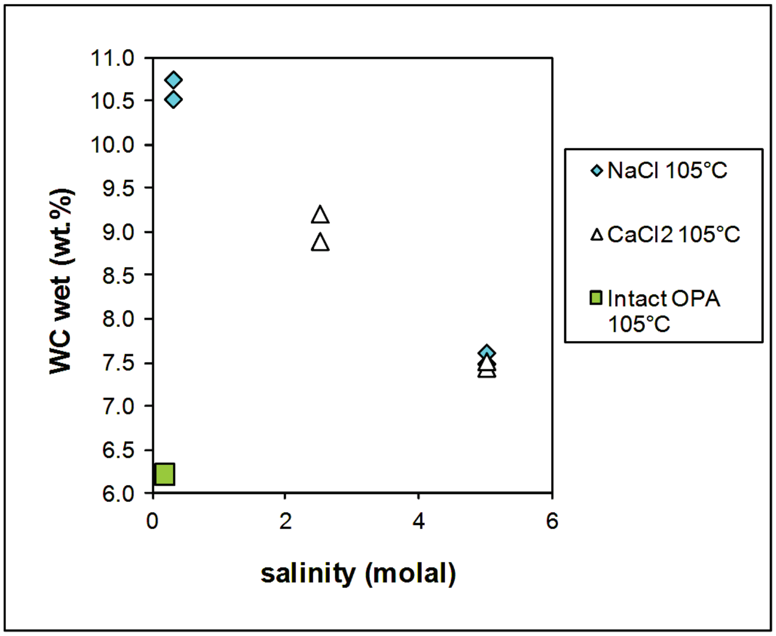


Figure 44: Wet Water Content (WC) of Intact Porewater-saturated Opalinus Clay (OPA), and Following Equilibration with Synthetic Solutions of Various Salinity and Salt Type; Water Contents were Obtained by Drying at 105°C

Table 19: Water Content of Opalinus Clay Before and After Equilibration with Saline Solutions

Expt. #	Sample ID	Type of synthetic solution	Water content from lowest mass when drying at 105°C*	
			$WC_{grav.}$ wet (wt%)	$WC_{grav.}$ dry (wt%)
Original water content of OPA rock used in experiments				
	OPA-1A	None	6.24	6.66
	OPA-1B	None	6.20	6.61
	Average	*None*	*6.22*	*6.63*
Water content of OPA rock equilibrated with synthetic Vittel solutions				
40	S40VIT-A	0.3m NaCl	10.63	11.90
40	S40VIT-B	0.3m NaCl	10.41	11.62
40	*Average*	*0.3m NaCl*	*10.52*	*11.76*
41	S41VIT-A	0.3m NaCl	10.78	12.09
41	S41VIT-B	0.3m NaCl	10.70	11.99
41	*Average*	*0.3m NaCl*	*10.74*	*12.04*
42	S42VIT-A	5m NaCl	7.52	8.13
42	S42VIT-B	5m NaCl	7.46	8.06
42	*Average*	*5m NaCl*	*7.49*	*8.09*
43	S43VIT-A	5m NaCl	7.60	8.23
43	S43VIT-B	5m NaCl	7.62	8.25
43	*Average*	*5m NaCl*	*7.61*	*8.24*
44	S44VIT-A	2.5m $CaCl_2$	8.82	9.67
44	S44VIT-B	2.5m $CaCl_2$	8.96	9.85
44	*Average*	*2.5m* $CaCl_2$	*8.89*	*9.76*
45	S45VIT-A	2.5m $CaCl_2$	9.09	10.00
45	S45VIT-B	2.5m $CaCl_2$	9.32	10.28
45	*Average*	*2.5m* $CaCl_2$	*9.21*	*10.14*
46	S46VIT-A	5m $CaCl_2$	7.33	7.91
46	S46VIT-B	5m $CaCl_2$	7.55	8.16
46	*Average*	*5m* $CaCl_2$	*7.44*	*8.04*
47	S47VIT-A	5m $CaCl_2$	7.52	8.13
47	S47VIT-B	5m $CaCl_2$	7.51	8.12
47	*Average*	*5m* $CaCl_2$	*7.52*	*8.13*

Table 20: Water Content of OPA Rock Samples After Isotope Diffusive Exchange Experiments

Exper. #	Sample ID	Type of synthetic solution	Water content from lowest mass when drying at 105°C		Water content from lowest mass when drying at 150°C	
			$WC_{grav.}$ Wet (wt%)	$WC_{grav.}$ dry (wt%)	$WC_{grav.}$ wet (wt%)	$WC_{grav.}$ dry (wt%)
40	OPA1LAB	0.3m NaCl	10.43	11.64	10.44	11.65
40	OPA1TEW	0.3m NaCl	10.75	12.05	10.85	12.18
40	*Average*	0.3m NaCl	10.59	11.85	10.64	11.91
41	OPA1ALAB	0.3m NaCl	10.58	11.83	10.61	11.86
41	OPA1ATEW	0.3m NaCl	10.32	11.51	10.39	11.59
41	*Average*	0.3m NaCl	10.45	11.67	10.50	11.73
42	OPA2LAB	5m NaCl	7.37	7.95	7.68	8.31
42	OPA2TEW	5m NaCl	7.50	8.11	7.83	8.49
42	*Average*	5m NaCl	7.43	8.03	7.75	8.40
43	OPA2ALAB	5m NaCl	7.38	7.97	7.71	8.35
43	OPA2ATEW	5m NaCl	7.11	7.65	7.40	7.99
43	*Average*	5m NaCl	7.25	7.81	7.56	8.17
44	OPA3LAB	2.5m $CaCl_2$	8.49	9.27	8.72	9.56
44	OPA3TEW	2.5m $CaCl_2$	8.45	9.23	8.82	9.67
44	*Average*	2.5m $CaCl_2$	8.47	9.25	8.77	9.61
45	OPA3ALAB	2.5m $CaCl_2$	8.62	9.44	9.02	9.92
45	OPA3ATEW	2.5m $CaCl_2$	8.74	9.58	9.10	10.01
45	*Average*	2.5m $CaCl_2$	8.68	9.51	9.06	9.97
46	OPA4LAB	5m $CaCl_2$	7.12	7.67	7.53	8.15
46	OPA4TEW	5m $CaCl_2$	7.03	7.56	7.45	8.05
46	*Average*	5m $CaCl_2$	7.08	7.61	7.49	8.10
47	OPA4ALAB	5m $CaCl_2$	7.03	7.56	7.49	8.10
47	OPA4ATEW	5m $CaCl_2$	7.01	7.54	7.47	8.07
47	*Average*	5m $CaCl_2$	7.02	7.55	7.48	8.09

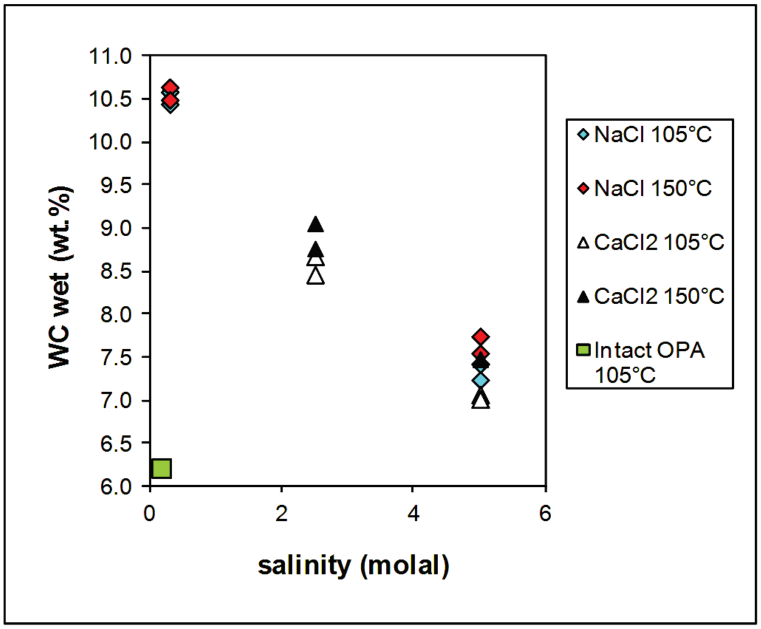


Figure 45: Wet Water Content (WC) of OPA Rock Determined After Isotope Diffusive Exchange Experiments with Rock Saturated with Synthetic Porewater of Various Salinity and Salt Type; Water Contents were Obtained by Drying at 105 and 150°C; Values for Intact Porewater-saturated Opalinus Clay are Shown for Comparison

6.7.1.4 Mineralogy

The mineralogical compositions (whole rock X-ray diffraction) of the Opalinus Clay rock samples before and after equilibration with Vittel synthetic standard solutions are given in Table 21. Equilibration with saline solutions did not induce measurable mineralogical changes within the analytical uncertainty of the method employed, and the observed variations are interpreted to reflect small-scale variability in the formation.

Table 21: Mineralogical Composition of OPA Samples Before and After Equilibration with Vittel Standard Solutions

Sample	Note	C_{inorg} wt%	C_{org} wt%	S wt%	Calcite wt%	Dolomite wt%	Quartz wt%	K-feldspar wt%	Plagioclase wt%	Total sheet sil. wt%	Additional phases
DR-17 (9.35-9.50)	Intact saturated core	2.2	0.2	0.1	18.3	0.0	17.3	2.4	0.0	62.1	illite, siderite, clinochlore
S40VIT-A	Equil. at 0.3m NaCl	1.9	0.1	0.5	15.1	0.6	19.9	2.7	1.9	59.8	illite, clinochlore, pyrite
S41VIT-A	Equil. at 0.3m NaCl	1.7	0.2	0.1	13.9	0.2	19.8	2.1	0.3	63.8	pyrite, clinochlore, muscovite
S42VIT-A	Equil.at 5m NaCl	2.2	0.2	0.1	18.3	0.0	17.7	2.1	0.1	62.0	clinochlore, siderite, illite
S43VIT-A	Equil.at 5m NaCl	1.8	0.3	0.1	14.9	0.0	18.4	2.7	1.0	63.1	illite, clinochlore, siderite
S44VIT-A	Equil.at 2.5m $CaCl_2$	2.2	0.2	0.3	18.3	0.0	15.0	1.8	0.0	65.0	siderite, clinochlore
S45VIT-A	Equil.at 2.5m $CaCl_2$	1.6	0.3	0.2	12.7	0.6	16.1	3.0	1.3	66.4	ankerite, clinochlore, illite
S46VIT-A	Equil. at 5m $CaCl_2$	2.1	0.2	0.1	17.4	0.0	16.3	15.3	0.8	50.3	siderite, illite, clinochlore
S47VIT-A	Equil. at 5m $CaCl_2$	2.3	<0.1	0.1	19.1	0.0	13.3	2.0	1.3	64.4	siderite, illite, clinochlore

Note: Total sheet silicate content is obtained by difference with the total of calcite, dolomite, quartz, K-feldspar, and plagioclase. Additional phases are not quantified and the list might not be exhaustive. Clay mineralogy of the Opalinus Clay is known to include kaolinite, illite, illite/smectite mixed layers, and chlorite (Pearson et al., 2003).

6.7.2 Time-Series and Final Chemical Composition of Equilibrated Solution

The initial experiment conditions for equilibration of Opalinus Clay rock samples with synthetic Vittel saline solutions are given in Table 22. The rock/solution weight ratio was between 1.39 and 1.72. The amount of solution used in each experiment was determined by the amount necessary to cover all of the rock material.

Table 22: Equilibration of Opalinus Clay Samples: Initial Conditions (October 10, 2010)

Cell No	Wt of cell, lid & all fittings (& sticks) (g)	Wt of rock added (g)	Wt of cell & rock material (g)	Type of solution added	Start time (solution added) (h:m)	Wt of solution added (g)	Total wt of cell & contents at start of experiment (g)
OPA1	446.2	648	1094.2	0.3m NaCl	19:12	373.5	1467.7
OPA1A	430.8	654.1	1084.9	0.3m NaCl	19:17	381.0	1465.9
OPA2	448.5	672.6	1121.1	5m NaCl	19:22	427.8	1548.9
OPA2A	431.3	674.8	1106.1	5m NaCl	19:27	432.2	1538.3
OPA3	447.6	666.8	1114.4	2.5m $CaCl_2$	19:31	447.0	1561.4
OPA3A	430.3	707.5	1137.8	2.5m $CaCl_2$	19:36	429.1	1566.9
OPA4	445.8	698.9	1144.7	5m $CaCl_2$	19:40	501.1	1645.8
OPA4A	427.2	712.8	1140	5m $CaCl_2$	19:44	483	1623

A time-series of small aliquots (0.5 mL) of the standard solution were sampled to monitor the equilibration process. Sampling was done on containers OPA2 (5 m NaCl) and OPA3 (2.5 m $CaCl_2$). The porewater salinity (Cl^-) of saturated Opalinus Clay is around 0.17 molal (Pearson and Waber, 2006) and, therefore, significantly lower than the sampled standard solutions. Time-series samples were analyzed for anions (F^-, Cl^-, Br^-, SO_4^{-2}, NO_3^-). The results are given in Table 23, and plotted in Figures 46 and 47. The last sample, after 1502.3 hours of equilibration (= 62.6 days), corresponds to the end of the equilibration experiment and the start of the isotope diffusive exchange experiment. The chemical compositions of the equilibrated solutions are given in Table 24.

Figures 46 and 47 indicate that the equilibration time for chloride is fast – i.e., on the order of 24 hours. The composition is then maintained at a stable concentration until the end of the equilibration experiment. As shown in Figures 46 and 47, all data are within 2σ error and, therefore, the time-series evolution might not be significant. However, the time-series follow very consistent curves in both figures, suggesting that the errors are largely overestimated. This outcome implies that the data can be used to evaluate the equilibration time.

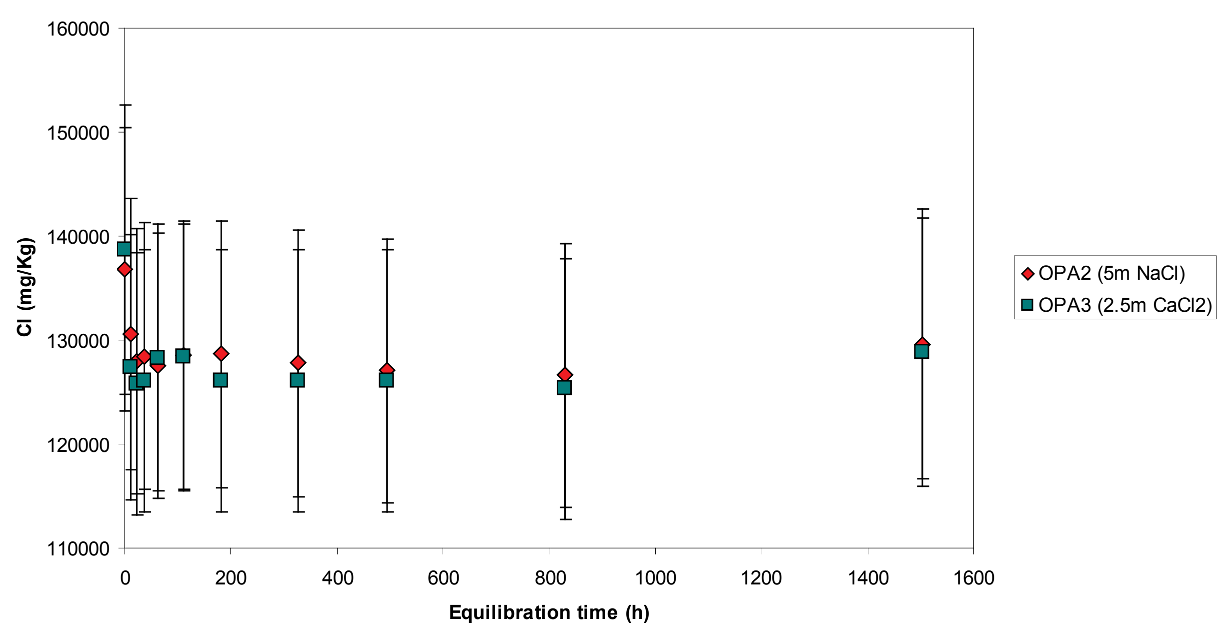


Figure 46: Time-Series Evolution of the Cl Content of Standard Solutions Equilibrating with Opalinus Clay; Error Bars are 10% (2σ) of the Value

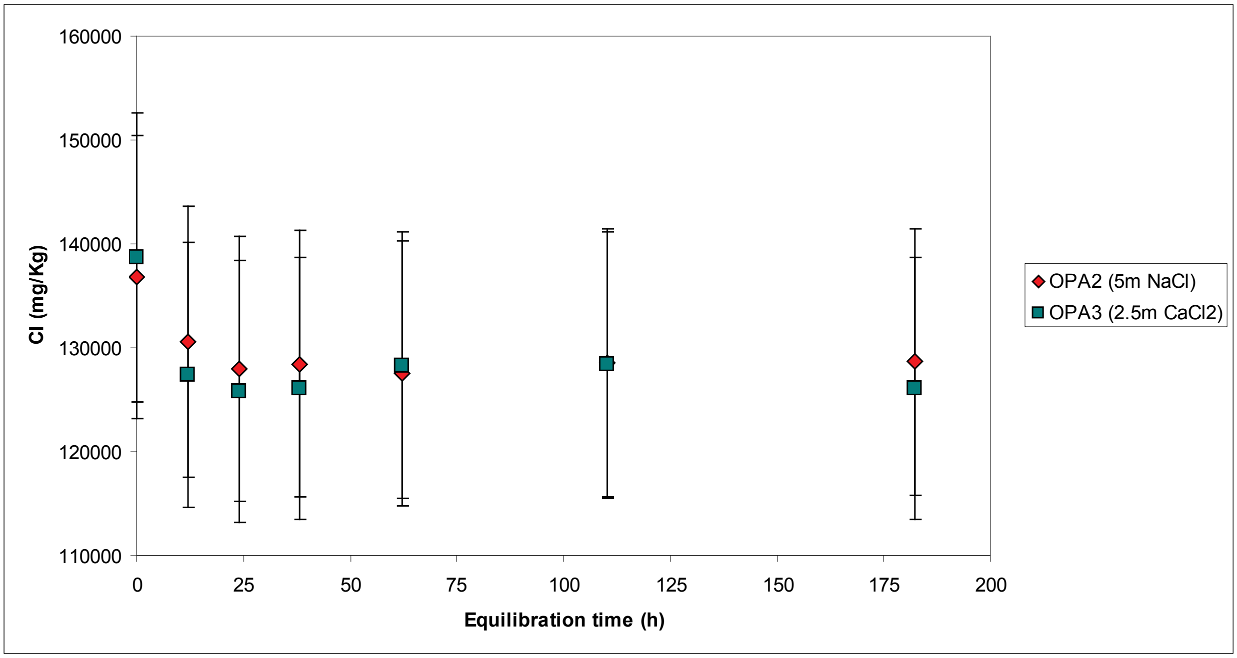


Figure 47: First 200 Hours of the Equilibration Experiments Shown in Figure 46; Error Bars are 10% (2σ) of the Value

Table 23: Time-Series Evolution of the Standard Solutions During Equilibration with Opalinus Clay

Container OPA2 filled with 5m NaCl	OPA2-0	OPA2-1	OPA2-2	OPA2-3	OPA2-4	OPA2-5	OPA2-6	OPA2-7	OPA2-8	OPA2-9	OPA2-equil. (S42VIT)
Elapsed time (h)	0	12.0	24.0	38.3	62.3	110.3	182.3	326.3	494.3	830.3	1502.3
Anions (mg/kg)											
Fluoride (F$^-$)		<5	<5	<5	<5	<5	<5	<5	<5	<5	<50
Chloride (Cl$^-$)	136800	130629	127971	128440	127529	128579	128632	127766	127051	126617	129601
Bromide (Br$^-$)		<5	<5	<5	<5	<5	<5	<5	<5	<5	<50
Sulfate (SO$_4^{2-}$)		*4169*	*4213*	*4140*	*4344*	*4297*	*4220*	*4152*	*4156*	*4358*	307
Nitrate (NO$_3^-$)		<5	<5	<5	<5	<5	<5	<5	<5	<5	<50
Container OPA3 filled with 2.5m CaCl$_2$	OPA3-0	OPA3-1	OPA3-2	OPA3-3	OPA3-4	OPA3-5	OPA3-6	OPA3-7	OPA3-8	OPA3-9	OPA3-equil. (S44VIT)
Elapsed Time (h)	0	12.0	24.0	38.3	62.3	110.3	182.3	326.3	494.3	830.3	1502.3
Anions (mg/kg)											
Fluoride (F$^-$)		<5	<5	<5	<5	<5	<5	<5	<5	<5	<50
Chloride (Cl$^-$)	138700	127406	125788	126101	128280	128349	126056	126139	126144	125356	128849
Bromide (Br$^-$)		<5	<5	<5	<5	<5	<5	<5	<5	<5	<50
Sulfate (SO$_4^{2-}$)		*4006*	*4116*	*4274*	*4069*	*4099*	*4068*	*4294*	*4403*	*4245*	235
Nitrate (NO$_3^-$)		<5	<5	<5	<5	<5	<5	<5	<5	<5	<50

Notes: numbers in *Italics* are semi-quantitative; measured values at these dilutions are below the lowest standard. Chlorine content of the initial step (t=0) is that of the synthetic solution, obtained by weighing of the respective components (see Table 15).

Table 24: Chemical Composition of Standard Solutions Equilibrated with Opalinus Clay

Sample	S40VIT	S41VIT	S42VIT	S43VIT	S44VIT	S45VIT	S46VIT	S47VIT
Type of standard solution	0.3m NaCl	0.3m NaCl	5m NaCl	5m NaCl	2.5m CaCl$_2$	2.5m CaCl$_2$	5m CaCl$_2$	5m CaCl$_2$
pH (lab)	6.95	6.95	6.25	6.25	5.17	5.16	4.36	4.38
pH at start of titration	7.04	6.96	6.24	6.24	5.16	5.19	4.45	4.47
Alkalinity (m)	7.41	7.48	4.68	4.53	2.19	1.98	0.49	0.44
water activity of equil. Sol. (measured)	1.000	1.000	0.831	0.845	0.856	0.857	0.590	0.597
CATIONS								
Sodium (Na$^+$) (mg/kg)	6153	6034	81299	82551	1420	1709	1313	1503
Potassium (K$^+$) (mg/kg)	86	80	337	326	211	230	234	232
Magnesium (Mg^{+2}) (mg/kg)	209.0	200.0	473	463	662	717	635	659.0
Calcium (Ca^{+2}) (mg/kg)	415.7	452.2	1166	823.9	70840	67737	118480	122700
Strontium (Sr^{+2}) (mg/kg)	43.3	42.6	118.0	118.0	152.0	169.0	162.0	167.0
ANIONS								
Fluoride (F$^-$) (mg/kg)	<50	<50	<50	<50	<50	<50	<50	<50
Chloride (Cl$^-$) (mg/kg)	10367	10169	129601	129792	128849	126861	212459	209119
Bromide (Br$^-$) (mg/kg)	<50	<50	<50	<50	<50	<50	<50	*147*
Sulfate (SO$_4^{-2}$) (mg/kg)	478.2	374.5	*307*	*292*	*235*	*276*	<50	<50
Nitrate (NO$_3^-$) (mg/kg)	<50	<50	<50	<50	<50	<50	<50	<50
Total Alkalinity (meq/L)	7.41	7.48	4.68	4.53	2.19	1.98	0.49	0.44
Total Alkalinity as HCO$_3$ (mg/kg)	452.1	456.4	285.6	276.4	133.6	120.8	29.9	26.8
CATIONS								
Sodium (Na$^+$) (molal)	2.726E-01	2.672E-01	4.496E+00	4.570E+00	7.744E-02	9.264E-02	8.561E-02	9.820E-02
Potassium (K$^+$) (molal)	2.230E-03	2.081E-03	1.096E-02	1.061E-02	6.765E-03	7.330E-03	8.973E-03	8.913E-03
Magnesium (Mg^{+2}) (molal)	8.758E-03	8.378E-03	2.474E-02	2.425E-02	3.415E-02	3.676E-02	3.917E-02	4.072E-02
Calcium (Ca^{+2}) (molal)	1.056E-02	1.149E-02	3.698E-02	2.617E-02	2.216E+00	2.106E+00	4.432E+00	4.598E+00
Strontium (Sr^{+2}) (molal)	5.033E-04	4.950E-04	1.712E-03	1.714E-03	2.175E-03	2.403E-03	2.772E-03	2.863E-03
ANIONS								
Fluoride (F$^-$) (molal)								
Chloride (Cl$^-$) (molal)	2.978E-01	2.920E-01	4.648E+00	4.660E+00	4.556E+00	4.459E+00	8.985E+00	8.859E+00
Bromide (Br$^-$) (molal)								2.756E-03
Sulfate (SO$_4^{-2}$) (molal)	5.070E-03	3.969E-03	4.058E-03	3.864E-03	3.063E-03	3.581E-03		
Nitrate (NO$_3^-$) (molal)								
Total Alkalinity as HCO$_3$ (molal)	7.547E-03	7.615E-03	5.950E-03	5.766E-03	2.745E-03	2.467E-03	7.347E-04	6.609E-04
Sum of analyzed constituents (mg/kg)	18129	17788	213459	214357	202327	197502	333017	334222
Amount of solvant/liter (kg)	0.982	0.982	0.787	0.786	0.798	0.802	0.667	0.666

Sample	S40VIT	S41VIT	S42VIT	S43VIT	S44VIT	S45VIT	S46VIT	S47VIT
Density (GWB Pitzer) (g/cm^3)	1.021	1.021	1.103	1.104	1.104	1.1	1.175	1.183
Charge Balance								
Sum Cations (meq/L)	3.067E+02	3.062E+02	3.653E+03	3.682E+03	3.658E+03	3.520E+03	6.028E+03	6.248E+03
Sum Anions (meq/L)	-3.098E+02	-3.021E+02	-3.667E+03	-3.672E+03	-3.641E+03	-3.586E+03	-5.993E+03	-5.901E+03
Difference/Total (%)	-0.50%	0.67%	-0.18%	0.14%	0.23%	-0.93%	0.29%	2.86%

Note: highlighted data were obtained by ICP, all others by IC. Values in italics are semi-quantitative, just below calibration range in most concentrated solution measured.

6.7.3 Aqueous Leach Data and Chloride-Accessible Porosity

Aqueous leaching was performed at a solid/liquid mass ratio of 1 on aliquots of equilibrated Opalinus Clay dried in an oxygen-free glove box. The chemical compositions of the aqueous extracts are given in Table 25.

The porewater chloride concentration was calculated by up-scaling the aqueous extract concentration, considering the water content obtained by drying the rock samples in the glove box (N_2 atmosphere + desiccant for 49 days) and in an oven at 105°C. Drying would have been more complete at 150°C and would have given higher water contents, especially for samples equilibrated with $CaCl_2$ solutions. Drying at this higher temperature was not performed for the equilibrated Opalinus Clay samples, but was performed on samples of the Queenston Shale (see Section 6.8). Underestimating the water content implies that the up-scaled porewater chloride concentration is overestimated. The up-scaling formula is:

$$Cl_{PW} = 100*Cl_{Aq} / WC_{dry} \qquad (16)$$

where Cl_{PW} is the chloride concentration in the porewater and Cl_{Aq} is the chloride concentration in the aqueous extract at a solid/liquid ratio of 1.

The ratio of the chloride-accessible and the water-loss porosities can be estimated by comparison of the calculated porewater chloride concentration (which corresponds to the sum of the concentrations of the chloride-accessible and chloride-free volumes) with the measured concentration in the equilibrated solution. Knowing that the chloride-accessible pores have the same salinity as the equilibrated solution, the fraction of chloride-accessible porosity relative to total porosity is as follows:

$$\text{Cl-accessible porosity [\% of total porosity]} = 100*Cl_{PW} / Cl_{sol} \qquad (17)$$

where Cl_{PW} is the calculated chloride concentration in the porewater (up-scaled to water-loss porosity) and Cl_{sol} is the chloride concentration in the equilibrated standard solution. Calculated Cl-accessible porosity fractions are given in Table 25. Values for samples equilibrated with $CaCl_2$ solutions are near or even above 100%. It is impossible to have more than 100% Cl-accessible porosity and the most probable explanation is that the drying at 105°C is not complete for $CaCl_2$-saturated samples, which implies an underestimation of the WC_{dry} and, by consequence, an overestimation of the porewater salinity.

Results show that near 80% of the porewater volume is Cl-accessible at 0.3 m NaCl solution, and 100% of it at 5 m NaCl solution. The percentages of Cl-accessible porosity for $CaCl_2$ saturated samples are overestimated because there is evidence that drying is not complete at 105°C. This implies they are probably <95% for 2.5 m $CaCl_2$ and near 100% for 5 m $CaCl_2$.

Table 25: Opalinus Clay: Aqueous Extract Data, Calculated Porewater Cl-Content and Chloride-Accessible Porosity Ratio

Sample	S40VITa-aq	S40VITb-aq	S41VITa-aq	S41VITb-aq	S42VITa-aq	S42VITb-aq	S43VITa-aq	S43VITb-aq	S44VITa-aq	S44VITb-aq	S45VITa-aq	S45VITb-aq	S46VITa-aq	S46VITb-aq	S47VITa-aq	S47VITb-aq
Standard solution	0.3m NaCl	0.3m NaCl	0.3m NaCl	0.3m NaCl	5m NaCl	5m NaCl	5m NaCl	5m NaCl	2.5m CaCl2	2.5m CaCl2	2.5m CaCl2	2.5m CaCl2	5m CaCl2	5m CaCl2	5m CaCl2	5m CaCl2
Liquid/solid ratio (g/g)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
CATIONS																
Sodium (Na^+) (mg/L)	760.2	786.7	777.9	785.2	8277.5	7152.5	6650.6	6621.1	216.0	218.1	248.8	248.3	193.6	193.4	202.0	199.8
Potassium (K^+) (mg/L)	30.7	31.4	31.2	30.0	90.5	88.1	85.2	88.4	161.0	154.0	132.0	131.0	125.0	122.0	123.0	123.0
Magnesium (Mg^{+2}) (mg/L)	4.6	4.7	4.2	4.3	26.9	26.8	22.2	22.0	139.0	142.0	118.0	120.0	138.0	139.0	145.0	143.0
Calcium (Ca^{+2}) (mg/L)	19.8	19.8	16.0	20.9	61.4	62.5	54.1	55.2	6798.9	7013.7	7081.0	6974.7	11714.3	11460.3	11500.2	11597.2
Strontium (Sr^{+2}) (mg/L)	1.0	1.0	1.0	1.0	3.6	3.6	3.1	3.1	14.6	14.6	16.1	16.1	15.5	15.3	15.9	15.9
ANIONS																
Fluoride (F^-) (mg/L)	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Chloride (Cl^-) (mg/L)	941.3	969.1	970.6	981.3	10449.9	10509.7	9985.5	9943.4	12271.2	12447.2	12151.5	12178.8	20496.4	20209.8	20036.4	20224.7
Bromide (Br^-) (mg/L)	<5	<5	<5	<5	<5	<5	<5	<5	14.7	14.8	14.9	14.9	25.2	25.0	25.8	25.3
Sulfate (SO_4^{-2}) (mg/L)	206.1	212.5	183.5	187.3	95.1	94.1	83.2	83.6	66.0	66.6	97.9	98.6	113.5	113.3	96.2	96.4
Nitrate (NO_3^-) (mg/L)	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Total Alkalinity (meq/L)	4.24	4.28	4.03	4.04	5.73	5.75	5.52	5.59	1.65	1.68	1.14	1.19	1.71	1.75	1.82	1.74
Total Alkalinity as HCO_3 (mg/L)	258.7	261.2	245.9	246.5	349.6	350.8	336.8	341.1	100.7	102.5	69.6	72.6	104.3	106.8	111.1	106.2
PARAMETERS CALCULATED FROM ANALYTICAL DATA																
Sum of constituents (mg/L)	2228	2343	2235	2261	19352	18287	17220	17156	19674	20096	19854	19772	32850	32300	32096	32737
Charge Balance																
Sum Cations (meq/L)	3.534E+01	3.824E+01	3.591E+01	3.640E+01	3.677E+02	3.188E+02	2.961E+02	2.949E+02	3.562E+02	3.694E+02	3.718E+02	3.661E+02	6.023E+02	5.887E+02	5.858E+02	6.203E+02
Sum Anions (meq/L)	-3.525E+01	-3.620E+01	-3.539E+01	-3.579E+01	-3.027E+02	-3.044E+02	-2.891E+02	-2.879E+02	-3.495E+02	-3.543E+02	-3.462E+02	-3.470E+02	-5.827E+02	-5.747E+02	-5.695E+02	-5.747E+02
Difference/Total (%)	0.12%	2.73%	0.72%	0.85%	9.69%	2.31%	1.19%	1.20%	0.96%	2.08%	3.56%	2.67%	1.65%	1.20%	1.41%	3.81%
WATER CONTENT																
WCdry (glove box) (wt%)	11.81	11.81	11.58	11.58	7.21	7.21	6.37	6.37	6.91	6.91	7.09	7.09	4.23	4.23	4.27	4.27
WCdry 105°C (wt%)	11.76	11.76	12.04	12.04	8.09	8.09	8.24	8.24	9.76	9.76	10.14	10.14	8.04	8.04	8.13	8.13
WCdry 150°C (wt%)	no data															
CHLORINE CONTENT IN PORE WATER (by scaling up with WCdry)																
Cl^- (WCdry glove box) (mg/kg)	7968	8203	8385	8477	144963	145792	156798	156137	177589	180136	171413	171799	484467	477691	469256	473665
Cl^- (WCdry 105°C) (mg/kg)	8006	8242	8063	8152	129123	129861	121200	120688	125716	127519	119848	120117	255007	251441	246579	248896
Cl^- (WCdry 150°C) (mg/kg)	no WCdry 150°C data															
CHLORINE CONTENT OF SOLUTION AT EQUILIBRIUM																
Sample	S40VIT	S40VIT	S41VIT	S41VIT	S42VIT	S42VIT	S43VIT	S43VIT	S44VIT	S44VIT	S45VIT	S45VIT	S46VIT	S46VIT	S47VIT	S47VIT
Cl^- (mg/kg)	10367	10367	10169	10169	129601	129601	129792	129792	128849	128849	126861	126861	212459	212459	209119	209119
CHLORINE-ACCESSIBLE POROSITY (calculated with WCdry 105°C)																
Cl accessible porosity (% of total	77	79	79	80	100	100	93	93	98	99	94	95	120	118	118	119

Note: highlighted data were obtained by ICP, others by IC.

6.7.4 Stable Water Isotope Composition of Solutions After Equilibration

The stable water isotope composition of the Vittel saline solution after equilibration with Opalinus Clay rock was analysed using the 120°C distillation technique. NaF treatment was performed for $CaCl_2$ solutions. Results are shown in Table 26.

The isotopic composition of the equilibrated Vittel solutions (Figure 48) is not significantly modified by mixing with the porewater initially contained in the Opalinus Clay. This is because the Vittel mineral water ($\delta^{18}O$ = -8.57‰, $\delta^{2}H$ = -55.56‰ VSMOW) has an isotope composition almost identical to the Opalinus Clay porewater of the DR-17 sample ($\delta^{18}O$ = -7.74‰, $\delta^{2}H$ = -54.7‰ VSMOW; T. Gimmi – personal communication, 2012).

Table 26: Stable Water Isotope Composition of Vittel Solutions Equilibrated with Opalinus Clay

Expt. #	PVC container ID	Equil. Sol. ID	Salinity (initial)		$\delta^{18}O$	2σ	$\delta^{2}H$	2σ
			NaCl (molal)	$CaCl_2$ (molal)	(‰ VSMOW)	(‰ VSMOW)	(‰ VSMOW)	(‰ VSMOW)
40	OPA1	S40VIT1	0.3		-8.3	0.4	-54.3	1.4
40	OPA1	S40VIT2	0.3		-8.4	0.4	-54.6	1.4
41	OPA1A	S41VIT1	0.3		-8.4	0.4	-54.9	1.4
41	OPA1A	S41VIT2	0.3		-8.4	0.4	-55.2	1.4
42	OPA2	S42VIT1	5		-8.6	0.4	-55.1	1.4
42	OPA2	S42VIT2	5		-8.5	0.4	-55.1	1.4
43	OPA2A	S43VIT1	5		-8.6	0.4	-55.5	1.4
43	OPA2A	S43VIT2	5		-8.2	0.4	-54.5	1.4
44	OPA3	S44VIT1		2.5	-8.2	0.4	-55.3	1.4
44	OPA3	S44VIT2		2.5	-8.3	0.4	-55.3	1.4
45	OPA3A	S45VIT1		2.5	-8.3	0.4	-55.6	1.4
45	OPA3A	S45VIT2		2.5	-8.4	0.4	-55.6	1.4
46	OPA4	S46VIT1		5	-7.8	0.4	-55.0	1.4
46	OPA4	S46VIT2		5	-8.3	0.4	-56.0	1.4
47	OPA4A	S47VIT1		5	-8.5	0.4	-56.3	1.4
47	OPA4A	S47VIT2		5	-8.2	0.4	-55.4	1.4

Note: NaF addition (for $CaCl_2$ solutions), distillation and stable water isotope analysis were performed in duplicate for the solutions from each equilibration container.

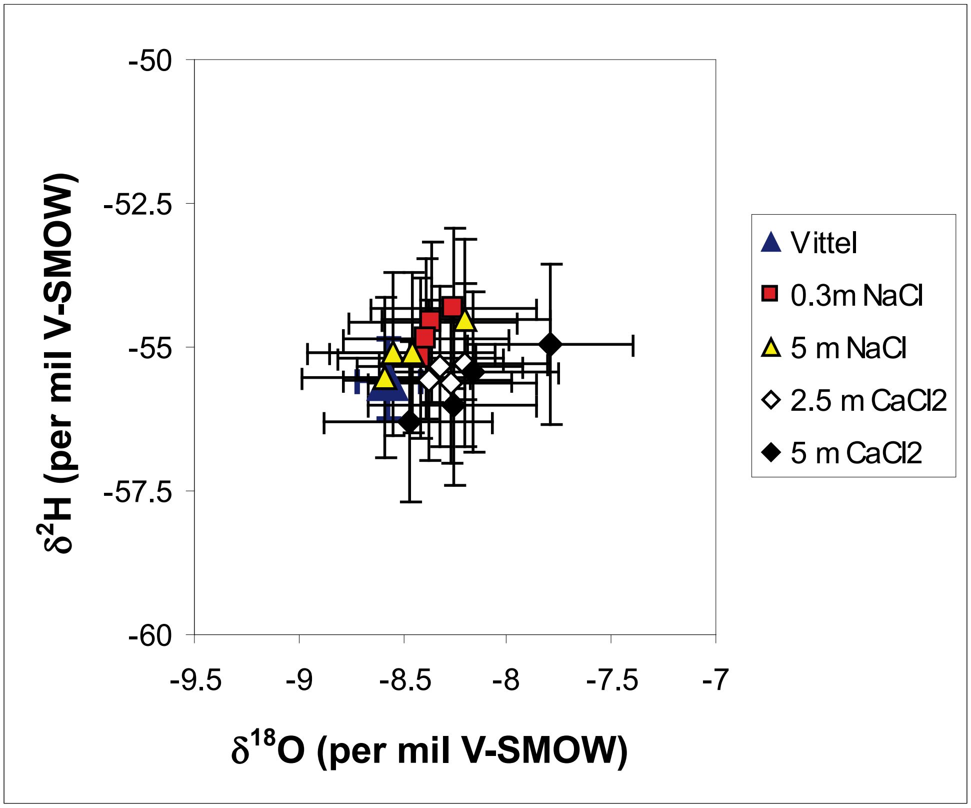


Figure 48: Isotopic Composition of the Synthetic Vittel Solutions After Equilibration with Opalinus Clay Compared with Data for Pure Vittel Mineral Water; Error Bars are 2σ

6.8 QUEENSTON SHALE RESULTS

6.8.1 Physical and Mineralogical Properties Before and After Equilibration

6.8.1.1 Bulk Density

The bulk wet densities of the intact porewater-saturated Queenston Shale samples are given in Table 27, while bulk wet densities of the same rocks, equilibrated with Vittel synthetic solutions, are given in Table 28. The data plotted in Figure 49 show that bulk wet density of intact rock is higher, and that density increases with the salinity of the synthetic solution. A similar, but much more pronounced, behaviour was observed in the rock stability experiments for Opalinus Clay (Section 6.2). The salinity of the original porewater present in the Queenston samples used for the experiments is unknown but the porewater salinity of the Queenston Shale is reported to range between 2.5 and 5 molal (Hobbs et al., 2011). Measured densities of Queenston Shale rock equilibrated with 5 molal NaCl and $CaCl_2$ solutions compare well with the value of the intact rock. This suggests that immersion of the rock samples in the synthetic solution did not affect significantly the rock properties, particularly the densities and water contents. Volume increase due to pressure release is probably not significant. Furthermore, swelling clays content is negligible in the Queenston Shale and this might limit the “density lowering” observed in other samples upon immersion under atmospheric pressure. These results contrast with those obtained for the Opalinus Clay (Section 6.7.1.1).

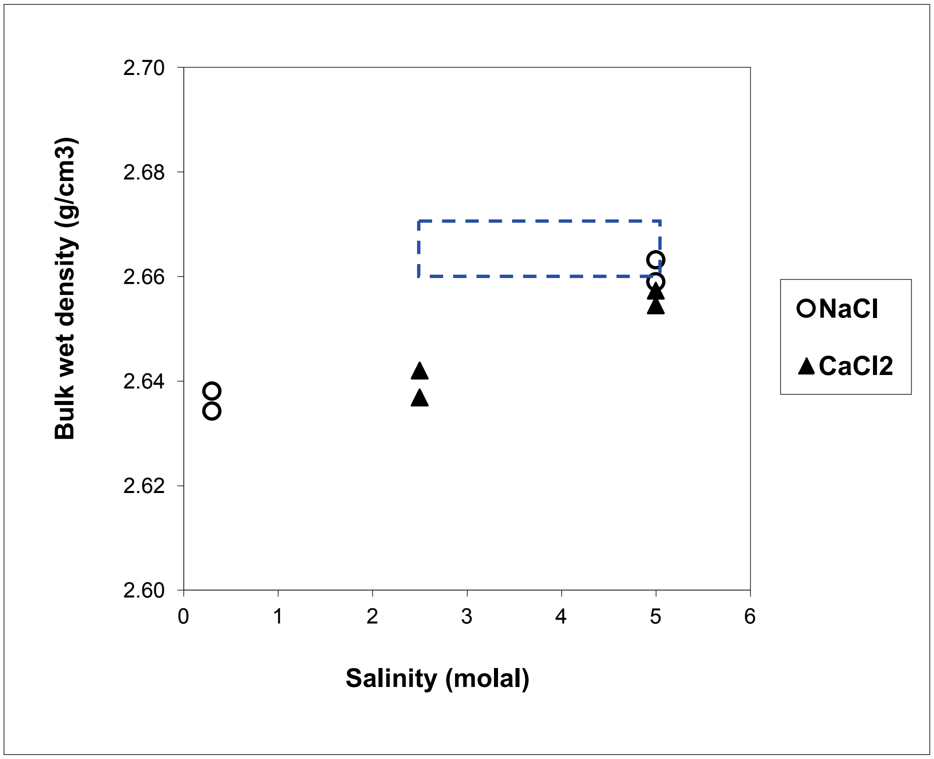


Figure 49: Bulk Wet Density of Queenston Shale Equilibrated with Synthetic Solutions of Various Salinities; Range of Density Values for the Intact Porewater-saturated Rock (Hobbs et al., 2011) is Shown as a Blue Dashed Box

Table 27: Bulk Wet Density of Intact Porewater-Saturated Queenston Shale

Sample ID	Density of paraffin (g/cm^3)	Replicate A Wt of rock in air (g)	Wt of rock in paraffin (g)	Calculated bulk density (g/cm^3)	Replicate B Wt of rock in air (g)	Wt of rock in paraffin (g)	Calculated bulk density (g/cm^3)	Average calculated bulk density (g/cm^3)
DGR4-451.08	0.86	20.2909	13.7237	2.657	13.9969	9.4646	2.656	2.66
DGR4-453.11	0.86	35.2939	23.9463	2.675	10.6958	7.2388	2.661	2.67

Table 28: Bulk Wet Density of Queenston Shale Samples After Equilibration with Synthetic Solutions

Exp. #	Solution salinity	Type	PWC container D	Density of paraffin (g/cm^3)	Replicate A Wt. of rock in air (g)	Wt. of rock in paraffin (g)	Calc. bulk density (g/cm^3)	Replicate B Wt. of rock in air (g)	Wt. of rock in paraffin (g)	Calc. bulk density (g/cm^3)	Ave. calc. bulk density (g/cm^3)
50	0.3	NaCl	CAN1	0.861	18.3540	12.3686	2.640	22.2180	14.9610	2.636	2.64
51	0.3	NaCl	CAN1A	0.861	14.4762	9.7478	2.636	15.0060	10.0983	2.633	2.63
52	5	NaCl	CAN2	0.861	13.2863	8.9836	2.659	18.6327	12.6002	2.659	2.66
53	5	NaCl	CAN2A	0.861	12.1784	8.2420	2.664	10.9159	7.3862	2.663	2.66
54	2.5	$CaCl_2$	CAN3	0.861	25.3154	17.0662	2.642	16.0588	10.8251	2.642	2.64
55	2.5	$CaCl_2$	CAN3A	0.861	8.6571	5.8261	2.633	18.4955	12.4655	2.641	2.64
56	5	$CaCl_2$	CAN4	0.861	23.1999	15.6735	2.654	14.1208	9.5416	2.655	2.65
57	5	$CaCl_2$	CAN4A	0.861	16.4547	11.1222	2.657	16.9373	11.4505	2.658	2.66

6.8.1.2 Grain Density

Grain density of the Queenston Shale equilibrated with synthetic saline solutions has been measured on 2 to 4 replicate samples by kerosene pycnometry. Data are given in Table 29 and plotted in Figure 50.

The density measured for samples equilibrated at 0.3 molal NaCl is higher than that of samples equilibrated at 5 molal NaCl, as well as 2.5 and 5 molal $CaCl_2$ solutions. The water content measured for samples dried in the N_2 glove box are lower than those obtained by drying at 105°C and 150°C, which suggests drying was not complete in the glove box. This might affect the grain density value because part of the measured weight would correspond to remnants of porewater, thus causing a lowering of the measured density. Because salts are hydrophilic, the difficulty in fully drying the samples is higher at high salinity. This might explain the higher grain density measured at 0.3 molal NaCl (low salinity). After drying, the rock material includes salts precipitated from the porewater, as well as rock matrix material. However, Hobbs et al. (2011) showed that correction for the presence of salts would be negligible compared to the error of the measured density.

Considering the problems discussed above, the obtained grain density values are considered not to be reliable.

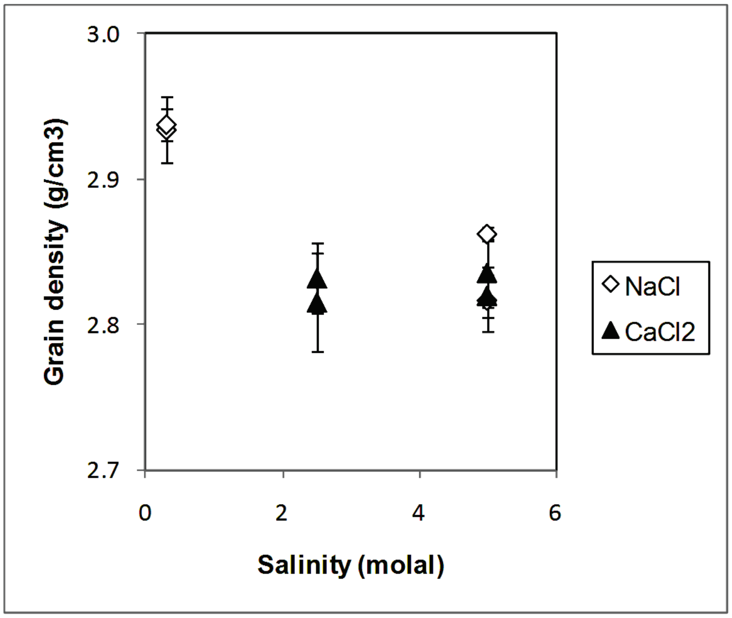


Figure 50: Grain Density of Equilibrated Queenston Shale versus Salinity of the NaCl or $CaCl_2$ Standard Solution; Samples were Dried in Glove Box in N_2 Atmosphere Before Milling and Grain Density Measurement

Table 29: Grain Density of Queenston Shale

Sample	Ave. grain density (g/cm^3)	STD
S50VIT-AQ	2.9338	0.023 (n=2)
S51VIT-AQ	2.9374	0.011 (n=2)
S52VIT-AQ	2.8624	0.005 (n=2)
S53VIT-AQ	2.8169	0.022 (n=3)
S54VIT-AQ	2.8316	0.024 (n=3)
S55VIT-AQ	2.8149	0.034 (n=4)
S56VIT-AQ	2.8195	0.015 (n=2)
S57VIT-AQ	2.8354	0.023 (n=2)

Note: all samples dried in N_2 atmosphere

6.8.1.3 Water Content

Water content (WC) was measured by drying rock samples first at 105°C and then at 150°C until rock samples reach a constant weight (at each temperature). The aim of drying at 150°C was to remove more water from the $CaCl_2$-saturated samples ($CaCl_2$ likely does not completely dehydrate at 105°C). The rock sample minimum weight has been used to calculate the WC at 105°C and 150°C. The WC corresponds to the pure water contained in the porewater, which does not account for the mass of dissolved salts.

WC of intact porewater-saturated Queenston Shale, and of samples equilibrated with synthetic solutions, are presented in Table 30 and plotted in Figure 51. The WC of Queenston Shale samples, after isotope diffusive exchange experiments, are given in Table 31 and plotted in Figure 52.

Figures 51 and 52 show that the WC of Queenston Shale samples equilibrated with synthetic solutions are similar before and after isotope diffusive exchange experiments. As expected, samples equilibrated with $CaCl_2$ solutions are more completely dried at 150°C than at 105°C, and the WC obtained at 150°C is, therefore, slightly higher than at 105°C, the difference being <10% of the WC at 105°C.

As for the Opalinus Clay, there is a good inverse correlation between salinity and WC, which apparently is not related to the chlorinity, but is related to the molality of cations (Ca^{+2} or Na^+).

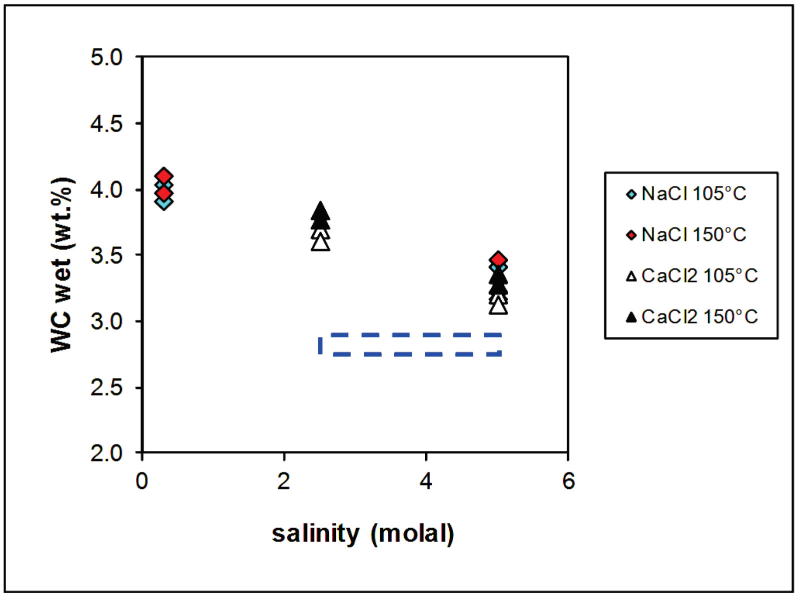


Figure 51: Wet Water Content (WC) of Queenston Shale After Equilibration with Synthetic Solutions; Water Contents were Obtained by Drying at 105 and 150°C; Water Content (drying at 105°C) of Queenston Shale, Saturated with its Original Porewater, is Shown as a Blue Dashed Box

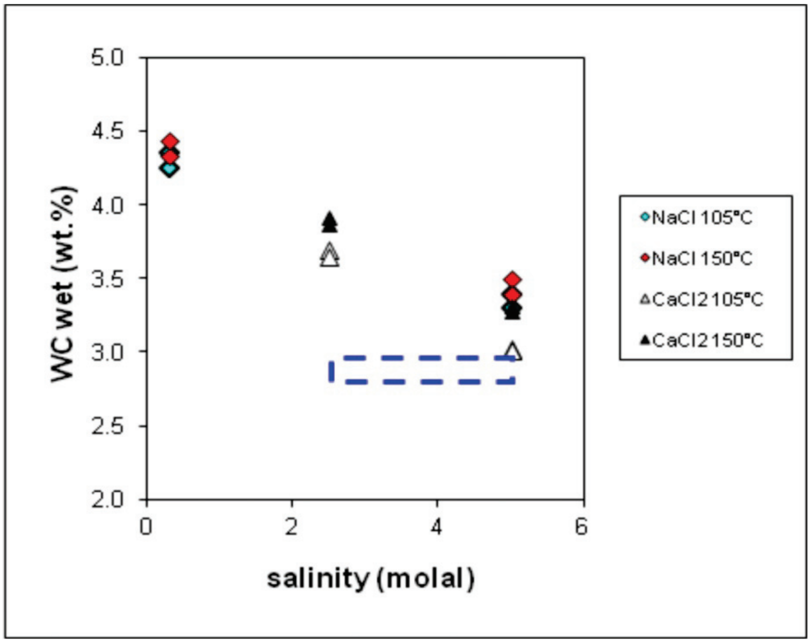


Figure 52: Wet Water Content (WC) of Queenston Shale After Equilibration with Synthetic Solutions and Isotope Diffusive Exchange Experiments; Water Contents were Obtained by Drying at 105 and 150°C; Water Content (105°C) of Queenston Shale Saturated with its Original Porewater is Shown as a Blue Dashed Box

Table 30: Water Content of Queenston Shale Before and After Equilibration with Saline Solutions

Exper. #	Sample ID	Type of synthetic solution	Water content from lowest mass when drying at 105°C		Water content from lowest mass when drying at 150°C	
			$WC_{grav.}$ wet	$WC_{grav.}$ dry	$WC_{grav.}$ Wet	$WC_{grav.}$ dry
			wt%	wt%	wt%	wt%
Original water content of Queenston Shale rock used in experiments						
	DGR4-453.11A	none	2.96	3.05		
	DGR4-453.11B	none	2.97	3.06		
	Average	*none*	*2.97*	*3.06*		
	DGR4-451.08A	none	2.87	2.96		
	DGR4-451.08B	none	2.85	2.93		
	Average	*none*	*2.86*	*2.95*		
Water content of OPA rock equilibrated with synthetic Vittel solutions						
50	S50VIT-A	0.3m NaCl	4.04	4.21	4.11	4.29
51	S51VIT-A	0.3m NaCl	3.92	4.08	3.98	4.14
52	S52VIT-A	5m NaCl	3.42	3.54	3.47	3.60
53	S53VIT-A	5m NaCl	3.18	3.28	3.23	3.34
54	S54VIT-A	2.5m $CaCl_2$	3.71	3.85	3.85	4.00
55	S55VIT-A	2.5m $CaCl_2$	3.61	3.75	3.78	3.93
56	S56VIT-A	5m $CaCl_2$	3.21	3.32	3.37	3.48
57	S57VIT-A	5m $CaCl_2$	3.13	3.24	3.29	3.40

6.8.1.4 Mineralogy

The mineralogical compositions (by whole rock X-ray diffraction) of Queenston Shale rock samples before and after equilibration with Vittel synthetic standard solutions are given in Table 32. Equilibration with saline solutions did not induce measurable mineralogical changes, within the analytical uncertainty of the methods employed.

Table 31: Water Content of Queenston Shale After Isotope Diffusive Exchange Experiments

Exp. #	Sample ID	Type of synthetic solution	Water content from lowest mass when drying at 105°C *		Water content from lowest mass when drying at 150°C	
			$WC_{grav.}$ wet (wt%)	$WC_{grav.}$ dry (wt%)	$WC_{grav.}$ wet (wt%)	$WC_{grav.}$ dry (wt%)
50	CAN1LAB	0.3m NaCl	4.30	4.49	4.38	4.58
50	CAN1TEW	0.3m NaCl	4.19	4.38	4.28	4.47
50	*Average*	0.3m NaCl	4.25	4.43	4.33	4.53
51	CAN1ALAB	0.3m NaCl	4.36	4.56	4.43	4.64
51	CAN1ATEW	0.3m NaCl	4.36	4.56	4.43	4.64
51	*Average*	0.3m NaCl	4.36	4.56	4.43	4.64
52	CAN2LAB	5m NaCl	3.38	3.50	3.49	3.61
52	CAN2TEW	5m NaCl	3.42	3.54	3.51	3.64
52	*Average*	5m NaCl	3.40	3.52	3.50	3.63
53	CAN2ALAB	5m NaCl	3.31	3.42	3.41	3.53
53	CAN2ATEW	5m NaCl	3.28	3.39	3.38	3.50
53	*Average*	5m NaCl	3.29	3.41	3.39	3.51
54	CAN3LAB	2.5m $CaCl_2$	3.74	3.89	3.97	4.13
54	CAN3TEW	2.5m $CaCl_2$	3.65	3.79	3.86	4.02
54	*Average*	2.5m $CaCl_2$	3.70	3.84	3.92	4.08
55	CAN3ALAB	2.5m $CaCl_2$	3.67	3.81	3.89	4.04
55	CAN3ATEW	2.5m $CaCl_2$	3.63	3.76	3.84	4.00
55	*Average*	2.5m $CaCl_2$	3.65	3.78	3.86	4.02
56	CAN4LAB	5m $CaCl_2$	3.01	3.10	3.30	3.42
56	CAN4TEW	5m $CaCl_2$	3.04	3.14	3.33	3.44
56	*Average*	5m $CaCl_2$	3.02	3.12	3.32	3.43
57	CAN4ALAB	5m $CaCl_2$	3.02	3.12	3.29	3.41
57	CAN4ATEW	5m $CaCl_2$	3.00	3.09	3.27	3.38
57	*Average*	5m $CaCl_2$	3.01	3.11	3.28	3.39

Table 32: Mineralogical Composition of Queenston Shale Samples Before and After Equilibration with Vittel Standard Solutions

Sample	Note	C_{inorg} wt%	C_{org} wt%	S wt%	Calcite wt%	Dolomite wt%	Quartz wt%	K-feldspar wt%	Plagioclase wt%	Total sheet sil. wt%	Additional phases
DGR4-453.11A	Intact saturated core	4.3	<0.1	<0.1	23.5	11.6	10.3	1.0	0.5	53.1	illite, ankerite, hematite, clinochlore
S50VIT-A(453.11)	Equil. at 0.3m NaCl	4.0	0.1	<0.1	22.0	10.6	11.4	1.0	0.3	54.7	hematite, illite, clinochlore
S51VIT-A(453.11)	Equil. at 0.3m NaCl	4.1	0.1	<0.1	22.0	11.5	10.4	1.3	0.2	54.7	illite, clinochlore, hematite
S52VIT-A(453.11)	Equil. at 5m NaCl	4.2	0.1	<0.1	23.7	10.6	10.0	1.0	0.9	53.9	illite, clinochlore, hematite
S53VIT-A(453.11)	Equil. at 5m NaCl	4.7	0.1	<0.1	23.3	15.0	9.4	1.1	0.8	50.5	illite, clinochlore, hematite
DGR4-451.08A	Intact saturated core	3.9	0.1	<0.1	29.4	2.8	10.7	1.1	0.0	61.3	illite, hematite, clinochlore
S54VIT-A(451.08)	Equil. at 2.5m $CaCl_2$	4.0	<0.1	<0.1	27.6	5.4	10.6	1.2	0.4	54.9	illite, clinochlore, hematite
S55VIT-A(451.08)	Equil. at 2.5m $CaCl_2$	3.8	<0.1	<0.1	28.5	2.9	9.5	1.0	0.4	57.7	illite, clinochlore, hematite
S56VIT-A(451.08)	Equil. at 5m $CaCl_2$	3.9	<0.1	<0.1	30.1	2.2	9.4	1.2	0.0	57.2	illite, clinochlore, hematite
S57VIT-A(451.08)	Equil. at 5m $CaCl_2$	4.0	<0.1	<0.1	27.6	5.3	10.1	1.0	0.0	56.0	illite, clinochlore, hematite

Notes: Total sheet silicate content is obtained by difference with the total of calcite, dolomite, quartz, K-feldspar, and plagioclase. Additional phases are not quantified and the list might not be exhaustive. Previous studies showed illite and chlorite are the main clay minerals, with minor contents of an illite-rich illite/smectite mixed-layer phase (Koroleva et al., 2009).

6.8.2 Time-Series and Final Chemical Composition of Solution After Equilibration

The initial experimental conditions for equilibration of Queenston Shale samples with synthetic Vittel saline solutions are given in Table 33. The rock / solution weight ratio was between 1.20 and 1.48.

Table 33: Equilibration of Queenston Samples: Initial Conditions (January 26, 2011)

Cell No	Wt. of cell, lid & all fittings (&stick) (g)	Sample ID	Wt. of rock added (g)	Wt. of cell & rock material (g)	Type of solution added	Wt. of solution added (g)	Total wt. of cell & contents at start of experiment (g)
CAN1	446.73	Queenston DGR4-453.11	504.37	951.10	0.3m NaCl	346.79	1297.89
CAN1A	431.64	Queenston DGR4-453.11	500.07	931.71	0.3m NaCl	346.50	1277.97
CAN2	446.02	Queenston DGR4-453.11	502.02	948.04	5m NaCl	364.61	1312.65
CAN2A	427.82	Queenston DGR4-453.11	506.22	934.04	5m NaCl	422.42	1356.46
CAN3	444.31	Queenston DGR4-451.08	656.02	1100.33	2.5m$CaCl_2$	454.99	1555.32
CAN3A	431.45	Queenston DGR4-451.08	653.13	1084.58	2.5m$CaCl_2$	457.21	1541.79
CAN4	445.92	Queenston DGR4-451.08	664.59	1110.51	5m $CaCl_2$	487.9	1598.41
CAN4A	430.41	Queenston DGR4-451.08	705.08	1135.49	5m $CaCl_2$	483.37	1618.86

A time-series of small aliquots (0.5 mL) of the standard solutions were sampled to monitor the equilibration process. Sampling was done on containers CAN1 (0.3 m NaCl) and CAN3 (2.5 m $CaCl_2$). The porewater salinity of saturated Queenston Shale before equilibration ranges from 2.5 to 5.5 molal, which is much higher than the average 0.6 mol/L of seawater.

Time-series samples were analyzed for anions (F^-, Cl^-, Br^-, SO_4^{-2}, NO_3^-) and cations (Na^+, K^+, Mg^{+2}, Ca^{+2}, Sr^{+2}); the results are given in Tables 34 and 35 and plotted in Figures 53 and 54. The last samples, after 2174 hours of equilibration (= 90.6 days), correspond to the end of the equilibration experiment and the start of the isotope diffusive exchange experiment. The chemical compositions of the equilibrated solutions are given in Table 36.

Figures 53 shows the time-series evolution of the chemical composition of the 0.3 molal NaCl solution during equilibration with Queenston Shale (SO_4^{-2} and Br^- are at very low concentrations and are not plotted). Cl^-, Na^+, Ca^{+2}, Mg^{+2} and K^+ concentrations reached a plateau after 110 hours (~4 days) of equilibration. The strange behavior of the Na^+ concentration in the first 3 samples, specifically the anomalously low value of the second sample, is not explained. The higher concentrations observed in sample CAN1-5 (Table 34) suggests that some evaporation occurred between sampling and analysis (possibly because the vial in which the sample was stored was poorly sealed).

Figures 54 shows the time-series evolution of the chemical composition of the 2.5 molal $CaCl_2$ solution during equilibration with Queenston Shale (SO_4^{-2} and Br^- are at very low concentrations and are not plotted). Cl^- and Ca^{+2} reached a plateau after 19 hours (<1 days) of equilibration. In contrast, Na^+, Mg^{+2}, and K^+ concentrations required 326 hours before reaching equilibrium. This suggests that these last three elements may be involved in non-conservative reactions with minerals (e.g., sheet silicates, feldspar or carbonates?). It is probable that Ca^{+2} does not behave as a conservative element, but due to its high concentration in the standard synthetic solution, the effect of carbonate dissolution is not detectable. In conclusion, 326 hours (~14 days) are needed to attain equilibrium among the synthetic solution, the natural porewater and the minerals in the rock.

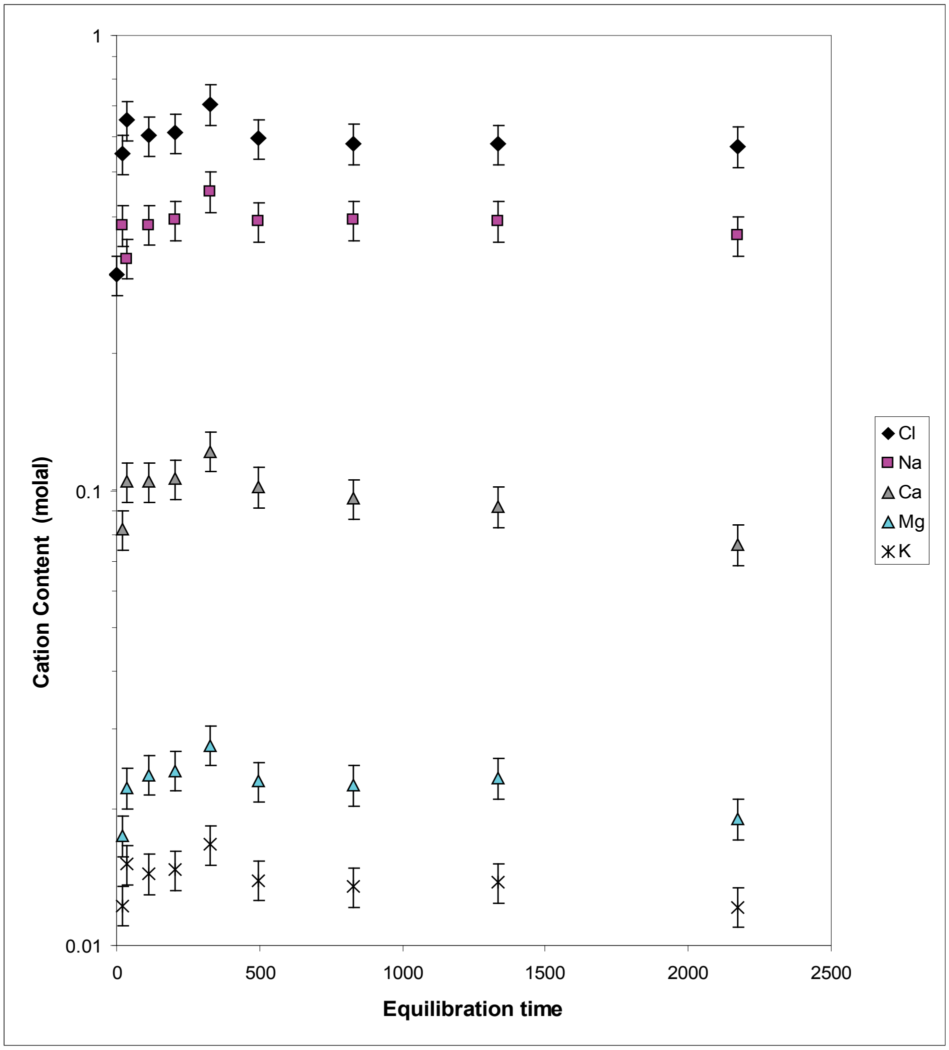


Figure 53: Time-Series Evolution of Cl and Major Cation Contents of 0.3 Molal NaCl Standard Solution Equilibrating with Queenston Shale (Container CAN1)

Table 34: Time-Series Evolution of the 0.3 m NaCl Standard Solution During Equilibration with Queenston Shale

Container CAN1 filled with 0.3m NaCl		**CAN1-0**	**CAN1-1**	**CAN1-2**	**CAN1-3**	**CAN1-4**	**CAN1-5**	**CAN1-6**	**CAN1-7**	**CAN1-8**	**CAN1-equil. (S50VIT-Sol)**
Equilibration time	h	0	19	38	110	206	326	494	830	1334	2174
CATIONS											
Sodium (Na^{+})	mg/kg	6736	8533	7176	8509	8715	10021	8679	8716	8694	8105
Potassium (K$^{+)}$)	mg/kg		464	568	543	554	625	525	508	520	460
Magnesium (Mg^{+2})	mg/kg		410	522	557	569	643	539	530	549	447
Calcium (Ca^{+2})	mg/kg		3186	4044	4047	4110	4688	3948	3722	3573	2954
Strontium (Sr^{+2})	mg/kg		<100	<100	<100	<100	<100	<100	<100	<100	64.3
ANIONS											
Fluoride (F^{-})	mg/kg		<7.5	<7.5	<7.5	<7.5	<7.5	<7.5	<7.5	<7.5	<50
Chloride (Cl^{-})	mg/kg	10390	18874	22256	20645	20947	24045	20327	19848	19758	19576
Bromide (Br^{-})	mg/kg		103	134	128	124	134	116	111	111	94
Sulfate (SO$_4^{-2}$)	mg/kg		130	145	129	139	145	135	136	140	137
Nitrate (NO$_3^{-}$)	mg/kg		<7.5	<7.5	<7.5	<7.5	<7.5	<7.5	<7.5	<7.5	<50
Total Alkalinity	meq/l										1.23
Total Alkalinity as HCO$_3$	mg/kg										75.1
CATIONS											
Sodium (Na^{+})	molal	2.981E-01	3.833E-01	3.234E-01	3.834E-01	3.929E-01	4.542E-01	3.909E-01	3.923E-01	3.912E-01	3.641E-01
Potassium (K$^{+)}$)	molal		1.225E-02	1.506E-02	1.439E-02	1.469E-02	1.666E-02	1.392E-02	1.345E-02	1.376E-02	1.215E-02
Magnesium (Mg^{+2})	molal		1.744E-02	2.224E-02	2.373E-02	2.425E-02	2.756E-02	2.295E-02	2.256E-02	2.337E-02	1.900E-02
Calcium (Ca^{+2})	molal		8.209E-02	1.045E-01	1.046E-01	1.063E-01	1.219E-01	1.020E-01	9.608E-02	9.221E-02	7.614E-02
Strontium (Sr^{+2})	molal										7.580E-04
ANIONS											
Fluoride (F^{-})	molal										
Chloride (Cl^{-})	molal	2.982E-01	5.498E-01	6.504E-01	6.033E-01	6.124E-01	7.067E-01	5.937E-01	5.793E-01	5.765E-01	5.703E-01
Bromide (Br^{-})	molal		1.336E-03	1.737E-03	1.659E-03	1.614E-03	1.752E-03	1.499E-03	1.438E-03	1.434E-03	1.214E-03
Sulfate (SO$_4^{-2}$)	molal		1.394E-03	1.565E-03	1.387E-03	1.505E-03	1.572E-03	1.460E-03	1.464E-03	1.507E-03	1.475E-03
Total Alkalinity as HCO$_3$	molal										1.271E-03
PARAMETERS CALCULATED FROM ANALYTICAL DATA											
Sum of Analysed	mg/kg	17126	31707	34851	34692	35165	40306	34274	33575	33350	31881
Mass of solvent/liter	kg	0.9829	0.9683	0.9651	0.9653	0.9648	0.9597	0.9657	0.9664	0.9667	0.9681
Solution density (GWB Pitzer)	g/cm^3	1.021	1.028	1.028	1.029	1.030	1.032	1.029	1.029	1.029	1.027
Charge Balance:											
Sum Cations	meq/l		5.758E+02	5.714E+02	6.347E+02	6.452E+02	7.387E+02	6.323E+02	6.214E+02	6.149E+02	5.497E+02
Sum Anions	meq/l		-5.367E+02	-6.328E+02	-5.868E+02	-5.955E+02	-6.832E+02	-5.778E+02	-5.643E+02	-5.619E+02	-5.574E+02
Difference/Total	%		3.51%	-5.10%	3.92%	4.00%	3.91%	4.50%	4.82%	4.51%	-0.69%

Note: highlighted cation concentrations were obtained by ICP, all the others by IC.

Table 35: Time-Series Evolution of the 2.5 m $CaCl_2$ Standard Solution During Equilibration with Queenston Shale

Container CAN1 filled with 2.5m $CaCl_2$		**CAN3-0**	**CAN3-1**	**CAN3-2**	**CAN3-3**	**CAN3-4**	**CAN3-5**	**CAN3-6**	**CAN3-7**	**CAN3-8**	**CAN3-equil (S54VIT-Sol)**
Equilibration time	h	0	19	38	110	206	326	494	830	1334	2174
CATIONS											
Sodium (Na^+)	mg/kg		1394	1891	2216	1973	2366	2380	2365	2469	2117
Potassium ($K^{+)}$)	mg/kg		*304*	*342*	*526*	*460*	*646*	*569*	*666*	*726*	570
Magnesium (Mg^{+2})	mg/kg		*519*	*558*	*573*	*638*	*838*	*799*	*744*	*878*	762
Calcium (Ca^{+2})	mg/kg	78320	92062	96885	94934	91028	92024	97021	92170	92482	69759
Strontium (Sr^{+2})	mg/kg		<100	<100	<100	<100	<100	<100	<100	<100	104.0
ANIONS											
Fluoride (F^-)	mg/kg		<50	<50	<50	<50	<50	<50	<50	<50	<250
Chloride (Cl^-)	mg/kg	138600	138916	149167	144740	138709	140556	137013	141077	142159	135679
Bromide (Br^-)	mg/kg		217	259	262	248	262	262	219	258	*205*
Sulfate (SO_4^{-2})	mg/kg		103	112	111	107	111	114	115	115	<250
Nitrate (NO_3^-)	mg/kg		<50	<50	<50	<50	<50	<50	<50	<50	<250
Total Alkalinity	meq/l		n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.81
Total Alkalinity as HCO_3	mg/kg										49.4
CATIONS											
Sodium (Na^+)	molal		7.912E-02	1.096E-01	1.274E-01	1.119E-01	1.349E-01	1.359E-01	1.349E-01	1.412E-01	1.164E-01
Potassium ($K^{+)}$)	molal		1.015E-02	1.163E-02	1.778E-02	1.533E-02	2.167E-02	1.911E-02	2.234E-02	2.440E-02	1.843E-02
Magnesium (Mg^{+2})	molal		2.784E-02	3.059E-02	3.116E-02	3.425E-02	4.518E-02	4.317E-02	4.013E-02	4.749E-02	3.964E-02
Calcium (Ca^{+2})	molal	2.495E+00	2.997E+00	3.220E+00	3.131E+00	2.962E+00	3.008E+00	3.177E+00	3.015E+00	3.033E+00	2.201E+00
Strontium (Sr^{+2})	molal										1.501E-03
ANIONS											
Fluoride (F^-)	molal										
Chloride (Cl^-)	molal	4.992E+00	5.112E+00	5.604E+00	5.396E+00	5.102E+00	5.195E+00	5.073E+00	5.218E+00	5.270E+00	4.839E+00
Bromide (Br^-)	molal		3.550E-03	4.311E-03	4.335E-03	4.046E-03	4.298E-03	4.296E-03	3.588E-03	4.243E-03	3.249E-03
Sulfate (SO_4^{-2})	molal		1.400E-03	1.556E-03	1.534E-03	1.446E-03	1.517E-03	1.551E-03	1.572E-03	1.574E-03	
Total Alkalinity as HCO_3	molal										1.024E-03
PARAMETERS CALCULATED FROM ANALYTICAL DATA											
Sum of Analysed	mg/kg	216920	233529	249230	243380	233180	236823	238175	237370	239106	209113
Mass of solvent/liter	kg	0.7831	0.7665	0.7508	0.7566	0.7668	0.7632	0.7618	0.7626	0.7609	0.7909
Solution density (GWB Pitzer)	g/cm^3	1.143	1.134	1.142	1.139	1.134	1.136	1.143	1.136	1.137	1.105
Charge Balance:											
Sum Cations	meq/l		4.705E+03	4.971E+03	4.894E+03	4.692E+03	4.780E+03	5.025E+03	4.780E+03	4.813E+03	3.646E+03
Sum Anions	meq/l		-3.924E+03	-4.214E+03	-4.089E+03	-3.919E+03	-3.971E+03	-3.871E+03	-3.985E+03	-4.016E+03	-3.830E+03
Difference/Total	%		9.05%	8.25%	8.96%	8.99%	9.25%	12.97%	9.07%	9.02%	-2.46%

Note: highlighted cation concentrations were obtained by ICP, all the others by IC.

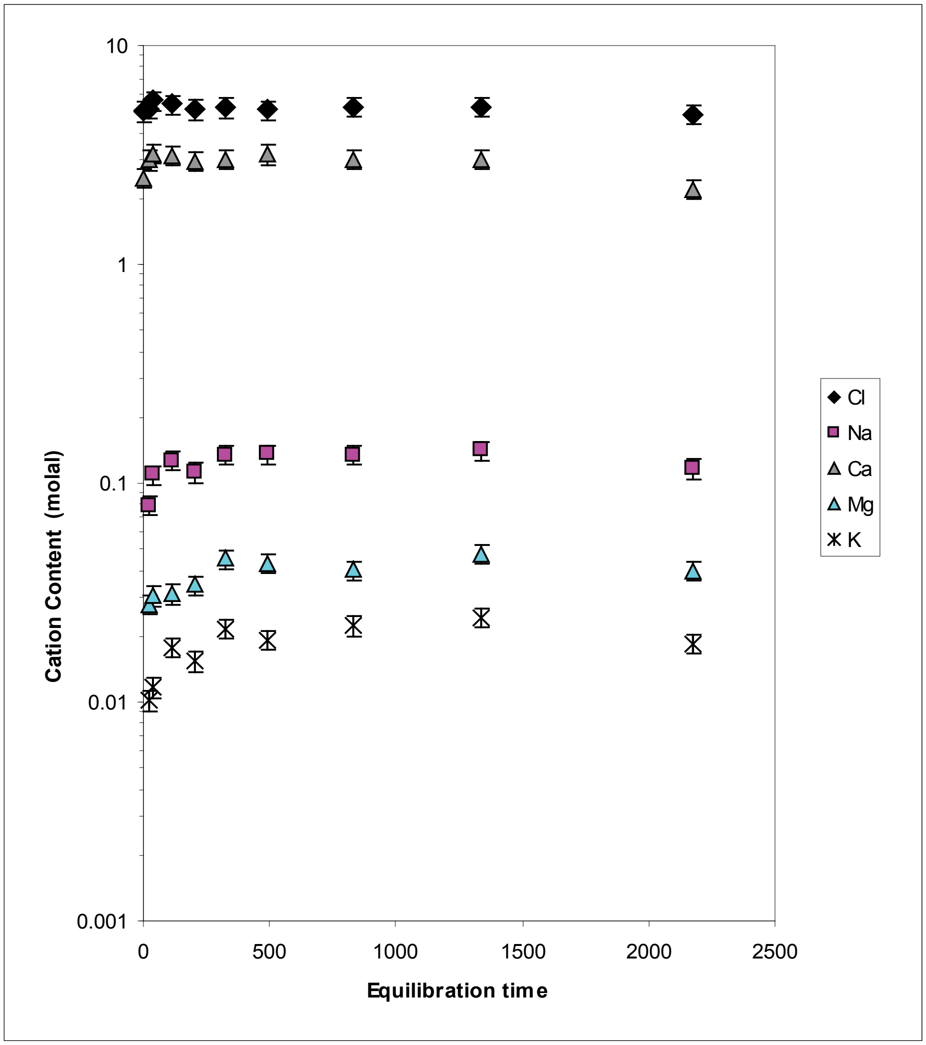


Figure 54: Time-Series Evolution of Cl and Major Cation Contents of 2.5 Molal $CaCl_2$ Standard Solution Equilibrating with Queenston Shale (Container CAN3)

Table 36: Chemical Composition of Standard Solutions Equilibrated with Queenston Shale

Sample		**S50VIT-Sol**	**S51VIT-Sol**	**S52VIT-Sol**	**S53VIT-Sol**	**S54VIT-Sol**	**S55VIT-Sol**	**S56VIT-Sol**	**S57VIT-Sol**
Type of standard solution		0.3m NaCl	0.3m NaCl	5m NaCl	5m NaCl	2.5m $CaCl_2$	2.5m $CaCl_2$	5m $CaCl_2$	5m $CaCl_2$
MISCELLANEOUS PROPERTIES (mesured on aliquots day after sampling)									
pH (lab), UniBe	-log(H+)	7.13	7.15	6.64	6.69	5.69	5.65	5.15	5.04
pH at start of titration	-log(H+)	7.21	7.2	6.93	6.74	5.72	5.73	5.18	5.09
Alkalinity	m	1.23	0.94	0.83	0.46	0.81	0.81	0.76	0.72
CHEMICAL COMPOSITION									
CATIONS									
Sodium (Na^+)	mg/kg	8105	8189	84533	86831	2117	2098	1926	2047
Potassium (K^+)	mg/kg	460	474	735	642	570	559	541	559
Magnesium (Mg^{+2})	mg/kg	447	442	400	336	762	720	552	572
Calcium (Ca^{+2})	mg/kg	2954	3108	3567	3161	69759	77192	125105	127301
Strontium (Sr^{+2})	mg/kg	64.3	62.9	67.6	56.6	104.0	102.0	116.0	119.0
ANIONS									
Fluoride (F^-)	mg/kg	<50	<50	<250	<250	<250	<250	<250	<250
Chloride (Cl^-)	mg/kg	19576	19704	139990	139709	135679	135103	216910	217852
Bromide (Br^-)	mg/kg	93.9	99.5	<250	<250	*205*	*211*	*281*	*286*
Sulfate (SO_4^{-2})	mg/kg	137.2	145.1	<250	<250	<250	<250	<250	<250
Nitrate (NO_3^-)	mg/kg	<50	<50	<250	<250	<250	<250	<250	<250
Total Alkalinity	meq/l	1.23	0.94	0.83	0.46	0.81	0.81	0.76	0.72
Total Alkalinity as HCO_3	mg/kg	75.1	57.4	50.6	28.1	49.4	49.4	46.4	43.9
CATIONS									
Sodium (Na^+)	molal	3.641E-01	3.681E-01	4.771E+00	4.907E+00	1.164E-01	1.164E-01	1.279E-01	1.367E-01
Potassium (K^+)	molal	1.215E-02	1.253E-02	2.439E-02	2.134E-02	1.843E-02	1.824E-02	2.112E-02	2.195E-02
Magnesium (Mg^{+2})	molal	1.900E-02	1.879E-02	2.135E-02	1.796E-02	3.964E-02	3.779E-02	3.467E-02	3.613E-02
Calcium (Ca^{+2})	molal	7.614E-02	8.013E-02	1.155E-01	1.025E-01	2.201E+00	2.457E+00	4.765E+00	4.876E+00
Strontium (Sr^{+2})	molal	7.580E-04	7.418E-04	1.001E-03	8.393E-04	1.501E-03	1.485E-03	2.021E-03	2.085E-03
ANIONS									
Fluoride (F^-)	molal								
Chloride (Cl^-)	molal	5.703E-01	5.743E-01	5.123E+00	5.120E+00	4.839E+00	4.861E+00	9.340E+00	9.433E+00
Bromide (Br^-)	molal	1.214E-03	1.287E-03			*3.249E-03*	*3.364E-03*	*5.364E-03*	*5.500E-03*
Sulfate (SO_4^{-2})	molal	1.475E-03	1.560E-03						
Nitrate (NO_3^-)	mg/kg								
Total Alkalinity as HCO_3	molal	1.271E-03	9.714E-04	1.077E-03	5.977E-04	1.024E-03	1.033E-03	1.160E-03	1.105E-03
PARAMETERS CALCULATED FROM ANALYTICAL DATA									
Sum of Analysed Constituents	mg/kg	31881	32276	229301	230369	209113	216033	344972	348584
Mass of solvent/liter	kg	0.9681	0.9677	0.7707	0.7696	0.7909	0.7840	0.6550	0.6514
Solution density (GWB Pitzer)	g/cm^3	1.027	1.028	1.112	1.114	1.105	1.115	1.19	1.194
Charge Balance:									
Sum Cations	meq/l	5.497E+02	5.629E+02	3.913E+03	3.951E+03	3.646E+03	4.020E+03	6.355E+03	6.500E+03
Sum Anions	meq/l	-5.574E+02	-5.610E+02	-3.949E+03	-3.941E+03	-3.830E+03	-3.814E+03	-6.122E+03	-6.149E+03
Difference/Total	%	-0.69%	0.17%	-0.46%	0.13%	-2.46%	2.63%	1.86%	2.78%

Note: highlighted cation concentrations were obtained by ICP, the others by IC. Values in italics are semi-quantitative (Cl peak interference and just below range of standardization).

6.8.3 Aqueous Leach Data and Chloride-Accessible Porosity

Aqueous leaching was performed at a solid/liquid mass ratio of 1 on aliquots of equilibrated Queenston Shale. The chemical compositions of the obtained aqueous extracts are given in Table 37.

The porewater chloride composition has been calculated by up-scaling the aqueous extract concentration, and considering the water content obtained by drying in the glove box (N_2 atmosphere + desiccant for 96 days) and in an oven at 105°C and 150°C. The most complete drying was obtained at 150°C, especially for rocks equilibrated with $CaCl_2$ solution. It is, however, probable that some water could not be removed from $CaCl_2$, even at 150°C. Underestimating the water content implies that the up-scaled chloride concentration calculated is somewhat higher than the actual porewater concentration. The chloride concentration in the porewater is calculated using the up-scaling formula (16).

Chloride-accessible porosity is calculated using equation (17) and calculated Cl-accessible porosity percentages are given in Table 37. Except for rock equilibrated with 0.3 molal NaCl solution, all the data are above 100% (up to 139% for 5 molal $CaCl_2$ solution), which is impossible. It might be that the drying at 150°C is not complete for $CaCl_2$-saturated samples, which implies an underestimate of the WC_{dry} and an overestimate of the porewater salinity, but such incomplete drying is difficult to envisage for the 5 molal NaCl solution.

6.8.4 Water Isotope Composition of Solutions after Equilibration

The stable water isotope composition of the Vittel saline solution after equilibration with Queenston Shale rock was analysed using the 120°C distillation technique (see Section 4). NaF treatment was performed for $CaCl_2$ solutions, as described in Section 4. Results are shown in Table 38 and plotted in Figure 55.

The isotopic composition of the porewater contained in the Queenston Shale has been measured by diffusive exchange using saline test solutions on one sample of DGR4 (DGR4-472.78; Hobbs et al., 2011), giving: $\delta^{18}O = +1.7 \pm 0.7‰$ V-SMOW (2σ error) and $\delta^{2}H = -39.3 \pm 2.0‰$ V-SMOW (2σ error).

Alternative measurements using a 150°C vacuum distillation technique were performed at the University of Ottawa and yielded values close to -3‰ V-SMOW for $\delta^{18}O$, and -48‰ V-SMOW for $\delta^{2}H$ (as described in Intera, 2008 and 2009).

Table 37: Queenston Shale: Aqueous Extract Data, Calculated Porewater Cl-Content, and Chloride-Accessible Porosity Ratio

Sample	S50VITa-aq	S50VITb-aq	S51VITa-aq	S51VITb-aq	S52VITa-aq	S52VITb-aq	S53VITa-aq	S53VITb-aq	S54VITa-aq	S54VITb-aq	S55VITa-aq	S55VITb-aq	S56VITa-aq	S56VITb-aq	S57VITa-aq	S57VITb-aq
Standard solution	0.3m NaCl	0.3m NaCl	0.3m NaCl	0.3m NaCl	5m NaCl	5m NaCl	5m NaCl	5m NaCl	2.5m $CaCl_2$	2.5m $CaCl_2$	2.5m $CaCl_2$	2.5m $CaCl_2$	5m $CaCl_2$	5m $CaCl_2$	5m $CaCl_2$	5m $CaCl_2$
Liquid/solid ratio	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
CATIONS																
Sodium (Na^+) (mg/L)	407.7	406.8	397.4	391.8	3418.8	3406.1	3365.5	3278.1	135.8	134.7	133.4	134.1	136.9	136.1	147.1	146.0
Potassium ($K^{+)}$) (mg/L)	131.5	131.0	131.1	128.8	176.7	167.0	160.8	148.7	395.4	396.4	341.1	340.6	391.1	369.7	423.0	443.9
Magnesium (Mg^{+2}) (mg/L)	<10	<10	<10	<10	<50	<50	<50	<50	162.2	152.1	123.1	127.9	140.1	141.9	171.6	171.5
Calcium (Ca^{+2}) (mg/L)	31.6	30.6	28.0	26.6	63.2	62.8	<50	<50	2983.3	3183.9	3313.2	3274.4	5419.3	5399.2	5408.8	5430.3
Strontium (Sr^{+2}) (mg/L)	<10	<10	<10	<10	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50
ANIONS																
Fluoride (F^-) (mg/L)	5.5	5.5	5.3	5.2	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25
Chloride (Cl^-) (mg/L)	741.9	736.8	716.7	717.9	5416.3	5405.6	5272.5	5299.4	5934.0	6002.8	6191.7	6138.9	10053.7	10077.8	10274.6	10277.4
Bromide (Br^-) (mg/L)	<5	<5	<5	<5	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25
Sulfate (SO_4^{-2}) (mg/L)	40.1	39.8	52.7	52.3	36.1	36.9	34.7	35.0	30.1	29.9	34.4	32.5	38.4	38.2	35.7	36.8
Nitrate (NO_3^-) (mg/L)	<5	<5	<5	<5	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25
Total Alkalinity (meq/L)	1.63	1.65	1.66	1.67	2.06	2.07	2.07	2.10	0.36	0.37	0.37	0.36	0.37	0.38	0.39	0.38
Total Alkalinity as HCO_3 (mg/L)	99.5	100.7	101.3	101.9	125.7	126.3	126.3	128.1	22.0	22.6	22.6	22.0	22.6	23.2	23.8	23.2
PARAMETERS CALCULATED FROM ANALYTICAL DATA																
Sum of constituents (mg/L)	1471	1463	1440	1432	9270	9244	9034	8973	9671	9931	10167	10079	16210	16194	16492	16537
Charge Balance																
Sum Cations (meq/L)	2.349E+01	2.335E+01	2.268E+01	2.227E+01	1.581E+02	1.573E+02	1.542E+02	1.507E+02	1.782E+02	1.874E+02	1.900E+02	1.885E+02	2.979E+02	2.965E+02	3.012E+02	3.028E+02
Sum Anions (meq/L)	-2.372E+01	-2.358E+01	-2.325E+01	-2.328E+01	-1.562E+02	-1.560E+02	-1.521E+02	-1.529E+02	-1.688E+02	-1.707E+02	-1.762E+02	-1.746E+02	-2.851E+02	-2.859E+02	-2.913E+02	-2.915E+02
Difference/Total (%)	-0.48%	-0.51%	-1.23%	-2.21%	0.61%	0.44%	0.69%	-0.74%	2.72%	4.65%	3.78%	3.81%	2.19%	1.82%	1.67%	1.91%
WATER CONTENT																
WCdry (glove box) (wt%)	4.02	4.02	3.99	3.99	3.22	3.22	4.18	4.18	3.50	3.50	3.59	3.59	2.61	2.61	2.74	2.74
WCdry 105°C (wt%)	4.21	4.21	4.08	4.08	3.54	3.54	3.28	3.28	3.85	3.85	3.75	3.75	3.32	3.32	3.24	3.24
WCdry 150°C (wt%)	4.29	4.29	4.14	4.14	3.60	3.60	3.34	3.34	4.00	4.00	3.93	3.93	3.48	3.48	3.40	3.40
CHLORINE CONTENT IN PORE WATER (by scaling up with WCdry)																
Cl^- (WCdry glove box) (mg/kg)	18463	18334	17967	17996	167984	167653	126161	126806	169321	171282	172365	170894	384604	385529	375307	375409
Cl^- (WCdry 105°C) (mg/kg)	17611	17488	17578	17605	152941	152639	160692	161515	154222	156008	165101	163692	303040	303768	317570	317657
Cl^- (WCdry 150°C) (mg/kg)	17313	17192	17291	17319	150474	150177	157949	158757	148238	149955	157698	156352	288718	289411	302413	302496
CHLORINE CONTENT OF SOLUTION AT EQUILIBRIUM																
Sample	S50VIT	S50VIT	S51VIT	S51VIT	S52VIT	S52VIT	S53VIT	S53VIT	S54VIT	S54VIT	S55VIT	S55VIT	S56VIT	S56VIT	S57VIT	S57VIT
Cl^- (mg/kg)	19576	19576	19704	19704	139990	139990	139709	139709	135679	135679	135103	135103	216910	216910	217852	217852
CHLORINE-ACCESSIBLE POROSITY (calculated with WCdry 150°C)																
Cl accessible porosity (% of total)	88	88	88	88	107	107	113	114	109	111	117	116	133	133	139	139

For comparison with the actual measured data, the isotopic composition of the equilibrated Vittel solution was calculated based on the isotopic compositions of the Queenston Shale porewater (diffusive exchange data in Hobbs et al., 2011; vacuum distillation in Intera, 2008, 2009) and Vittel standard water using the mass-balance equation:

$$\text{delta}_{EQU} \text{ (per mil)} = (PW * \text{delta}_{PW} + SOL * \text{delta}_{SOL}) / (PW+SOL) \qquad (18)$$

where delta_{EQU} is the isotopic composition ($\delta^{18}O$ or $\delta^{2}H$) of the solution and porewater at equilibrium, PW is the initial weight of water in the equilibrated rock, SOL is the initial weight of water in the Vittel standard solution used for equilibration, delta_{PW} is the initial isotopic composition of the porewater, and delta_{SOL} is the isotope composition of the standard Vittel water. Results are given in Table 38 and plotted in Figure 56A.

There is good correspondence (within the relatively large error) between the measured and calculated values when the data of Hobbs et al. (2011) are used. This gives confidence both in the obtained results for equilibrated Vittel solutions and in the fact that these fluids equilibrated with the original porewater.

In contrast, the isotopic compositions of the equilibrated solutions calculated using the Queenston Shale porewater isotopic composition obtained by 150°C vacuum distillation (Intera, 2008, 2009) are less strongly shifted towards positive values (see Table 38 and Figure 56B), and the correspondence of the calculated values with the measured isotopic compositions of the equilibrated solutions (Figure 55) is not as good as compositions obtained from diffusive exchange data (Hobbs et al., 2011; Figure 56A).

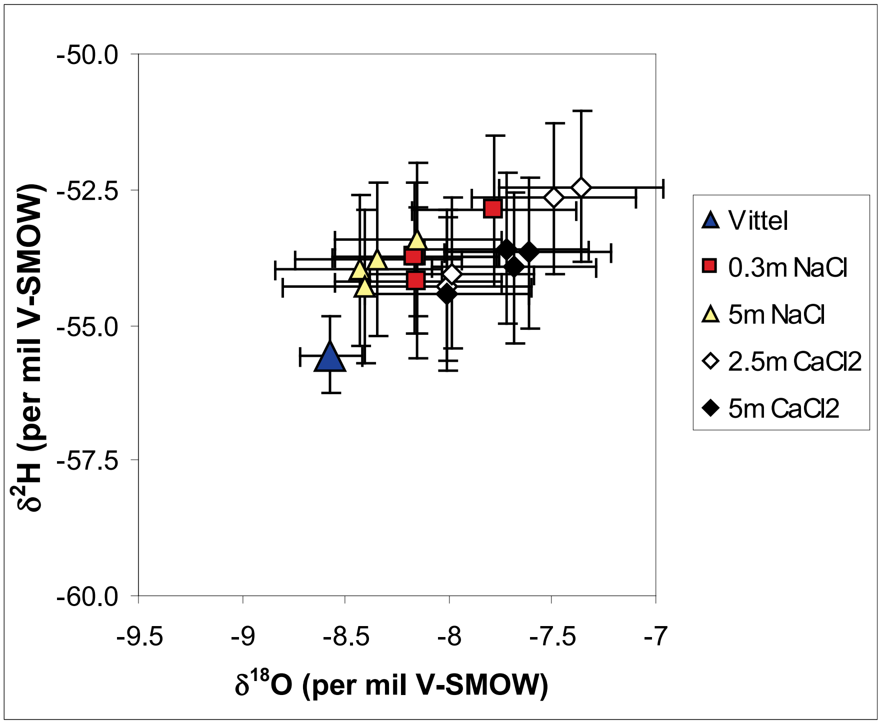


Figure 55: Isotopic Composition of the Synthetic Vittel Solutions After Equilibration with Queenston Shale Compared with Data for Pure Vittel Mineral Water; Error Bars are 2σ

Table 38: Water Isotope Composition of Vittel Solutions Equilibrated with Queenston Shale (Measured and Calculated)

Expt. #	PVC container ID	Equilibrated solution ID	Initial salinity of Vittel solution		Equilibrated solutions				WCwet 105°C of fresh rock	Weight of rock	Amount of water in rock	Weight of solution	Salinity of standard solution	Amount of water in solution	Calculated composition of equilibrated solution (using diffusive-exchange data)		Calculated composition of equilibrated solution (using vacuum distillation data)	
			NaCl (molal)	$CaCl_2$ (molal)	$\delta^{18}O$ ‰ V-SMOW	2σ ‰ V-SMOW	$\delta^{2}H$ ‰ V-SMOW	2σ ‰ V-SMOW	wt%	(g)	(g)	(g)	wt%	(g)	$\delta^{18}O$ ‰ V-SMOW	$\delta^{2}H$ ‰ V-SMOW	$\delta^{18}O$ ‰ V-SMOW	$\delta^{2}H$ ‰ V-SMOW
50	CAN1	S50VIT1	0.299	0	-8.1	0.4	-54.2	1.4	2.965	504.380	14.957	346.790	1.742	340.748	-8.1	-54.9	0.2	-55.2
50	CAN1	S50VIT2	0.299	0	-7.8	0.4	-52.9	1.4	2.965	504.380	14.957	346.790	1.742	340.748	-8.1	-54.9	-8.3	-55.2
51	CAN1A	S51VIT1	0.299	0	-8.2	0.4	-53.8	1.4	2.965	500.070	14.829	345.500	1.742	339.481	-8.1	-54.9	-8.3	-55.2
51	CAN1A	S51VIT2	0.299	0	-8.2	0.4	-53.8	1.4	2.965	500.070	14.829	345.500	1.742	339.481	-8.1	-54.9	-8.3	-55.2
52	CAN2	S52VIT1	4.980	0	-8.4	0.4	-54.0	1.4	2.965	502.010	14.887	363.770	29.193	257.576	-8.0	-54.7	-8.3	-55.1
52	CAN2	S52VIT2	4.980	0	-8.3	0.4	-53.8	1.4	2.965	502.010	14.887	363.770	29.193	257.576	-8.0	-54.7	-8.3	-55.1
53	CAN2A	S53VIT1	4.980	0	-8.4	0.4	-54.3	1.4	2.965	506.200	15.011	421.650	29.193	298.559	-8.1	-54.8	-8.3	-55.2
53	CAN2A	S53VIT2	4.980	0	-8.2	0.4	-53.4	1.4	2.965	506.200	15.011	421.650	29.193	298.559	-8.1	-54.8	-8.3	-55.2
54	CAN3	S54VIT1	0	2.499	-7.5	0.4	-52.7	1.4	2.860	656.020	18.762	454.120	27.693	328.363	-8.0	-54.7	-8.3	-55.2
54	CAN3	S54VIT2	0	2.499	-7.4	0.4	-52.5	1.4	2.860	656.020	18.762	454.120	27.693	328.363	-8.0	-54.7	-8.3	-55.2
55	CAN3A	S55VIT1	0	2.499	-8.0	0.4	-54.3	1.4	2.860	653.130	18.680	456.380	27.693	329.997	-8.0	-54.7	-8.3	-55.2
55	CAN3A	S55VIT2	0	2.499	-8.0	0.4	-54.0	1.4	2.860	653.130	18.680	456.380	27.693	329.997	-8.0	-54.7	-8.3	-55.2
56	CAN4	S56VIT1	0	4.991	-7.7	0.4	-53.9	1.4	2.860	664.590	19.007	487.110	55.515	216.691	-7.7	-54.2	-8.1	-55.0
56	CAN4	S46VIT2	0	4.991	-8.0	0.4	-54.4	1.4	2.860	664.590	19.007	487.110	55.515	216.691	-7.7	-54.2	-8.1	-55.0
57	CAN4A	S57VIT1	0	4.991	-7.6	0.4	-53.7	1.4	2.860	705.080	20.165	482.630	55.515	214.699	-7.7	-54.2	-8.1	-54.9
57	CAN4A	S57VIT2	0	4.991	-7.7	0.4	-53.6	1.4	2.860	705.080	20.165	482.630	55.515	214.699	-7.7	-54.2	-8.1	-54.9

Notes: NaF addition (for $CaCl_2$ solutions), distillation, and water isotope analysis were performed in duplicate for the solution of each container. Calculated isotope composition of equilibrated Vittel solution has been done considering the porewater in the Queenston Shale has $\delta^{18}O$ of +1.7‰ and $\delta^{2}H$ of -39.3‰ (diffusive exchange results in Hobbs et al, 2011), or $\delta^{18}O$ of -3‰ and $\delta^{2}H$ of -48‰ (vacuum distillation data, Intera 2008 and 2009). Pure Vittel water is at $\delta^{18}O$ of -8.57‰ and $\delta^{2}H$ of -55.56‰ VSMOW.

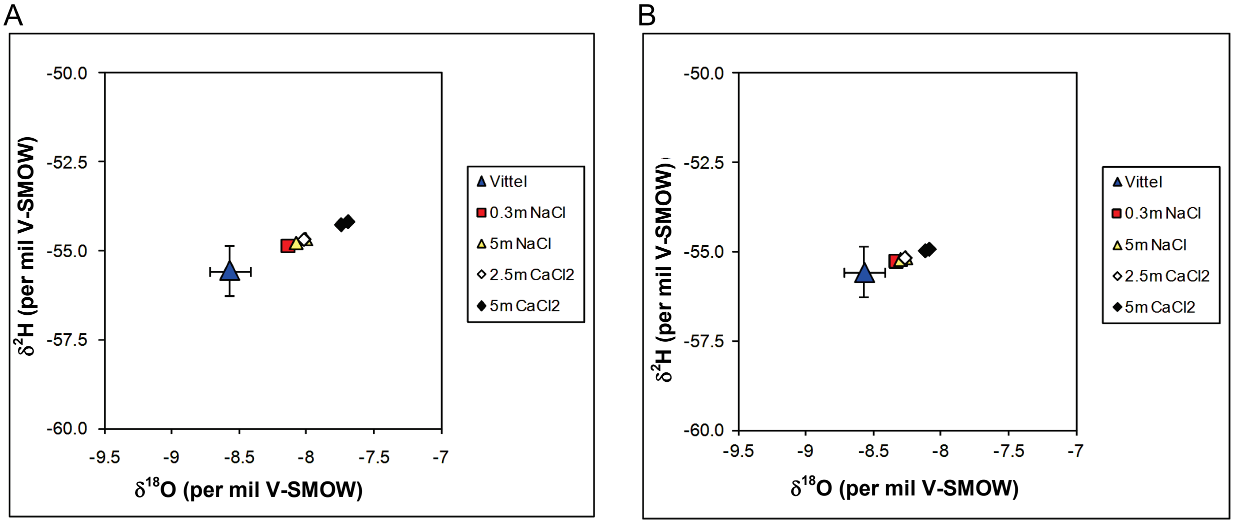


Figure 56: A) Calculated Isotope Composition of Equilibrated Vittel Solutions Considering the Queenston Shale Initial Isotope Porewater Composition Obtained by Diffusive Exchange at +1.7‰ δ^{18}O and -39.3‰ δ^{2}H VSMOW (Hobbs et al., 2011; Table 38); B) Calculated Isotope Composition of Equilibrated Vittel Solutions Considering an Initial Isotope Porewater Composition of -3‰ δ^{18}O and -48‰ δ^{2}H VSMOW (corresponds to average of data obtained by 150°C vacuum distillation, as in Intera, 2010; see Table 38)

7. ISOTOPE DIFFUSIVE EXCHANGE EXPERIMENTS

Isotope diffusive exchange experiments were performed in duplicate for rock samples previously equilibrated with Vittel solutions (Sections 6.7.4 and 6.8.4) and having the chemical compositions specified in Table 39. In these experiments, diffusive exchange via the vapour phase occurred between the porewater of the rock samples and test solutions prepared with LAB and TEW waters. Because porewater-saturated rocks were first equilibrated with synthetic Vittel solutions, the isotopic composition of the porewater and the surrounding Vittel solution (hereafter called artificial porewater) following equilibration should be the same. Therefore, diffusive exchange results should fit with data shown in Tables 36 and 38 for the Opalinus Clay and Queenston Shale experiments, respectively.

Initial and final weights of test solutions and rock samples for both the Opalinus Clay and Queenston Shale experiments are given in Table 40. All standard test solutions were analysed for δ^{18}O and δ^{2}H after 120°C distillation, with addition of NaF to $CaCl_2$ solutions. Analytical data and calculated water contents and isotopic compositions of the porewaters are given separately in the Opalinus Clay and Queenston Shale experiments in the following subsections.

Table 39: Diffusive Exchange Experiments

Experiment #	Salinity	
	NaCl (molal)	$CaCl_2$ (molal)
Opalinus Clay		
40 & 41	0.3	
42 & 43	5	
44 & 45		2.5
46 & 47		5
Queenston Shale		
50 & 51	0.3	
52 & 53	5	
54 & 55		2.5
56 & 57		5

Table 40: Weights of Test Solutions and Samples during Opalinus Clay and Queenston Shale Experiments

Expt.#	Start of expt.	End of expt.	Initial weight of test solutio[1]	Initial weight of test water (no salt)[1,2]	Final weight of test solution[1]	Final weight of test water (no salt)[1,2]	Weight difference: test solution (end-ini.)	Initial weight of sample rock[3]	Final weight of sample rock[3]	Weight difference: rock sample (end-ini.)	Initial mass of system[4]	Final mass of system[4]	Delta mass (end-ini.)
	(d.m.y)	(d.m.y)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)
Diffusive exchange with Opalinus Clay samples saturated with Vittel solutions													
40 LAB	19.01.2011	09.03.2011	5.049	4.962	4.998	4.911	-0.051	119.078	119.064	-0.014	738.983	738.908	-0.075
41 LAB	19.01.2011	09.03.2011	5.044	4.957	4.957	4.870	-0.087	118.801	118.801	0.000	727.621	727.562	-0.059
42 LAB	19.01.2011	09.03.2011	5.822	4.502	6.032	4.712	0.210	122.468	122.217	-0.251	734.036	734.011	-0.025
43 LAB	19.01.2011	09.03.2011	5.857	4.529	6.070	4.742	0.213	120.746	120.499	-0.247	737.376	737.366	-0.010
44 LAB	19.01.2011	09.03.2011	5.899	4.614	6.109	4.824	0.210	122.106	121.789	-0.317	733.93	733.839	-0.091
45 LAB	19.01.2011	09.03.2011	5.933	4.641	6.171	4.879	0.238	111.041	110.751	-0.290	724.641	724.594	-0.047
46 LAB	19.01.2011	09.03.2011	6.649	4.276	6.931	4.558	0.282	129.773	129.456	-0.317	750.233	750.212	-0.021
47 LAB	19.01.2011	09.03.2011	6.623	4.259	6.926	4.562	0.303	125.523	125.176	-0.347	735.452	735.439	-0.013
40 TEW	19.01.2011	09.03.2011	5.062	4.975	5.016	4.929	-0.046	144.701	144.693	-0.008	752.426	752.375	-0.051
1 TEW	19.01.2011	09.03.2011	5.039	4.952	4.964	4.877	-0.075	113.587	113.625	0.038	729.476	729.451	-0.025
42 TEW	19.01.2011	09.03.2011	5.817	4.499	6.012	4.694	0.195	113.196	112.946	-0.250	729.918	729.873	-0.045
43 TEW	19.01.2011	09.03.2011	5.819	4.500	6.015	4.696	0.196	129.809	129.569	-0.240	751.807	751.791	-0.016
44 TEW	19.01.2011	09.03.2011	5.951	4.654	6.134	4.837	0.183	109.095	108.829	-0.266	724.127	724.089	-0.038
45 TEW	19.01.2011	09.03.2011	5.100	3.988	5.320	4.208	0.220	107.054	106.796	-0.258	725.934	725.898	-0.036
46 TEW	19.01.2011	09.03.2011	6.653	4.280	6.951	4.578	0.298	157.437	157.100	-0.337	767.11	767.093	-0.017
47 TEW	19.01.2011	09.03.2011	6.631	4.266	6.874	4.509	0.243	120.291	119.846	-0.445	737.514	737.318	-0.196
Diffusive exchange with Queenston Shale samples saturated with Vittel solutions													
50LAB	25.05.2011	10.08.2011	5.055	4.967	4.421	4.333	-0.634	130.143	130.716	0.573	741.903	741.844	-0.059
51LAB	25.05.2011	10.08.2011	5.062	4.974	4.376	4.288	-0.686	122.200	122.816	0.616	741.564	741.497	-0.067
52LAB	25.05.2011	10.08.2011	5.812	4.494	5.711	4.393	-0.101	126.463	126.525	0.062	740.816	740.784	-0.032
53LAB	25.05.2011	10.08.2011	5.787	4.475	5.696	4.384	-0.091	130.727	130.786	0.059	747.813	747.784	-0.029
54LAB	25.05.2011	10.08.2011	6.013	4.703	5.881	4.571	-0.132	152.538	152.617	0.079	768.879	768.826	-0.053
55LAB	25.05.2011	10.08.2011	5.998	4.691	5.890	4.583	-0.108	172.024	172.100	0.076	785.149	785.12	-0.029
56LAB	25.05.2011	10.08.2011	6.631	4.264	6.679	4.312	0.048	165.591	165.533	-0.058	774.772	774.761	-0.011
57LAB	25.05.2011	10.08.2011	6.719	4.321	6.763	4.365	0.044	159.002	158.940	-0.062	783.488	783.47	-0.018
50TEW	25.05.2011	10.08.2011	5.029	4.942	4.423	4.336	-0.606	108.876	109.442	0.566	728.278	728.245	-0.033
51TEW	25.05.2011	10.08.2011	5.041	4.954	4.309	4.222	-0.732	144.614	145.264	0.650	763.024	762.945	-0.079
52TEW	25.05.2011	10.08.2011	5.799	4.485	5.677	4.363	-0.122	123.352	123.415	0.063	739.456	739.404	-0.052
53TEW	25.05.2011	10.08.2011	5.775	4.466	5.688	4.379	-0.087	150.700	150.754	0.054	764.284	764.262	-0.022
54TEW	25.05.2011	10.08.2011	5.998	4.691	5.813	4.506	-0.185	163.673	163.700	0.027	779.755	779.605	-0.150
55TEW	25.05.2011	10.08.2011	5.995	4.688	5.865	4.558	-0.130	173.278	173.329	0.051	784.453	784.387	-0.066
56TEW	25.05.2011	10.08.2011	6.573	4.229	6.619	4.275	0.046	170.797	170.741	-0.056	796.512	796.502	-0.010
57TEW	25.05.2011	10.08.2011	6.723	4.325	6.769	4.371	0.046	196.204	196.148	-0.056	821.274	821.264	-0.010

[1] Test solutions are LAB or TEW (experiment label). [2] Calculated from the salinity (see Table 15). [3] All sample rocks were equilibrated with Vittel water. [4] System = container + rock sample + test solution + Petri dishes

7.1 OPALINUS CLAY RESULTS

In Table 41, the $\delta^{18}O$ and $\delta^{2}H$ values of the artificial porewaters (standard Vittel solutions that were equilibrated with the Opalinus Clay samples) are compared with the isotope composition of the porewater, as calculated from the results of the diffusive exchange experiments.

Figure 57 compares the $\delta^{18}O$ and $\delta^{2}H$ values of the porewaters in Opalinus Clay to that of the artificial porewaters. Results are identical within 2σ error. Figure 58 shows that the calculated isotopic compositions ($\delta^{18}O$ and $\delta^{2}H$ values) of the porewaters do not depend on salinity or type of salt (NaCl or $CaCl_2$).

Water contents (wt%) were calculated using the $\delta^{18}O$ and $\delta^{2}H$ data by the diffusive exchange experiments and are reported as $WC_{\delta 18O}$ and $WC_{\delta 2H}$ (Table 42). Figure 59 shows a good correlation between $WC_{\delta 18O}$ and $WC_{\delta 2H}$, with all the data plotting on a 1:1 slope within 2σ error. The water contents correlate inversely with salinity (Figure 60), which is consistent with the decreased swelling capacity of smectite clay with increasing salinity. Water contents measured gravimetrically by drying the rocks at 105°C or 150°C after the diffusive exchange experiments are lower than the values obtained by diffusive exchange, especially at low salinity (Figure 60 and Table 20).

Table 41: Calculated Isotope Composition of Porewater in Opalinus Clay Experiments

Expt. #	Test Water Salinity (molal)		Test Solution "LAB" (‰ V-SMOW)				Test Solution "TEW" (‰ V-SMOW)				Calculated Porewater Isotopic Composition (‰ V-SMOW)				Artificial Porewater Isotopic Composition (‰ V-SMOW)			
	NaCl	$CaCl_2$	Initial $\delta^{18}O$	Final $\delta^{18}O$	Initial $\delta^{2}H$	Final $\delta^{2}H$	Initial $\delta^{18}O$	Final $\delta^{18}O$	Initial $\delta^{2}H$	Final $\delta^{2}H$	$\delta^{18}O$	2σ	$\delta^{2}H$	2σ	$\delta^{18}O$	2σ	$\delta^{2}H$	2σ
40	0.3	0.0	-11.00	-8.64	-77.07	-60.27	-27.09	-11.99	-208.68	-86.03	-7.9	0.7	-55.1	2.2	-8.3	0.3	-54.5	1.0
41	0.3	0.0	-11.00	-8.76	-77.07	-59.84	-27.09	-12.82	-208.68	-93.03	-8.0	0.6	-54.3	2.2	-8.4	0.3	-55.0	1.0
42	5.0	0.0	-11.00	-9.01	-77.07	-61.72	-27.09	-14.35	-208.68	-105.52	-8.1	0.7	-54.7	2.4	-8.5	0.3	-55.1	1.0
43	5.0	0.0	-11.00	-9.02	-77.07	-61.68	-27.09	-13.95	-208.68	-102.54	-8.1	0.7	-54.1	2.6	-8.4	0.3	-55.0	1.0
44	0.0	2.5	-11.00	-8.70	-77.07	-61.19	-27.09	-13.73	-208.68	-102.97	-7.8	0.7	-54.8	2.3	-8.3	0.3	-55.3	1.0
45	0.0	2.5	-11.00	-8.89	-77.07	-61.70	-27.09	-12.69	-208.68	-96.15	-8.1	0.7	-55.5	2.4	-8.3	0.3	-55.6	1.0
46	0.0	5.0	-11.00	-8.90	-77.07	-62.18	-27.09	*-12.74*	-208.68	-95.08	-8.1	0.7	-56.0	2.4	-8.0	0.3	-55.5	1.0
47	0.0	5.0	-11.00	-8.85	-77.07	-62.14	-27.09	-13.28	-208.68	-101.05	-8.1	0.6	-56.2	2.3	-8.3	0.3	-55.9	1.0

Note: “Artificial porewater” refers to the Vittel solution equilibrated with the rock and its original porewater (see Table 26).

Table 42: Water Contents Calculated from Opalinus Clay Experiments

Exper. #	Test Water Salinity		Calculated Water Content (Wet)			
	NaCl (molal)	$CaCl_2$ (molal)	$WC_{\delta 18O}$ (wt%)	2STD (wt%)	$WC_{\delta 2H}$ (wt%)	2STD (wt%)
40	0.3	0.0	12.6	2.8	13.7	1.4
41	0.3	0.0	13.0	2.4	13.0	1.0
42	5.0	0.0	8.1	1.3	8.1	0.5
43	5.0	0.0	7.7	1.3	7.6	0.6
44	0.0	2.5	9.6	1.5	9.4	0.6
45	0.0	2.5	11.8	2.3	10.3	0.8
46	0.0	5.0	8.3	1.7	7.9	0.7
47	0.0	5.0	9.4	1.6	8.5	0.6

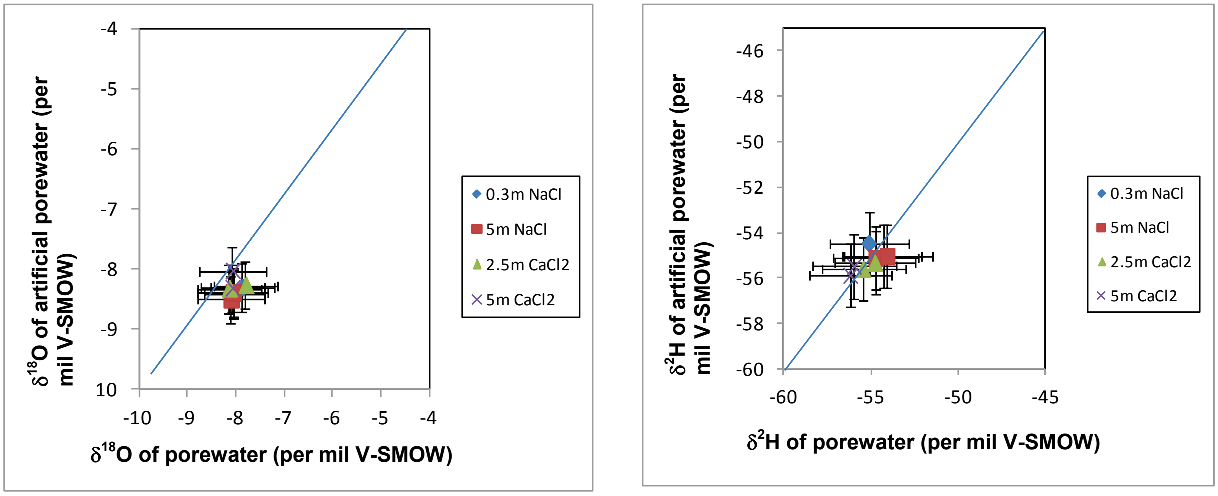


Figure 57: Measured $\delta^{18}O$ and $\delta^{2}H$ Values of Artificial Porewater versus Isotopic Composition of the Respective Porewater in Opalinus Clay, Obtained by Diffusive Exchange; Error Bars are 2σ and Data is Presented in Table 41

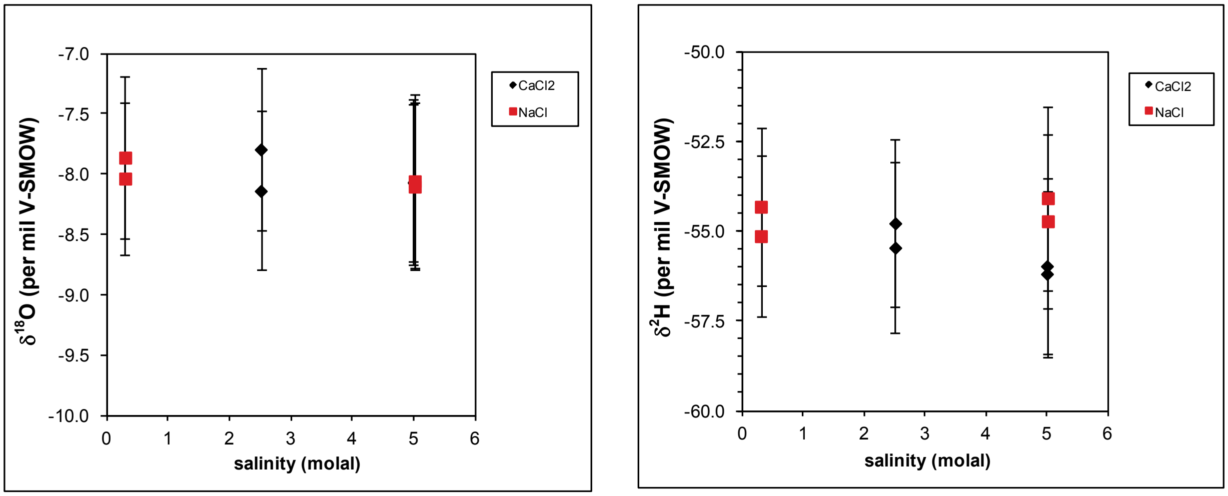


Figure 58: Porewater $\delta^{18}O$ and $\delta^{2}H$ Values Calculated from Diffusive-Exchange Experiments versus Salinity of the Corresponding Artificial Porewater in Opalinus Clay Experiments

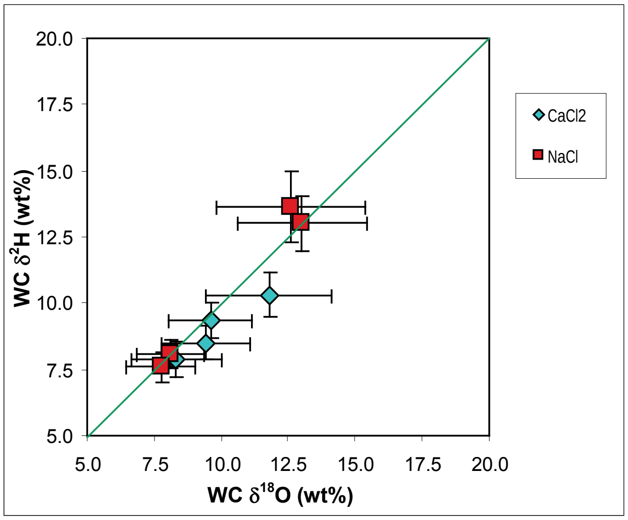


Figure 59: Calculated $WC_{\delta 18O}$ versus $WC_{\delta 2H}$ Values of Opalinus Clay Rock Equilibrated with Vittel Synthetic Solutions; Error Bars are 2σ

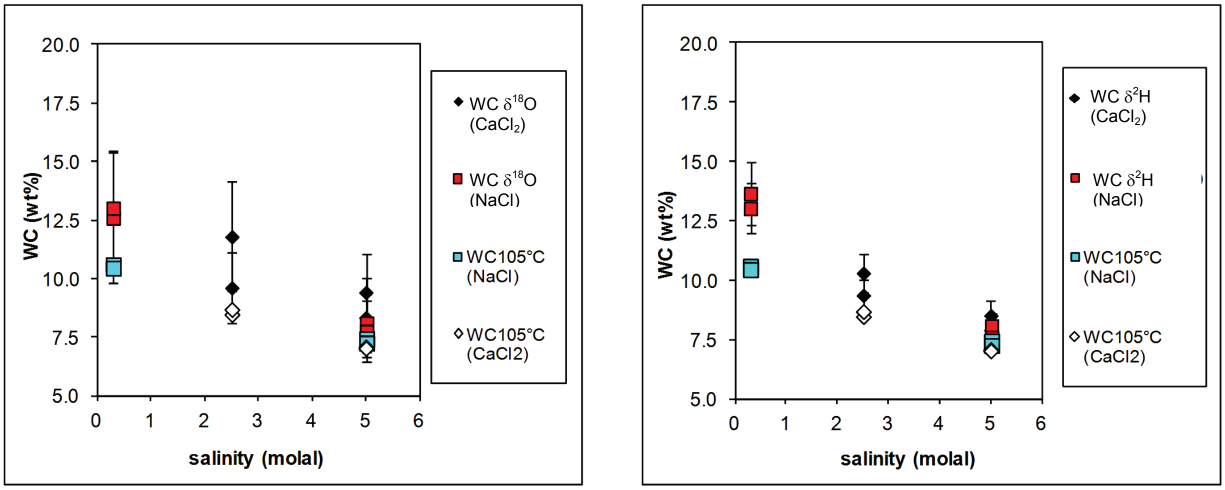


Figure 60: Calculated WC$_{\delta 18O}$ and WC$_{\delta 2H}$ Values versus Salinity of Synthetic Porewater in Opalinus Clay Samples, Compared with Gravimetric Water Contents Obtained by Drying at 105°C After Diffusive Exchange Experiment; Water Contents Obtained by Drying at 150°C (not shown, see Table 20) are Slightly Higher for the 2.5 and 5 Molal Experiments, and Correlation with WC$_{\delta 18O}$ and WC$_{\delta 2H}$ is Slightly Better; Error Bars are 2σ

7.2 QUEENSTON SHALE RESULTS

In Table 43, the δ^{18}O and δ^{2}H values of the artificial porewater (standard Vittel solutions that were equilibrated with the Queenston Shale samples) are compared with the isotopic composition of the porewater, as calculated from the results of the diffusive exchange experiments.

Figure 61 compares the δ^{18}O and δ^{2}H values of the porewaters in Queenston Shale with the respective values of the artificial porewaters. With the exception of one experiment (experiment 50), all the data coincide within the 2σ error, with the calculated porewater compositions being slightly more positive than the values of the equilibrated solutions. Experiment 50 shows values significantly shifted towards heavier isotopic compositions, which likely indicates vapour loss during distillation. In this perturbed experiment, Queenston Shale was equilibrated with a 0.3 molal NaCl Vittel solution.

Figure 62 compares the porewater δ^{18}O and δ^{2}H values with the salinity of the artificial porewater. Excluding experiment 50, the measured isotope compositions are independent of the salinity and type of salt of the artificial solution.

Table 43: Calculated Isotope Composition of Porewater in Queenston Shale Experiments

Expt. #	Test Water Salinity (molal)		Test Solution "LAB" (‰ V-SMOW)				Test Solution "TEW" (‰ V-SMOW)				Calculated Porewater Isotopic Composition (‰ V-SMOW)				Artificial Porewater Isotopic Composition (‰ V-SMOW)			
	NaCl	$CaCl_2$	Initial $\delta^{18}O$	Final $\delta^{18}O$	Initial $\delta^{2}H$	Final $\delta^{2}H$	Initial $\delta^{18}O$	Final $\delta^{18}O$	Initial $\delta^{2}H$	Final $\delta^{2}H$	$\delta^{18}O$	2STD	$\delta^{2}H$	2STD	$\delta^{18}O$	2STD	$\delta^{2}H$	2STD
50	0.3	0.0	-11.00	-7.90	-77.07	-60.64	-27.09	-16.40	-208.68	-121.58	-5.2	1.04	-49.2	2.96	-8.0	0.4	-53.6	1.4
51	0.3	0.0	-11.00	-8.82	-77.07	-62.67	-27.09	-14.87	-208.68	-110.17	-7.2	0.91	-52.7	3.00	-8.2	-8.2	-8.2	-8.2
52	5.0	0.0	-11.00	-9.27	-77.07	-64.64	-27.09	-16.96	-208.68	-127.91	-7.7	0.93	-53.4	3.31	-8.4	0.4	-53.9	1.4
53	5.0	0.0	-11.00	-8.95	-77.07	-64.17	-27.09	-16.19	-208.68	-122.28	-6.9	1.05	-52.1	3.47	-8.3	0.4	-53.9	1.4
54	0.0	2.5	-11.00	-8.55	-77.07	-63.10	-27.09	-14.71	-208.68	-114.73	-6.9	0.88	-53.3	2.97	-7.4	0.4	-52.6	1.4
55	0.0	2.5	-11.00	-8.43	-77.07	-62.09	-27.09	-15.05	-208.68	-114.31	-6.6	0.90	-52.1	2.90	-8.0	0.4	-54.2	1.4
56	0.0	5.0	-11.00	-8.74	-77.07	-63.71	-27.09	-15.65	-208.68	-116.94	-7.0	0.93	-54.2	2.95	-7.8	0.4	-54.2	1.4
57	0.0	5.0	-11.00	-8.76	-77.07	-64.00	-27.09	-15.46	-208.68	-114.34	-6.7	1.05	-53.6	3.18	-7.7	0.4	-53.6	1.4

Note: “Artificial porewater” refers to the Vittel solution equilibrated with the rock and its original porewater (see Table 38).

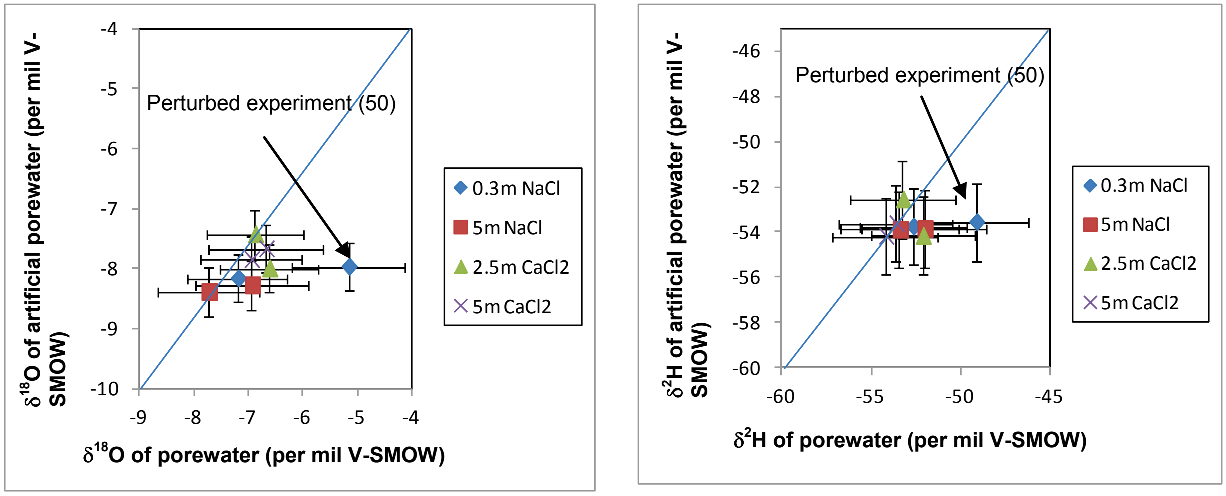


Figure 61: Measured δ^{18}O and δ^{2}H Values of Artificial Porewaters versus Isotope Compositions of the Respective Porewaters in Queenston Shale; Error Bars are 2σ; Experiment 50 is Perturbed

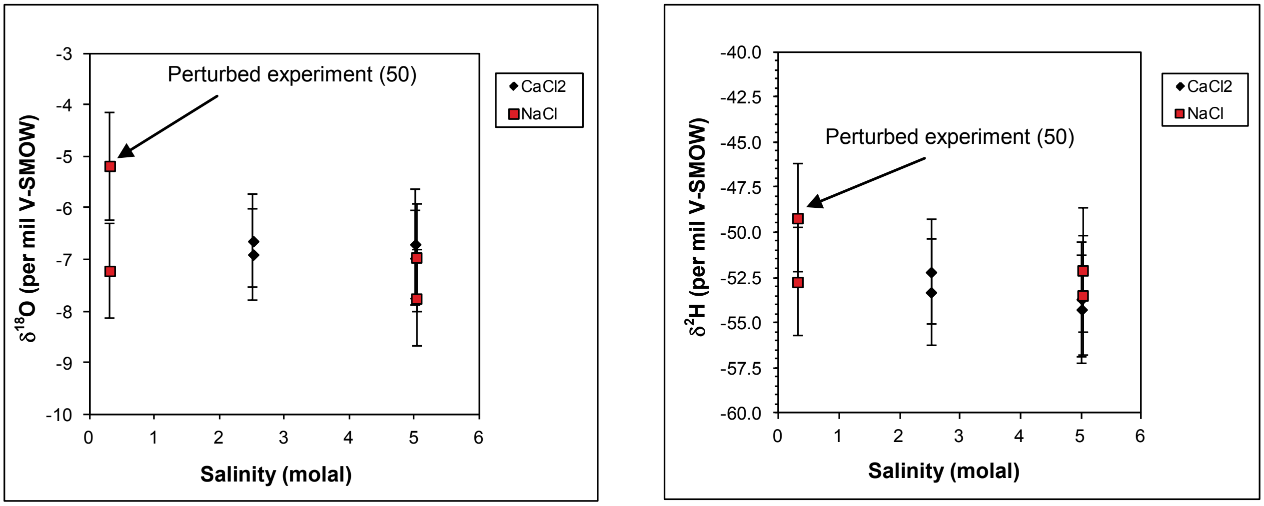


Figure 62: Calculated δ^{18}O and δ^{2}H Porewater Values versus Salinity of the Corresponding Artificial Porewater in Queenston Shale Experiments; Error Bars are 2σ; the Perturbed Experiment (experiment 50) is Shown

Water contents (wt% wet) were calculated using the δ^{18}O and δ^{2}H data of the diffusive exchange experiments and are reported as $WC_{\delta18O}$ and $WC_{\delta2H}$ (Table 44). Figure 63 shows that water contents obtained from both test solutions are the same, within error, except for the perturbed experiment 50. Comparisons of $WC_{\delta18O}$ and $WC_{\delta2H}$ with water contents obtained gravimetrically (by drying at 150°C) are shown in Figure 64. There is a relatively good correlation between diffusive exchange and gravimetric data, except for 0.3 molal NaCl values, which tend to be higher than the gravimetric data. Experiment 50 is perturbed, but data from the other experiment (experiment 51) shows also that $WC_{\delta18O}$ and $WC_{\delta2H}$ are systematically higher than the gravimetric data.

Table 44: Water Contents Calculated from Queenston Shale Diffusive Exchange Experiments

Experiment	Test water salinity		Calculated water content (wet)			
	NaCl (molal)	$CaCl_2$ (molal)	$WC_{\delta18O}$ (wt%)	2σ (wt%)	$WC_{\delta2H}$ (wt%)	2σ (wt%)
50	0.3	0.0	4.3	0.6	5.5	0.3
51	0.3	0.0	5.5	0.9	5.9	0.4
52	5.0	0.0	4.0	0.6	3.9	0.2
53	5.0	0.0	3.5	0.5	3.6	0.2
54	0.0	2.5	4.5	0.7	4.4	0.3
55	0.0	2.5	3.9	0.6	4.1	0.3
56	0.0	5.0	3.3	0.5	3.6	0.2
57	0.0	5.0	2.9	0.5	3.4	0.2

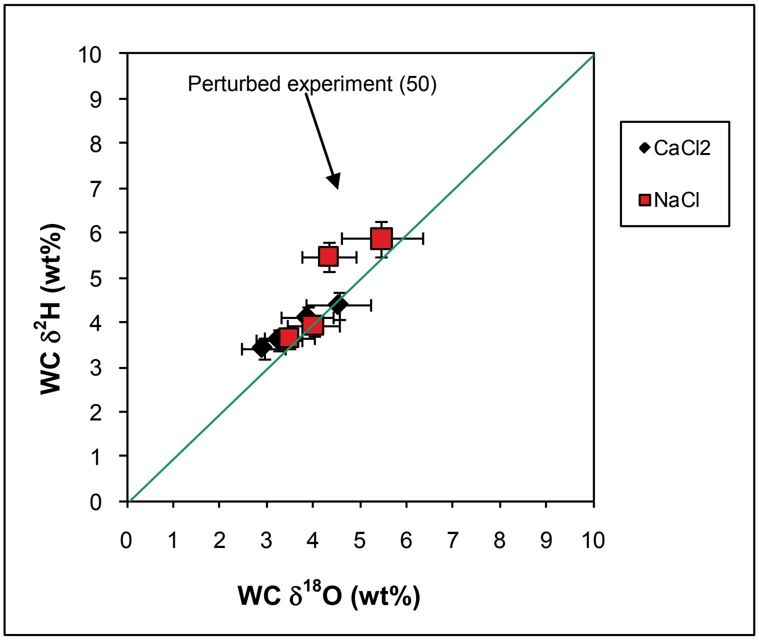


Figure 63: Calculated $WC_{\delta18O}$ versus $WC_{\delta2H}$ Values of Queenston Shale Rock Equilibrated with Vittel Synthetic Solutions; Error Bars are 2σ; Experiment 50 is Perturbed

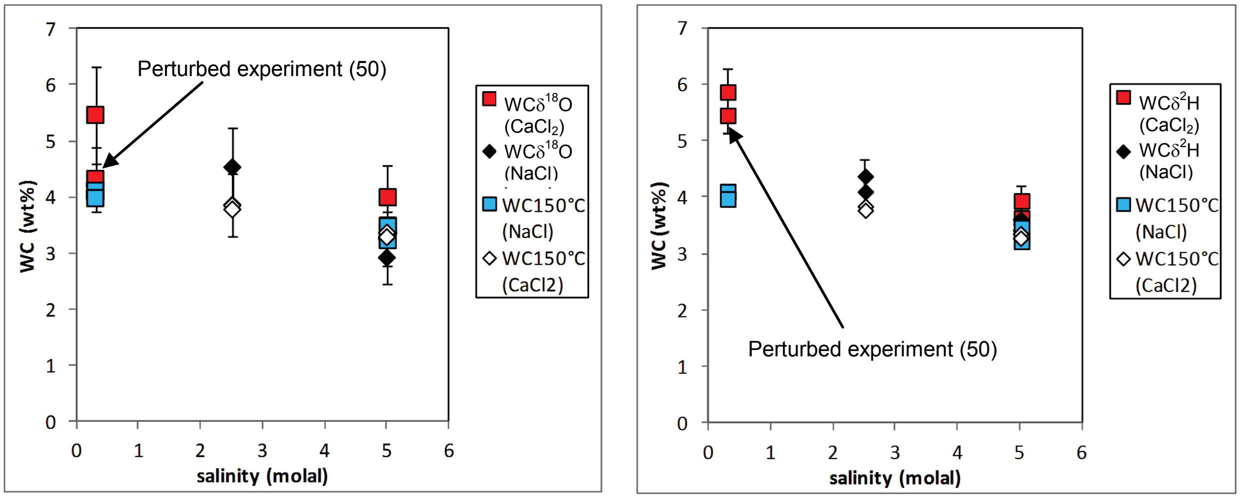


Figure 64: Calculated WC$_{\delta 18O}$ and WC$_{\delta 2H}$ Values versus Salinity of Artificial Porewater in Queenston Shale Samples Compared with Gravimetric Water Contents Obtained by Drying at 150°C After Diffusive Exchange Experiment; WC Obtained by Drying at 105°C (not shown, see Table 31) are a Little Bit Lower; Error Bars on WC by Diffusive Exchange are 2σ

8. DISCUSSION

8.1 EVIDENCE FOR ATTAINMENT OF EQUILIBRIUM

For the purpose of benchmarking the diffusive exchange method, it is most important to ensure that both oxygen and hydrogen isotopic equilibrium is attained between the porewater and the equilibrating solution. Because equilibration times for chloride concentration are higher than for water isotopes (see Table B.5), it follows that attainment of equilibrium for chloride implies that the water isotopes have already equilibrated.

Two clay-rich rocks were considered for the benchmarking of the diffusive-exchange method adapted to saline porewaters: the Opalinus Clay from northern Switzerland, and the Queenston Shale from Ontario, Canada. For an intact rock core of the Opalinus Clay, times of 11, 14 and 44 days were predicted, respectively, for $\delta^{18}O$, $\delta^{2}H$ and Cl^- to reach equilibrium between the synthetic solution and the porewater (Appendix B, Table B.5). To be on the safe side, smaller rock pieces, with diameters of approximately 2 to 4 cm, and a longer equilibration time (62 days for the Opalinus Clay) were used. For intact core samples of the Queenston Shale, much longer equilibration times of 62, 55, and 130 days for $\delta^{18}O$, $\delta^{2}H$ and Cl^-, respectively, were predicted between the equilibrating synthetic solution and the porewater (Appendix B, Table B.5). In these experiments, rock pieces with diameters of approximately 2 to 4 cm and an equilibration time of 90 days were used in an attempt to ensure that equilibrium had been reached.

For the Opalinus Clay, the time-series Cl^- concentrations measured during equilibration suggest a slight decrease in concentration from the start of the experiment to 24 hours; following that the concentrations remained stable (Figures 36 and 37). Although these results may indicate that equilibration between the porewater in the core and equilibrating solution occurred quickly, it must be noted that the Cl^- concentrations measured in the original Vittel solution and in all time-series samples are the same within the estimated 2σ analytical uncertainty of ± 10%. However, the fact that both equilibration experiments using 0.3 molal NaCl and 2.5 molal $CaCl_2$ solutions follow the same pattern (Figures 36 and 37) suggests that the real error associated with these data is probably far less than the estimated 10% relative 2σ error, which would imply that the equilibration time-series profile is meaningful. In the equilibrations conducted for the Opalinus Clay, the stable water isotopic composition of the final, equilibrated Vittel solution was the same as the original Vittel mineral water, within analytical uncertainty. This is because the $\delta^{18}O$ and $\delta^{2}H$ values of Vittel mineral water are similar to those of the porewater of the Opalinus Clay sample used in the experiments (T. Gimmi – personal communication, 2012). Consequently, the only data that support equilibration was attained are the results of the chloride time-series. Although the shift in chloride content during equilibration of the synthetic solutions is below the 2σ error, we estimate that the equilibrated material is suited for the benchmarking of the isotope diffusive exchange technique with porewater of different salinities.

The time-series measurements of Cl^- for the Queenston Shale suggest that approximately 4 days were required to attain equilibrium between the original Vittel solution and Cl^- in the porewater (Figures 53 and 54). In this case, the difference between the Cl^- concentration of initial Vittel solution and the time-series measurements for the equilibration experiment using solution at 0.3 m NaCl is greater than the analytical uncertainty and can therefore be reliably interpreted as an evidence for equilibrium attainment for Cl^-, and indirectly for $\delta^{18}O$ and δ^2H. Time-series for cations (Na^+, K^+, Ca^{+2}, and Mg^{+2}) gave similar results to those for Cl^-.

After equilibration with rock pieces of the Queenston Shale, the final isotopic composition ($\delta^{18}O$, δ^2H) of the synthetic Vittel solutions was significantly different from that of the original synthetic Vittel solutions (Figure 55, Tables 14 and 38), with an enrichment of up to 1.2‰ for $\delta^{18}O$ and 3.1‰ for δ^2H. The obtained values correspond well with the isotopic composition of the equilibrated synthetic solution calculated using the porewater compositions determined for the Queenston Shale by Hobbs et al. (2011) using the diffusive exchange technique and by Intera (2008, 2009) using vacuum distillation. A better fit was obtained using the Hobbs et al. (2011) data than the Intera (2008 and 2009) data.

The chloride content of the porewater obtained by up-scaling of the aqueous leach data permits the evaluation of the fraction of the chloride-accessible porosity relative to the total porosity. Results for Opalinus Clay showed chloride-accessible porosity percentage of 79 ± 1% for 0.3 m NaCl solutions, 97 ± 3.5% for 5 m NaCl solutions, 96.5 ± 2.5% for 2.5 m $CaCl_2$ solutions, and 119 ± 1.5% for 5 m $CaCl_2$ solutions. For the Queenston Shale, results were 88 ± 0% for 0.3 m NaCl solutions, 110 ± 3% for 5 m NaCl solutions, 113 ± 4% for 2.5 m $CaCl_2$ solutions, and 136 ± 3% for 5 m $CaCl_2$ solutions. These results are, at least, in part, overestimated (it is impossible to have more than 100% of porewater-accessible porosity). There is no clear explanation for this result, as the eventual incomplete drying of the $CaCl_2$ solution at 150°C might not explain the value of 110% obtained for the Queenston Shale saturated with 5 m NaCl.

8.2 BENCHMARKING OF THE DIFFUSIVE EXCHANGE TECHNIQUE

Calculated porewater isotopic composition of Opalinus Clay rock equilibrated with synthetic Vittel saline solutions fit within 2σ errors of the isotopic composition of the corresponding equilibrated synthetic solutions at all salinities. This indicates that the porewater salinity does not play a role in the diffusive exchange method when using test water with similar salinity and chemistry. The benchmarking of the method is, therefore, successful in defining the isotopic composition of the porewater at very different salinities and salt compositions.

In contrast, and for unknown reasons, the calculated water contents of the equilibrated samples tend to be slightly higher than the values obtained by the gravimetric method (drying at 105°C and 150°C), especially at low salinity.

9. CONCLUSIONS AND RECOMMENDATIONS

Diffusive exchange experiments using NaCl test and sample solutions, or $CaCl_2$ test and sample solutions, with salinities of 0.3, 1, 2.5 and 5 molal, produced accurate results. All calculated isotopic compositions and water contents were in agreement with the EVIAN sample solution within 2σ error. It follows that the adapted diffusive exchange technique works well when chemical composition and water activities are matched on both sides of the experiment (standard test solution and sample).

Diffusive exchange experiments performed with 5 molal NaCl test and sample solutions, but at different sample-to-test solution mass ratios, showed that acceptable errors are obtained only at ratios >0.5. The relative mass ratio of test and sample solutions only affects the magnitude of the error, but the tested isotopic compositions are independent of this ratio. The practical implication of these results is that, for successful diffusive exchange experiments, the connected porewater content of the rock sample must be >0.5 wt% when using 3 grams of water in the test solution (which is a practical minimum for the distillation-isotope analysis procedure) and ~300 grams of rock sample is required (which is a practical maximum). Reducing the rock sample size or its water content would lead to increased errors, such that the determined isotopic compositions would be meaningless.

The results show that matching of water activity between the test solution and sample is critical, because the time needed to equilibrate two solutions in terms of water activity (or salinity) by transferring water through the vapour phase can be longer than 30 days (i.e., longer than the routinely-used equilibration time). Because water activity equilibration is faster at higher salinities, it is recommended to use test water with lower than or equal water activity to that of the sample.

Having similar water activities but different chemical compositions (e.g., NaCl versus $CaCl_2$ solutions) on both sides of the experiment (i.e., in the test and sample solutions) has a significant effect on the $\delta^{18}O$ value of the test water, but a nearly negligible effect on the $\delta^{2}H$ value. The isotopic fractionation coefficient between liquid water and vapour depends on the salinity and the type of salt, and, therefore, the test and sample solutions may have different isotopic composition at equilibrium, depending on their chemical compositions.

Because of the very limited $\delta^{2}H$ shift observed in these experiments, $\delta^{2}H$ data obtained by the adapted diffusive exchange technique are probably reliable within <5‰, independent of the salt composition, provided the water activity matching is adequate ($\Delta a_w < 0.05$). Maximum deviation for $\delta^{18}O$, due to isotopic fractionation in the NaCl-$CaCl_2$ system, is about 1‰. This shift can be corrected if good constraints on the chemical composition of the sample solutions are available. These considerations are valid for brines dominated by NaCl and/or $CaCl_2$, but the effect of the salt-induced isotope fractionation might be higher if $MgCl_2$ and/or KCl are dominant species (see Figure 1).

Experiments using Cambrian groundwater (NaCl-$CaCl_2$ dominated complex brine) from borehole DGR3 at the Bruce Nuclear Site (sample OGW-10; Heagle and Pinder, 2009) showed that: i) direct NaF treatment and distillation is an effective way to analyze the water isotope composition of complex brines and an alternative to the direct H_2 and CO_2 equilibration method (GasBench), in which the measured isotopic compositions must be corrected for salt-induced water isotope fractionation following Horita et al. (1993a and 1993b); and ii) the results obtained by the diffusive exchange method using NaCl or $CaCl_2$ test water to match the brine water activity gave slightly shifted values, significant only for $\delta^{18}O$ (up to 1‰), but still within or very close to the 2σ error. When a standard correction is applied, considering only the major components of the brine (i.e., NaCl and $CaCl_2$), the correction appears sufficient to correct these shifts.

The adapted diffusive exchange technique works if the following criteria have been met:

(1) Good matching (Δa_w <0.05) of the water activity of the test solution with the sample solution – the test water has lower or equal water activity compared to that of the sample;
(2) The mass of water in the sample solution must be at least 0.5 times the mass of water in the test solution; and
(3) The effect of differing chemical compositions in the test solution and in the sample is weak to negligible for the calculated $\delta^{2}H$ value, but weak to just significant (up to 1‰ in the NaCl-$CaCl_2$ system) for the $\delta^{18}O$ value (i.e., very close to the 2σ error). Correction of these deviations can be made, at least broadly, if constraints on the chemical composition of the sample solution are available.

Equilibration of synthetic solutions of 0.3 and 5 molal NaCl, and 2.5 and 5 molal $CaCl_2$ was achieved with samples of Opalinus Clay that were saturated with the original porewaters. This was achieved by immersing 2 to 4 cm diameter rock pieces into air-tight PVC containers for 62 days. The same result was achieved in 90 days for the Queenston Shale using the same method. In both cases, the rocks never disaggregated during these experiments, even at 0.3 molal NaCl. The density of the equilibrated rocks is, in all cases, lower than that of intact porewater-saturated rock, and increases with increasing salinity. The general lowering of rock density is probably due to the lowering of the confining pressure compared to in-situ conditions. The rock density correlates with the water content, which is higher at low salinity.

Data obtained from Opalinus Clay and Queenston Shale experiments indicate that the diffusive exchange method gives reliable results for the isotope composition of the porewater at all salinities. The benchmarking of the method for the porewater isotopic composition is, therefore, successful when chemistries of the porewaters and test waters are similar.

For unknown reasons, the use of the diffusive exchange method to obtain the rock water content gave good results at high salinities (≥2.5 molal), but slightly overestimated values at low salinity (0.3 molal).

Conceptually, comparison of the chemical composition of the equilibrated synthetic solution with the porewater chloride content calculated by up-scaling the aqueous leach data allows the calculation of the fraction of chloride-accessible porosity (over total porosity). The measured results are possibly realistic for the 0.3 molal NaCl equilibration experiments, but tend to be higher than 100% at higher salinities. Incomplete drying during the gravimetric measurements, even at 150°C, could be an explanation (in particular when $CaCl_2$ was used), but is not completely satisfactory.

The 0.8 chloride-accessible porosity ratio obtained from experiments with Opalinus Clay saturated with 0.3 molal NaCl artificial porewater is higher than the well established value of ~0.5 at Mont Terri (Pearson et al., 2003). There are two reasons for that difference. First, the water content of the Opalinus Clay saturated with the synthetic solution is higher than the original in-situ value (see Section 6.7.1.1 and 6.7.1.3), probably because stress release increases the pore space and the swelling capacity. Second, the 0.3 molal salinity is higher than that of the porewater of the Opalinus Clay sample used in the experiments, which is ~0.17 molal NaCl (Pearson and Waber, 2006).

The fact that the rock properties (water content, density, etc.) are not conserved during the equilibration with the standard Vittel synthetic solution is not an obstacle for the benchmarking purpose of the experiments because we compare the isotopic composition of the synthetic porewater with the composition of the equilibrated solution surrounding the rock. Because it has been shown that equilibrium was reached between the solution and the porewater, these should give similar isotopic compositions; an exception to this outcome could result if major isotopic fractionation processes occur between the anion-accessible and the anion-free porosity. Results showed that such fractionation processes, if any, have effects that are below the analytical errors of the method. These observations are valid for the two rocks (Opalinus Clay and Queenston Shale) and for all salinities used in the experiments.

Possible further investigation of the diffusive exchange method could include the following:

(1) Conduct diffusive exchange experiments using test water of significantly different chemical composition than the equilibrated porewater (e.g., NaCl test water with $CaCl_2$-dominated porewater);
(2) Test other solution compositions with SO_4^{-2} and Mg^{+2} as major components;
(3) Test the diffusive exchange method with rocks bearing minerals that might perturb the water isotopic system and/or the water activity equilibrium between the sample and the test water (e.g., anhydrite, gypsum, bentonite); and,
(4) Investigate the possible isotopic fractionation between bound water and free water in bentonite variously saturated with water of known isotopic composition.

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REFERENCES

Al, T., Y. Xiang, D. Loomer and L. Cavé. 2010. Measurement of diffusion properties by X-ray radiography and by through-diffusion techniques using iodide and tritium tracers: Core samples from DGR-3 and DGR-4. TR-08-27. Revision 0B, May 7, 2010. DGR Site Characterization Document, Intera Engineering Project 08-200.

Al, T., Y. Xiang and L. Cavé. 2008. Measurement of Diffusion Properties by X-Ray Radiography and by Through-Diffusion Techniques Using Iodide and Tritium Tracers: Core Samples from OS-1 and DGR-2. TR-07-17. DGR Site Characterization Document, Intera Engineering Project 08-200.

Altinier, M.V., S. Savoye, J.-L. Michelot, C. Beaucaire, M. Massault, D. Tessier and H.N. Waber. 2006. The isotopic composition of porewater from Tournemire argillite (France): An inter-comparison study. Physics and Chemistry of the Earth, v. 32, 209-218.

Clark, I., I. Liu, H. Mohammadzadeh, R. Mohapatra, P. Zhang and M. Wilk. 2009. Porewater and gas analyses in DGR-3 & DGR-4 core. Draft Technical Report TR-08-19, Revision 0E, November 19, 2009. DGR Site Characterization Document, Intera Engineering Project 08-200.

Coplen, T.B., J.D. Wildman and J. Chen. 1991. Improvement in the gaseous hydrogen-water equilibration technique for hydrogen isotope ratio analysis. Analytical Chemistry, 63, 910-912.

Crank, J. 1975. The Mathematics of Diffusion. Oxford University Press, Oxford, U.K.

CRC. 1987. Handbook of Chemistry and Physics, 1st Edition. Weast, R.C., ed., CRC Press Inc., Boca Raton, Florida, USA.

de Haller, A., J. Spangenberg and M. Koroleva. 2008. Analysis of stable water isotopes in brines: Methodology study. Progress Report PR 08-02, Rock-Water Interaction Group, Institute of Geological Sciences, University of Bern, Switzerland.

de Haller, A., J. Spangenberg, J. Smuda and M. Koroleva. 2009. The stable H and O isotope analysis of small highly saline water samples: a methodological study. Goldschmidt Conference Abstract 2009, Geochimica et Cosmochimica Acta, 73, A274.

Gimmi, T. and H.N. Waber. 2004. Modelling of tracer profiles in porewater of argillaceous rocks in the Benken Borehole: Stable water isotopes, chloride, and chlorine isotopes. Nagra Technical Report NTB 04-05, Wettingen (Switzerland), 91 p.

Gimmi, T., H.N. Waber, A. Gautschi and A. Rubel. 2007. Stable water isotopes in porewater of Jurassic argillaceous rocks as tracers for solute transport over large spatial and temporal scales. Water Res. 43, 4.

Heagle, D. and L. Pinder. 2009. Opportunistic groundwater sampling in DGR-3 and DGR-4. Draft Technical Report TR-08-18, Revision 0B, August 20th, 2009. DGR Site Characterization Document, Intera Engineering Project 08-200.

Hobbs, M.Y. and H.N. Waber. 2002. Porewater Chemistry (PC) Experiment: Evaluation of the diffusive exchange method for the determination of $\delta^{18}O$ and $\delta^{2}H$ in Opalinus Clay porewater from Mont Terri. Mont Terri Project, Technical Note 2002-24.

Hobbs, M., A. de Haller, M. Koroleva, M. Mazurek, J. Spangenberg, U. Mäder and D. Meier. 2011. Borehole DGR-3 and DGR-4 porewater investigations. TR-08-40. Revision 0, March 31, 2011. DGR Site Characterization Document, Intera Engineering Project 08-200.

Horita, J., D.J. Wesolowski and D.R. Cole. 1993a. The activity-composition relationship of oxygen and hydrogen isotopes in aqueous salt solutions: I. vapour-liquid water equilibration of single salt solutions from 50 to 100°C. Geochimica et Cosmochimica Acta, 57(12), 2797-2817.

Horita, J., D.R. Cole and D.J. Wesolowski. 1993b. The activity-composition relationship of oxygen and hydrogen isotopes in aqueous salt solutions: II. Vapour-liquid water equilibration of mixed salt solutions from 50 to 100°C and geochemical implications. Geochimica et Cosmochimica Acta, 57(19), 4703-4711.

Horita, J., D.R. Cole and D.J. Wesolowski. 1995. The activity-composition relationship of oxygen and hydrogen isotopes in aqueous salt solutions: III. Vapour-liquid water equilibration of mixed salt solutions from 50 to 100°C and geochemical implications. Geochimica et Cosmochimica Acta, v. 59(6), p. 1139-1151.

Intera. 2008. Porewater and Gas Analyses in DGR-1 & DGR-2 Core. TR-07-21. Revision 0C, May 5, 2008. DGR Site Characterization Document, Intera Engineering Project 06-219.

Intera. 2009. Porewater and Gas Analyses in DGR-3 & DGR-4 Core. TR-08-19. Revision 0E, November 19, 2010. DGR Site Characterization Document, Intera Engineering Project 08-200.

Intera. 2010. Vacuum distillation experiments on DGR core. TR-08-37. Revision 0, May 21, 2010. DGR Site Characterization Document, Intera Engineering Project 08-200.

Jackson, R. and I. Clark. 2008. Phase 2 Lab testing of opportunistic and Westbay samples of groundwater. Test Plan TP-08-13. DGR Site Characterization Document, Intera Engineering Project 08-200.

Jarrett, M.A., B. Gusler, T. Xiang and D. Clapper. 2004. Improved competence in water activity measurement. Paper presented at the AADE (American Association of Drilling Engineers) Technology Conference, Houston, Texas, April 6-7, 2004. AADE-04-DF-HO-31.

Jury, W.A., W.R. Gardner and W.H. Gardner. 1991. Soil Physics, 5th Edition. John Wiley & Sons Inc.

Koroleva, M., A. de Haller, U. Mäder, H.N. Waber and M. Mazurek. 2009. Borehole DGR-2: Porewater investigations. Technical Report TR 08-02, RWI Group, Institute of Geological Sciences, University of Bern, Switzerland, 127 p.

Mäder, U.K., H.N. Waber and A. Gautschi. 2004. New method for porewater extraction from claystone and determination of transport properties with results for Opalinus Clay (Switzerland). In: Wanty, R.B. and R.R. Seal II (eds.): Proceedings of the 11th Symposium on Water-Rock Interaction WRI-11, Saratoga Springs, NY, USA. Balkema/Taylor & Francis, Leiden, The Netherlands, p. 445 - 449.

Mazurek, M., P. Alt-Epping, A. Bath, T. Gimmi and H.N. Waber. 2009. Natural tracer profiles across argillaceous formations: The CLAYTRAC Project. OECD Nuclear Energy Agency, NEA No. 6253.

Nagra. 2002. Projekt Opalinuston: Synthese der geowissenschaftlichen Untersuchungsergebnisse: Entsorgungsnachweis für abgebrannte Brennelemente, verglaste hochaktive sowie langlebige mittelaktive Abfälle: Nagra Technischer Bericht NTB 02-03, Nagra, Wettingen, Switzerland.

Pearson, F.J., D. Arcos, A. Bath, J.Y. Boisson, A.M. Fernandez, H.E. Gaebler, E.C. Gaucher, A. Gautschi, L. Griffault, P. Hernan and H.N. Waber. 2003. Mont Terri Project - Geochemistry of Water in the Opalinus Clay Formation at the Mont Terri Rock Laboratory. Reports of the Federal Office of Water and Geology (FOWG), Geology Series No. 5.

Pearson, F.J. and H.N. Waber. 2006. DR Experiment: Experimental Water Chemistry. Mont Terri Project Technical Note 2006-26, 18 January 2006, 33 p.

Pitzer, K.S. 1987. A thermodynamic model for aqueous solutions of liquid-like density. In Thermodynamic Modeling of Geologic Materials: Minerals, Fluids and Melts, I.S.E. Carmichael and H.P. Eugster (eds.), Reviews in Mineralogy, 17, 97-142.

Rimstidt, J.D. 1997. Gangue mineral transport and deposition. In: Barnes, H.L. ed. Geochemistry of hydrothermal ore deposits, third edition: J. Wiley & sons, p. 487-515.

Robinson, R.A. and R.H. Stokes. 1959. Electrolyte Solutions. Butterworth & Co., Ltd., London, England, 559 p.

Rogge, T. 1997. Eine molecular-diffusive Methode zur Bestimmung des Poren-wassergehaltes und der Zusammensetzung von stabilen Isotopen im Poren-wasser von Gestein. Unpublished Master Thesis, University of Heidelberg, Germany.

Rübel, A.P., C. Sonntag, J. Lippmann, F.J. Pearson and A. Gautschi. 2002. Solute transport in formations of very low permeability: profiles of stable isotope and dissolved noble gas contents of porewater in the Opalinus Clay, Mont Terri, Switzerland. Geochimica et Cosmochimica Acta, 66, 1311-1321.

Spangenberg, J.E., B. Dold, M.L. Vogt and H.R. Pfeifer. 2007. The stable hydrogen and oxygen isotope composition of waters from porphyry copper mine tailings. Environmental Science & Technology 41, 1870-1876.

Spangenberg, J.E. and T.W. Vennemann. 2008. The stable hydrogen and oxygen isotope variation of water stored in polyethylene terephthalate (PET) bottles. Rapid Communications in Mass Spectrometry 22, 672-676.

Spangenberg J. E. 2012. Caution on the storage of waters and aqueous solutions in plastic containers for hydrogen and oxygen stable isotope analysis. Rapid Communications in Mass Spectrometry, 26, 2627-2636.

Sposito G. 1990. Molecular Models of Ion Adsorption on Mineral Surfaces. In: M.F. Hochella and A.F. White (Eds.). Mineral-Water Interface Geochemistry. Reviews in Mineralogy Vol. 23, Min. Soc. America, Washington D.C., 261-279.

Waber, H.N., U.K. Mäder, M. Koroleva and A. de Haller. 2007. Testing Methods for the Characterisation of Saline Porewater in an Ordovician Limestone (Cobourg Formation, St. Mary's Quarry, Ontario). Rock-Water Interaction (RWI), Institute of Geological Sciences, University of Bern, Switzerland, TR-07-01, 112 p.

Waber, H.N. (ed.). 2008. Borehole Oftringen: Mineralogy, Porosimetry, Geochemistry, Porewater Chemistry: Nagra, Wettingen, Switzerland, Nagra Arbeitsbericht NAB 08-18, 235 p.

Walsh, R. 2008. Phase 1 Compilation and consolidation of field and laboratory data for hydrogeological properties. Technical Report TR-08-10. DGR Site Characterization Document, Intera Engineering Project 08-200.

APPENDIX A: METHODOLOGY

CONTENTS

A.1 WATER ACTIVITY

Water activity (a_w) of the rock samples was measured directly from the relative humidity of the air immediately surrounding the sample, using a HygroPalm AW1 meter with a resolution of ±0.001a_w and an accuracy of ±0.015a_w. The water activity meter was operated in A_wQuick mode. The measurement was conducted immediately after unpacking the drillcore sample, on rock material that had been coarsely crushed using a hammer. The same procedure was applied to rocks equilibrated with synthetic solution.

A.2 GRAVIMETRIC WATER CONTENT

The only quantity of the porewater that is directly measurable is the water content obtained gravimetrically by drying. The weight proportion of water (i.e., H_2O only) in the rock is the water content (WC). In high-salinity systems, the water content is markedly lower than the porewater content (PWC), which is defined as the weight proportion of brine (i.e., water plus solutes) in the rock. In the literature, PWC is sometimes called brine content or fluid content. The water content (WC) is required to express porewater concentrations of solutes in molality units (mol/kg_{H2O}), whereas the porewater content (PWC) is required to use molarity or concentration units ($mol/L_{solution}$ or $g/L_{solution}$, respectively), or to estimate porosity (porewater-loss porosity).

The gravimetric water content, WC, was obtained by drying two saturated rock sample aliquots of approximately 75 to 300 g in an oven to a constant weight at a temperature of 105°C. Duplicate measurements were performed for all samples. The gravimetric water content $WC_{Grav.wet}$ (expressed as a weight fraction) relative to the wet mass m_{wet} of the rock was then calculated from the change in weight upon drying (m_{wet}-m_{dry}):

$$WC_{Grav.wet} = \frac{m_{wet} - m_{dry}}{m_{wet}} \tag{1}$$

with m_{wet} = wet mass of the rock and m_{dry} = dry mass of the rock. Water content $WC_{Grav.dry}$ as weight fraction related to dry mass can be calculated from:

$$WC_{Grav.dry} = \frac{m_{wet} - m_{dry}}{m_{dry}} \tag{2}$$

A.3 BULK WET DENSITY

Bulk wet density ($\rho_{b.wet}$) was measured in duplicate using the paraffin displacement method. The principle of the method is the calculation of bulk wet density from sample mass and volume, making use of Archimedes' principle. Measurements were done on two separate, homogeneous rock pieces with masses of between 7 and 40 g. The volume of each rock piece was determined by weighing the rock in air and during immersion into paraffin (ρ_p = 0.86 g/cm^3 at 20°C) using a density accessory kit (Mettler Toledo). The bulk wet density was calculated according to:

$$\rho_{b.wet} = \frac{\rho_p * m_{wet.rock}}{m_{wet.rock} - m_{(wet.rock)P}} \tag{3}$$

where $m_{wet.rock}$ is the mass of the rock in air and $m_{(wet.rock)P}$ is the mass of the rock in paraffin.

A.4 GRAIN DENSITY

The grain density, ρ_g, was measured by kerosene-pycnometry in duplicate. The volume of the pycnometer was derived from the weight of the pycnometer filled with kerosene initially ($m_{k1+pycn}$). The density of kerosene (ρ_k = 0.78 g/cm^3 at 20°C) was checked using an aerometer. Before the measurement, equilibrated rock samples (broken to 2-4 cm diameter) were dried in a N_2 atmosphere glove box with desiccants for 49 days (Opalinus Clay) and 96 days (Queenston Shale). Then, the rock samples were powdered in a tungsten carbide mill and put again in the glove box until analysis. Approximately 15 g of the sample were transferred into the pycnometer, which was subsequently filled with kerosene while continuously removing the air by vacuum pump. The rock sample volume was calculated as the difference between the volume of kerosene in the pycnometer with and without the rock material. The grain density was then obtained according to:

$$\rho_g = \frac{(m_{rock+pycn} - m_{pycn})}{m_{rock+pycn} - m_{pycn} + m_{k1+pycn} - m_{rock+k2+pycn}} * \rho_k \tag{4}$$

where $m_{rock+pycn}$ is the sum of the masses of the dry, powdered rock sample and the pycnometer, m_{pycn} is the mass of the pycnometer, $m_{k1+pycn}$ is the mass of the pycnometer filled with the kerosene up to the meniscus, and $m_{rock+k2+pycn}$ is the mass of the of the pycnometer with the rock sample inside and filled with the kerosene up to the meniscus.

The combined relative error on the grain density is approximately:

$$\frac{\sigma_{\rho_g}}{\rho_g} \approx \sqrt{6}\,\frac{\sigma_m}{m_{rock}} + \frac{\sigma_{\rho_k}}{\rho_k} \approx \frac{\sigma_{\rho_k}}{\rho_k} \tag{5}$$

The relative error (precision) on grain density is dominated by the error in kerosene density and amounts to 1.3% using σ_m = 0.002 g, m_{rock} = 15 g, σ_k = 0.01 g/cm^3 and ρ_k = 0.78 g/cm^3.

A.5 AQUEOUS LEACHING

Rock samples were weighed to three decimal places just after their removal from a glove box. Samples were then milled for about 1-2 minutes in a tungsten carbide ring mill. The powder must be still grainy (not as fine as for XRD), to minimize possible contribution from fluid inclusions. To minimize contact with air, samples were put back into the glove box immediately after milling (or at least stored in vacuumed desiccators until returned to the glove box). The ultra-pure water used for leaching was oxygen-free; it was prepared by bubbling with N_2 gas for 30 minutes in the glove box. Aqueous extraction was performed in a glove box in duplicate using ultra-pure water and 30 grams of powdered (<60 µm) rock material. The weighed powdered solid was put into a polypropylene tube and covered with de-oxygenated water to give a solid:liquid ratio of 1:1. Each sample was shaken end-over-end for 48 hours. This length of time was chosen to equilibrate the extracted solution with calcite in the rocks. The tubes were then centrifuged for 10 minutes to separate solution and solid phases. After filtration through a 0.45 µm syringe filter, the supernatant solutions were immediately analysed for pH and alkalinity (by titration). Two aliquots of the solution were prepared for cation (to be acidified with 1 to 2 drops of concentrated HNO_3) and anion (not acidified) analyses and placed into the refrigerator. The remaining rock powder was stored dry for grain density measurements.

A.6 CHEMICAL ANALYSIS OF SALINE SOLUTIONS

Major anions and cations were analysed by ion-chromatography on a Metrohm 861 Advanced Compact IC-system. The relative analytical error of these determinations is ≤10%.

Minor and trace concentrations of K^+, Mg^{+2} and Sr^{+2} were analysed by ICP optical emission spectrometry using a Varian ICP 720-ES system. The relative analytical error of these determinations is ≤10%.

Alkalinity and pH of the solutions were analysed by titration using a Metrohm Titrino 785 DMP system.

A.7 DIFFUSIVE EXCHANGE EXPERIMENTS

The details of the method are given in Section 5 of the report. The principle is that a known mass of porewater-saturated rock is equilibrated with two standard test waters of known weight and different isotopic composition in two sealed containers. The isotope compositions of the two equilibrated test waters are measured and these values allow the calculation of the isotope composition of the porewater and the water content of the rock. In order to prevent mass transfer and isotopic fractionation (e.g., Horita et al., 1993a and 1993b) between the test water and the porewater of the rock through desiccation-condensation mechanisms, the activity of the test water must be adjusted in an attempt to match it to the water activity of the rock sample. This is performed by addition of NaCl or $CaCl_2$. Such saline solutions must be distilled before isotopic analysis and NaF has to be added first to remove Ca^{+2} from $CaCl_2$ solution (de Haller et al., 2009).

Approximately 100-200 g of rock and 5 mL of test solution were used for the individual experiments. Because rocks were equilibrated with synthetic solutions of known composition, test solutions with the same chemical composition as the synthetic solution before equilibration were used, in order to closely match the water activity and major ion chemistry of the porewater. The equilibration time of the three-reservoir system (porewater in rock sample, test water in crystallisation dish, air inside the container) essentially depends on the size of the rock pieces, the rock permeability and the distance of the rock piece to the test water. Typical equilibration times for the Opalinus Clay range between 2.5 and 20 days (Rübel et al., 2002; Hobbs and

Waber, 2002). A conservative equilibration time of 49 days was used for the Opalinus Clay experiments, and 77 days for the Queenston Shale experiments.

The test water, rock material and the entire container were weighed before and after the equilibration experiment to check the tightness of the container and to ensure that no transfer of test water or porewater occurred. No transfer occurred if the weights of the test water and rock material are the same at the beginning and end of experiment. After equilibration, the test water was removed from the crystallization dish, stored in a vapour-tight small PE-flask prior to isotopic analysis. The rock material was dried in an oven to constant mass at 105ºC in order to obtain the gravimetric water content of the rock material.

REFERENCES

de Haller, A., J. Spangenberg, J. Smuda and M. Koroleva. 2009. The stable H and O isotope analysis of small highly saline water samples: a methodological study. Goldschmidt Conference Abstract 2009. Geochimica et Cosmochimica Acta 73, A274.

Hobbs, M.Y. and H.N. Waber. 2002. Pore Water Chemistry (PC) Experiment: Evaluation of the diffusive exchange method for the determination of $\delta^{18}O$ and $\delta^{2}H$ in Opalinus Clay pore water from Mont Terri. Mont Terri Project, Technical Note 2002-24.

Horita, J., D.J. Wesolowski and D.R. Cole. 1993a. The activity-composition relationship of oxygen and hydrogen isotopes in aqueous salt solutions: I. vapour-liquid water equilibration of single salt solutions from 50 to 100°C. Geochimica et Cosmochimica Acta 57(12), 2797-2817.

Horita, J., D.R. Cole and D.J. Wesolowski. 1993b. The activity-composition relationship of oxygen and hydrogen isotopes in aqueous salt solutions: II. Vapour-liquid water equilibration of mixed salt solutions from 50 to 100°C and geochemical implications. Geochimica et Cosmochimica Acta 57(19), 4703-4711.

Rübel, A.P., C. Sonntag, J. Lippmann, F.J. Pearson and A. Gautschi. 2002. Solute transport in formations of very low permeability: profiles of stable isotope and dissolved noble gas contents of pore water in the Opalinus Clay, Mont Terri, Switzerland. Geochimica et Cosmochimica Acta 66, 1311-1321

APPENDIX B

CONTENTS

B.1 EQUILIBRATION OF ROCK SAMPLES WITH SYNTHETIC POREWATER - SCOPING CALCULATIONS

In addition to the evaluations of the adapted diffusive exchange technique and associated analytical methods, the second objective of this research is to benchmark the technique. The approach investigated in this study is to develop a procedure to precondition natural rock materials to contain a porewater of known chemical and isotopic composition. The stable isotope compositions of the porewaters in these preconditioned rock materials could then be determined using the adapted diffusive exchange technique to provide a benchmark. As a first step in developing a preconditioning procedure, scoping calculations were conducted to investigate two different experimental techniques for replacing in-situ porewater in rock materials with a synthetic porewater of known composition. The times required to replace the in-situ porewater in saturated, intact rock samples using the in/out diffusion technique and the advective displacement technique were estimated. Scoping calculations were conducted for a total of three different formations relevant to Canadian and Swiss nuclear waste management programs:

- Queenston formation from southwestern Ontario, Canada;
- Cobourg formation from southwestern Ontario, Canada and
- Opalinus Clay, Switzerland.

The tracers considered in the scoping calculations include chloride (Cl^-) and stable water isotopes (δ^2H, $\delta^{18}O$).

B1.1 Description of Potential Porewater Replacement Techniques

The two different techniques considered in the scoping calculations for replacement of porewater in cores are i) in/out diffusion and ii) advective displacement. These methods are briefly described below.

In the in/out diffusion technique, a core sample is immersed in an experimental test solution of known chemical and isotopic (δ^2H, $\delta^{18}O$) composition, sealed in a container and stored at ambient temperature (nearly constant). The approach of the system to steady-state conditions can be monitored by withdrawing small (0.5 mL) subsamples of the experimental solution over time and measuring the concentration of chemically conservative anions (e.g., Cl^-, Br^-). After attainment of steady-state conditions, the experiment is terminated. The final mass of the core and its bulk wet density are determined and the final chemical (pH, alkalinity, major ions) and isotopic compositions of experimental test solution are measured.

In the advective displacement (or core infiltration) method, a synthetic porewater is used to displace the in-situ porewater by applying a hydraulic gradient across a core that is confined under a constant hydraulic pressure; this confining pressure must be greater than the applied, infiltration pressure (Mäder et al., 2004). Successful displacement of porewater using this method hinges on the presence of sufficient connected porosity, the absence of preferred flow paths and the ability to induce a relatively homogeneous advective-dispersive displacement front between the injected artificial porewater and the displaced in-situ porewater. Displaced porewater can be collected at the outlet side of the experimental apparatus and, if a sufficient volume is available, analyzed for pH, major ion concentrations and isotopic composition.

B.2 INPUT PARAMETERS

The scoping calculations require a variety of input parameters including the geometry of the sample, estimates of the natural (or in-situ) porewater composition, as well as hydrological and petrophysical parameters. The parameters employed in the scoping calculations are described below.

B.2.1 Sample Geometry

For the purpose of the scoping calculations and to enable comparisons between the times calculated for porewater replacement using the two experimental techniques, the sample is assumed to be an intact core segment of cylindrical shape. The same sample geometry was used for all rock formations examined (Table B1).

Table B1: Specifications for Sample Geometry (In/Out Diffusion and Advective Displacement)

Parameter	Value	Remarks
Radius of sample	3.8 cm	Measured on a sample from the DGR-3 borehole
Length of sample	20 cm	Maximum length of sample that can be used with equipment for in/out diffusion experiments
Volume of sample	907 cm^3	Calculated
Retardation coefficient	1	Corresponds to no sorption at all. This assumption is reasonable for both Cl^- and water isotopes

B.2.2 Hydrogeological, Geochemical and Petrophysical Properties

The hydrogeological, geochemical and petrophysical parameters required for the scoping calculations were taken from the literature (Table B2 through Table B4). The values were selected (or estimated, as documented in the tables) to provide a rough estimate of the time required to replace porewater. It is assumed that the core was drilled vertically through the bedding of each formation. Using the in/out diffusion technique, diffusion into and out of the core will be primarily in a direction parallel to bedding; therefore, the relevant pore diffusion coefficients are those determined parallel to bedding. If pore diffusion coefficients (D_p) were not available in the literature, a value was calculated from the effective diffusion coefficient (D_e) using the following relationship:

$$\mathrm{D}_p = \frac{D_e}{\phi_a} \tag{1}$$

where ϕ_a is the proportion of the total, physical porosity accessible to a particular ion (e.g., Cl^-) or to water molecules. In some cases, the only available value for the pore diffusion coefficient was determined normal to bedding. In this case, the observed anisotropy in the effective diffusion coefficients (e.g., for HTO) was used to estimate the pore diffusion coefficient parallel to bedding.

For both the Queenston and Cobourg formations, it was assumed that Cl^- ions had access to the water-accessible porosity; anion exclusion was not considered. Evidence from Al et al. (2008) supports this assumption for limestone from the Cobourg Formation, in which the I^--accessible porosity was observed to be similar to the water-accessible porosity. For samples from the Queenston Formation, there was evidence that the I^--accessible porosity may only be approximately 50% of the water-accessible porosity (Al et al., 2008).

In the advective displacement technique, the direction of flow through the core is perpendicular to bedding. Therefore, the relevant hydraulic conductivity is that measured normal to bedding.

Table B2: Hydrogeological, Geochemical and Petrophysical Input Parameters for Opalinus Clay, Mont Terri, Switzerland. All Values Are from Mazurek et al. (2009)

	Opalinus Clay, Mont Terri	
[1]Parameters	Value	Remarks
Water-accessible porosity in shaly unit	0.18	Assumption is made that total physical porosity is accessible to water molecules
Fraction of physical porosity accessible to anions in shaly unit	0.54	
Calculated Cl$^-$-accessible porosity in shaly unit	0.097	Calculated from water-accessible porosity using fraction accessible to anions
Pore diffusion coefficient for Cl$^-$,$\perp$ to bedding in shaly unit	4.8 x 10^{-11} m^2/s	
Pore diffusion coefficient for HTO, $\perp$ to bedding in shaly unit	7.9 10^{-11} m^2/s	
Anisotropy of D_p in shaly unit (II/$\perp$)	4	Refers to measured anisotropy in D_p, as reported by Mazurek et al. 2009
Calculated pore diffusion coefficient for Cl$^-$, II to bedding	1.9 10^{-10} m^2/s	Calculated from D_p $\perp$ using anisotropy in D_p
Calculated pore diffusion coefficient for HTO, II to bedding	3.2 10^{-10} m^2/s	Calculated using anisotropy in D_p
Hydraulic conductivity in shaly units, $\perp$ to bedding	4 $\cdot 10^{-14}$ m/s	Average value (range 4 $\cdot 10^{-15}$ to 4 $\cdot 10^{-13}$ m/s). This parameter is used in calculations for advective displacement technique where infiltration direction for fluid is normal to bedding
Initial Cl$^-$	0.39 mol/l	Maximum Cl$^-$ concentration within clay-rich unit
Initial δ^{18}O	-7.1‰	Maximum δ^{18}O value measured within the formation
Initial δ^{2}H	-46.6‰	Maximum δ^{2}H value measured within the formation

[1] Data listed refer to screened data sets employed in modeling of tracer profiles within the CLAYTRAC Project (Mazurek et al., 2009). HTO refers to tritiated water.

Table B3: Hydrogeological, Geochemical and Petrophysical Input Parameters for the Queenston Formation, Canada

		Queenston Formation	
Parameter	Value	Remarks	Reference
Water-accessible porosity	0.082	HTO-accessible porosity (rock capacity factor, α)	Al et al., 2008.
Pore diffusion coefficient for Cl^- at 22 ± 1 °C, II to bedding	$8.0 \cdot 10^{-11}$ m^2/s	Used average D_p for I^- as determined for two samples of the Queenston Formation measured parallel to bedding using X-ray Radiography.	Al et al., 2008
Effective diffusion coefficient for HTO, $\perp$ to bedding @ 20.5 ± 0.5 °C	$4.8 \cdot 10^{-12}$ m^2/s		Al et al., 2008
Pore diffusion coefficient for HTO, $\perp$ to bedding	$5.85 \cdot 10^{-11}$ m^2/s	Calculated from D_e for HTO using the water-accessible porosity (equation 1).	
Pore diffusion coefficient for HTO, II to bedding	$1.05 \cdot 10^{-10}$ m^2/s	Estimated from D_p HTO normal to bedding by multiplying by the average anisotropy of D_p for I^- (II/$\perp$) of 1.8, based on two samples from the Queenston Formation as reported by Al. et al. 2008.	
Hydraulic conductivity, $\perp$ to bedding	$4 \cdot 10^{-14}$ m/s	Used of value reported for Opalinus Clay from Mont Terri as a proxy. Comparable to hydraulic conductivity parallel to bedding (K_h) of $3 \cdot 10^{-14}$ reported for Queenston shale by Walsh, 2011, where K_v (perpendicular to bedding) was between 1 and 10 times less than K_h.	Mazurek et al., 2009
Initial Cl^- concentration	4.0 mol/L	Average apparent porewater concentration for two samples from DGR-3, with no evidence for presence of halite. It is assumed that Cl^- has access to full water-accessible porosity (i.e. anion exclusion is not considered).	Hobbs et al., 2011
Initial $\delta^{18}O$	-0.4‰	Median value between RWI and Uni Ottawa data [1]	Clark et al., 2009 (data from University of Ottawa) and Hobbs et al., 2011 (data from RWI, University of Bern).
Initial δ^2H	-41.7‰	Median value between RWI and Uni Ottawa data [1]	Clark et al., 2009 (data from University of Ottawa) and Hobbs et al., 2011 (data from RWI, University of Bern).

HTO refers to tritiated water.

[1] The porewater stable isotopic compositions reported by RWI (Hobbs et al., 2011) of $\delta^{18}O$ +1.6‰, δ^2H -39.3‰ are different than the values of $\delta^{18}O$ -2.4‰, δ^2H -44.1‰ reported by UniOttawa (Clark et al., 2009) . Because it is not currently known which are more representative of in-situ values, the median value between the two data sets was employed.

Table B4: Hydrogeological, Geochemical and Petrophysical Input Parameters for the Cobourg Formation

		Cobourg Formation	
Parameter	Value	Remarks	Reference
Water-accessible porosity	0.012	Average of 4 samples; water content determined by drying at 105 °C.	Al et al., 2010
Pore diffusion coefficient for Cl^- at 20 °C, II to bedding	$1.0 \cdot 10^{-10}$ m^2/s	Average D_p from out-diffusion experiments for two samples was $1.9\ 10^{-10}$ m^2/s at 45 °C. Temperature correction described by Mazurek et al. 2009 (Appendix A3) for the Opalinus Clay was applied.	Koroleva et al., 2009; Hobbs et al., 2011
Effective diffusion coefficient for HTO, II to bedding @ 21.5 ± 1.5°C	$1.4 \cdot 10^{-12}$ m^2/s	Average value based on measurements for 4 samples conducted parallel to bedding	Al et al., 2010.
Pore diffusion coefficient for HTO, II to bedding	$1.2 \cdot 10^{-10}$ m^2/s	Calculated from D_e for HTO measured parallel to bedding using equation 1 (see text)	
Hydraulic conductivity, ⊥ to bedding	$6 \cdot 10^{-14}$ m/s	Value reported for Effingen member (sandy limestone) used as a proxy Lowest laboratory value measured for *treated* (clean & dry core samples) from the Cobourg Formation was $4.05 \cdot 10^{-13}$ m/s (Walsh, 2008) is not considered representative of preserved, untreated core samples.	Waber, 2008
Initial Cl^- concentration	4.4 mol/L	Average apparent porewater concentration for 6 samples (4 from DGR-3 and two from DGR-4); samples from Lower Member of Cobourg Formation without evidence for presence of halite. It is assumed that Cl^- has access to full water-accessible porosity (i.e. anion exclusion is not considered).	Hobbs et al., 2011
Initial $\delta^{18}O$	-2.2‰	[1]Average of RWI and Uni Ottawa data	Clark et al., 2009 (data from University of Ottawa) and Hobbs et al., 2011 (data from RWI, University of Bern).
Initial $\delta^{2}H$	-44.6‰	[1]Average of RWI and Uni Ottawa data	Clark et al., 2009 (data from University of Ottawa) and Hobbs et al., 2011 (data from RWI, University of Bern).

[1] The porewater isotopic compositions reported by RWI and UniOttawa are substantially different. Because it is not currently known which are more representative of in-situ values, the average value for the formation based on the two data sets was employed. HTO refers to tritiated water.

B.3 SCOPING CALCULATIONS

B.3.1 In/out Diffusion Method

To estimate the time required for equilibration of intact core samples using the in/out diffusion technique, scoping calculations were performed using a one-dimensional radial transport equation for diffusion within a rock cylinder:

$$\theta \frac{\partial C}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(r D_e \frac{\partial C}{\partial r} \right), \quad (0 < r < a) \tag{2}$$

where θ: volumetric water content accessible to the solute species (i.e., the water-loss porosity for $\delta^{18}O$, $\delta^{2}H$ and also for Cl^-, if no anion exclusion occurs), C: porewater concentration, D_p: pore diffusion coefficient, $D_e = \theta \cdot D_p$: effective diffusion coefficient, a : radius of the core, r : space coordinate, and t : time.

The transport equation for diffusion was solved using the following analytical solution, which describes diffusion out of a cylinder into a well-mixed reservoir (Crank, 1975):

$$C(r,t) = C_{eq} - \left(C_i - C_{eq} \right) \sum_{n=1}^{\infty} \frac{4(\alpha+1)\exp\left(-D_p q_n^2 t / a^2 \right)}{\left(4 + 4\alpha + \alpha^2 q_n^2 \right)} \frac{J_0(q_n r / a)}{J_0(q_n)} \tag{3}$$

Here, $\alpha = V_w/(\pi a^2 L \theta)$: ratio of the reservoir volume to the volume of porewater within the cylinder, $C_{eq} = C_i / (\alpha+1)$: final equilibrium concentration, and the q_ns are the positive, non-zero roots of:

$$\alpha q_n J_0(q_n) + 2 J_i(q_n) = 0 \tag{4}$$

which were obtained for each value of α numerically with a Newton-Raphson algorithm. The $J_0(x)$ and $J_i(x)$ are Bessel functions of the first kind of order zero and one, respectively. This analytical solution considers diffusion from the sides of the cylinder only (i.e., not from the top or bottom). This is a reasonable approximation, given the elongated geometry of the core samples chosen for the scoping calculations (i.e., length » diameter of the sample).

Two synthetic porewaters were defined: i) a NaCl solution with a molarity of 0.3 M; and ii) a 5 M NaCl solution. The water isotopes in both synthetic porewaters correspond to tap water from the University of Bern, Switzerland ($\delta^{18}O$ = -11.1‰; $\delta^{2}H$ = -80.5‰). In the simulations, the volume of test solution was 200 mL, which corresponds to an annular gap filled with solution of 3 mm around the core, as well as a solution-filled space of 5 mm above and beneath the sample. The resulting solid:liquid ratio is therefore 4.5:1 on a volume basis.

For chloride ions, the criterion used to define steady-state is a difference of 5% between the Cl^- concentration in the center of the sample and that in the test solution. This corresponds to the analytical uncertainty in the measurement of Cl^- using ion chromatography (IC). For the water isotopes, an absolute difference of 1‰ in the case of oxygen and 5‰ in the case of hydrogen between the center of the sample and the test solution are used as the equilibrium criteria. These correspond approximately to the overall analytical uncertainties in determining the oxygen and hydrogen isotope compositions of porewater using the adapted diffusive exchange technique.

B.3.2 Advective Displacement

For the simple scoping calculations conducted here, plug flow of the synthetic porewater through the core is assumed (i.e., dispersion is ignored). The relationship between hydraulic conductivity rate, the hydraulic head and the sample geometry (e.g., Mäder et al., 2004) is given by:

$$K = \frac{Ql}{Ah} \tag{5}$$

where K [m/s] is the hydraulic conductivity of the sample, Q [m^3/s] is the average volumetric flow rate, l [m] is the sample length, A [m^2] is the cross sectional area and h [m_{H2O}] is the difference in hydraulic head applied during infiltration. Using the sample geometry given in Table B1 and the hydraulic conductivities of the formations (Table B2 through Table B4), equation 1 was rearranged to calculate the flow rate through a core. Using this flow rate and the calculated pore volume of the core (taken as equal to the water-accessible porosity), the amount of time required to replace one pore volume was calculated. A range of hydraulic head differences between the infiltration and outlet of the core were simulated (200 to 500 mH_2O). The highest simulated value of 500 m H_2O is the upper limit for the experimental equipment.

B.4 RESULTS

The results of simulations conducted for equilibration using the in/out diffusion technique are shown in Table B5. Figure B1 illustrates the simulated evolution of the Cl^- concentrations in the porewater and in the outer reservoir with time for each formation. The maximum estimated time required to fully equilibrate an intact core with respect to Cl^- and the stable isotopes is 154 days (≈7 months) for the Cobourg Formation and the minimum is 44 days for the Opalinus Clay (Mont Terri).

Table B5: Results for the Diffusion Calculation. "Case" Refers to the Parameter Modelled and in the Case of Cl^-, Concentration in the Initial Solution. Initial Isotopic Composition of the Test Solution was $\delta^{18}O$ = -11.1‰; δ^2H = -80.5‰ in All Simulations

Formation	Case	Time (days)	Calculated Equilibrium Value[1]	Absolute difference from initial value in test water
Queenston	Cl^-, 0.3 M	130	1.3 M	1.0 M
	$\delta^{18}O$	62	-8.2‰	2.9‰
	δ^2H	55	-70.0‰	10.5‰
Cobourg	Cl^-, 0.3 M	154	0.5 M	0.2 M
	$\delta^{18}O$	62	-10.6‰	0.5‰
	δ^2H	57	-78.6‰	1.9‰
Opalinus Clay, Mont Terri	Cl^-, 5 M	44	3.6 M	1.4 M
	$\delta^{18}O$	11	-9.3‰	1.8‰
	δ^2H	14	-65.3‰	15.2‰

[1] Value in test solution when equilibrium is reached. Equilibrium is defined as a difference in the Cl^- concentration between porewater in the center of the core and that in the test solution of less than 5%, or a difference in $\delta^{18}O$ of < 1‰ and δ^2H <5‰.

The time estimates for replacement of porewater using advective displacement are shown in Table B6. The calculated times reflect the time required to displace one pore volume of solution through the sample at a given hydraulic head difference between the inlet and outlet of the core within the apparatus. The calculations for cores from the Queenston and Opalinus Clay (Mont Terri) suggest that 2.7 years, or longer, is required to replace one pore volume within the core. For the Cobourg Formation, the time estimates suggest that a minimum of 8 months would be required to displace one pore volume of porewater from the core, if displacement was conducted at the highest hydraulic head difference of 500 mH_2O.

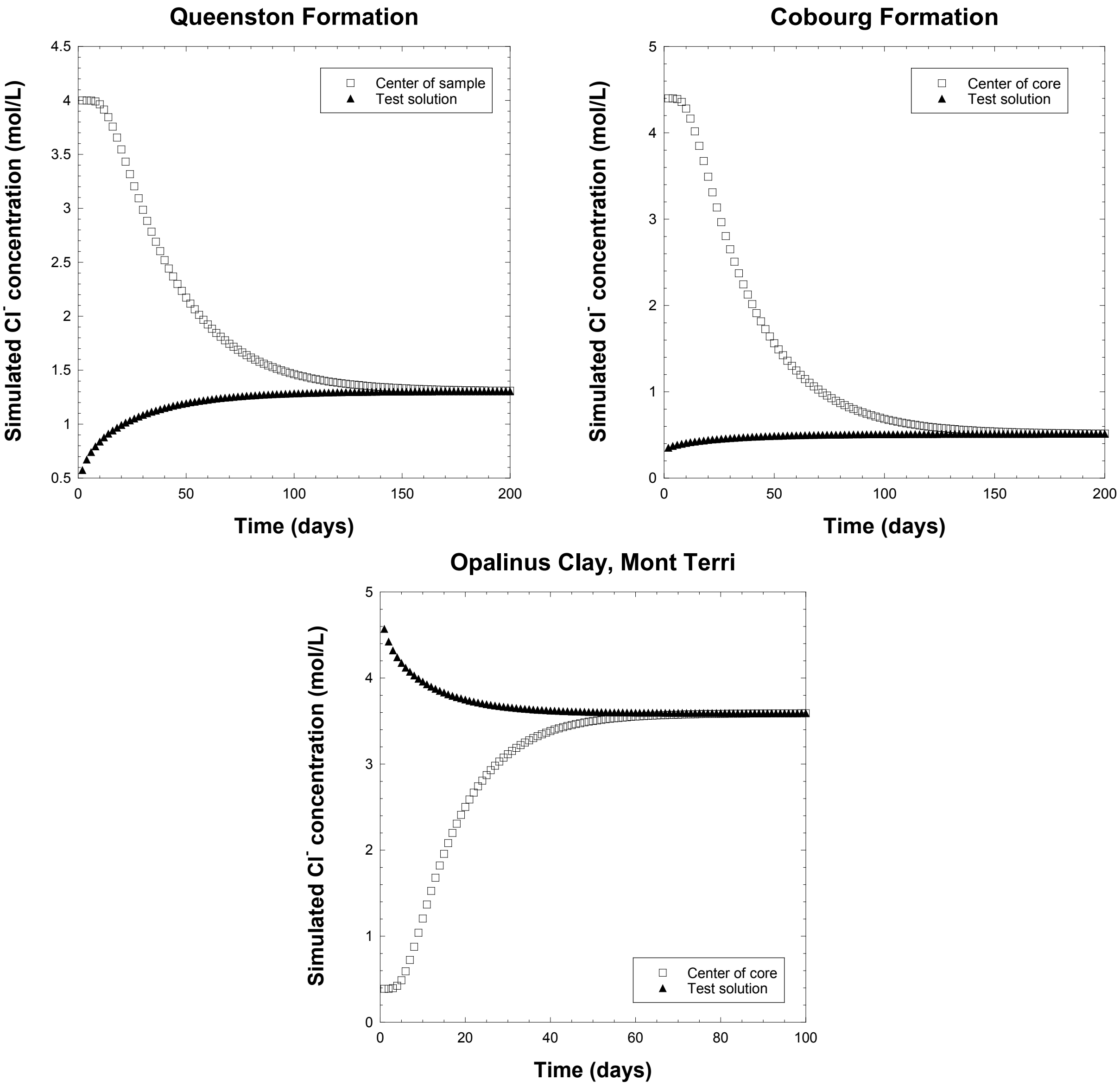

Figure B1: Simulated Change in Cl^- Concentration in Porewater at the Center of the Core Sample or In the Test Solution as a Function of Time during Equilibration Using the In/Out Diffusion Technique

Table B6: Results of Simulations for Replacement of Porewater Using Advective Displacement

Hydraulic head difference (m H_2O)	500	400	300	200
Rock	Time to displace one pore volume (days)			
Queenston	1898	2373	3164	4745
Cobourg	185	231	309	463
Opalinus Clay, Mont Terri	4167	5208	6944	10417

B.5 IMPLICATIONS FOR POREWATER REPLACEMENT

The scoping calculations reveal that replacement of the porewater by advective displacement is not practical for rocks with a very low hydraulic conductivity (ca. 10^{-14} m/s), such as those from all three formations examined here. In/out diffusion is therefore used to equilibrate rock materials with a synthetic porewater. To decrease the time required for full chemical and isotopic equilibration, smaller rock pieces could be used, rather than the intact core considered in the scoping calculations.

REFERENCES

Al, T., Y. Xiang and L. Cavé. 2008. Measurement of Diffusion Properties by X-Ray Radiography and by Through-Diffusion Techniques Using Iodide and Tritium Tracers: Core Samples from OS-1 and DGR-2. TR-07-17. DGR Site Characterization Document, Intera Engineering Project 08-200.

Clark, I., I. Liu, H. Mohammadzadeh, R. Mohapatra, P. Zhang and M. Wilk. 2009. Porewater and gas analyses in DGR-3 & DGR-4 core. Draft Technical Report TR-08-19, Revision 0E, November 19, 2009. DGR Site Characterization Document, Intera Engineering Project 08-200.

Crank, J. 1975. The Mathematics of Diffusion. Oxford University Press, Oxford, U.K.

Hobbs, M., A. de Haller, M. Koroleva, M. Mazurek, J. Spangenberg, U. Mäder and D. Meier. 2011. Borehole DGR-3 and DGR-4 porewater investigations, TR-08-40. Revision 0, March 31, 2011. DGR Site Characterization Document, Intera Engineering Project 08-200.

Koroleva, M., A. de Haller, U. Mäder, H.N. Waber and M. Mazurek. 2009. Borehole DGR-2: Porewater investigations. Technical Report TR 08-02, RWI Group, Institute of Geological Sciences, University of Bern, Switzerland, 127 p.

Mäder, U.K., H.N. Waber and A. Gautschi. 2004. New method for porewater extraction from claystone and determination of transport properties with results for Opalinus Clay (Switzerland). *In*: Wanty, R.B. and R.R. Seal II (eds.): Proceedings of the 11th Symposium on Water-Rock Interaction WRI-11, Saratoga Springs, NY, USA, Balkema/Taylor & Francis, Leiden, The Netherlands, p. 445 - 449.

Mazurek, M., P. Alt-Epping, A. Bath, T. Gimmi and H.N. Waber. 2009. Natural tracer profiles across argillaceous formations: The CLAYTRAC Project. OECD Nuclear Energy Agency, NEA No. 6253.

Waber, H.N. (ed.). 2008. Borehole Oftringen: Mineralogy, Porosimetry, Geochemistry, Porewater Chemistry: Nagra, Wettingen, Switzerland. Nagra Arbeitsbericht NAB 08-18, 235 p.