

Forsmark site characterisation

Borehole KFM22 and KFM23: Derivation of porewater data by diffusion experiments

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Preface

A methodology comparison for porewater extraction and characterisation techniques was initiated at the Forsmark site, Sweden. This involved two laboratories: The University of Bern, Switzerland and the United States Geological Survey in Denver, Colorado. The University of Bern's approach, together with results and interpretation, are presented in detail in this report. The USGS Denver results are briefly described, compared and discussed in a Memorandum presented in Appendix 1. Also included in this appendix are comments from the USGS Denver related to the Memorandum.

Summary

Within the Detum Project (Detailed Investigations in Forsmark) a ‘Methodology comparison for porewater extraction and characterisation techniques’ was initiated. This has centred on two shallow boreholes drilled at Söderviken within the northern part of the Forsmark characterisation site. The comparison includes different methodologies to characterise the chemical and isotopic composition of porewater residing in the connected pore space of the rock matrix. The present report describes the chemical and isotopic information of the porewater obtained by out-diffusion experiments and the diffusive isotope equilibration technique applied to originally water saturated drillcore samples. In addition, petrophysical data and solute transport properties of the rock matrix, all necessary for porewater characterisation, have also been elaborated.

Specially conditioned drillcore samples were obtained from depths of less than 100 m from boreholes KFM22 and KFM23. Porewater has been extracted successfully from seven samples by laboratory out-diffusion and diffusive isotope exchange methods. The methodology to extract and analyse the porewater is outlined and the analytical data are tabulated. The data are critically reviewed for potential experimental artefacts and their significance with respect to *in situ* conditions.

The connected pore space in the core material representing borehole KFM22 and KFM23 was measured on different types of originally saturated drillcore samples using gravimetric and isotope mass balance methods. Out-diffusion experiments were performed on kg-sized drillcore samples to derive the *in situ* concentration of the chemically conservative compounds chloride and bromide. The attainment of equilibrium conditions in the out-diffusion experiments was monitored by the concentration change of chloride and bromide as a function of time. The water isotope composition of porewater was determined by the diffusive isotope equilibration technique and by isotope mass balance calculation, which in addition delivers a measure for the water content.

In spite of the shallow origin of the drillcore samples from borehole KFM22 and KFM23 compared to the earlier Forsmark studies, porewater Cl^- and Br^- concentrations and $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values obtained for the porewater coincide with earlier porewater data produced on drillcore material from near-by boreholes (cf. Waber et al. 2009).

Sammanfattning

Inom detaljundersökningsprogrammet (Detum) i Forsmark har SKB låtit göra en jämförande studie mellan två olika metoder att extrahera matrisporvatten. Detta gjordes för två ytliga borrhål som borrades vid Söderviken i den norra delen av Forsmarks karakteriseringsområde. Jämförelsen inkluderade två olika metoder att karakterisera den kemiska sammansättningen och isotopsammansättningen porvattnet i bergmatrisen. Kemisk information inklusive isotoper har erhållits genom sk utdiffusionsexperiment och diffusiv isotopjämviktsteknik som tillämpats på vattenmättade borrhålsprover. Dessutom har petrofysiska data och transportegenskaper av lösta ämnen i bergsmatrisen, vilka behövs för porvattenkarakterisering, tagits fram.

Borrhållor som hanterats i enlighet med rutiner för provvattenundersökningar (se t ex Waber et al. 2009) erhöles från djup på mindre än 100 m från borrhål KFM22 och KFM23. Porvatten extraherades framgångsrikt från sju borrhålsprover i laboratorium genom utdiffusion och diffusivt isotopbyte. Metoden att extrahera och analysera porvatten finns beskrivet i denna rapport och de analytiska resultaten finns sammanställda i tabellform. Data har granskats kritiskt med avseende på potentiella experimentella artefakter samt deras signifikans med avseende på *in situ* förhållanden.

Det interkonnekterade porutrymmet i borrhållematrisen representerande borrhållen KFM22 och KFM23 mättes på prover med olika typer av ursprunglig vattenmättnad med hjälp av gravimetriska metoder och massbalansberäkningar på isotoper. Utdiffusionsexperimenten utfördes på kg-stora borrhålsprover för att bestämma, *in situ* koncentrationer hos de kemiskt konservativa komponenterna klorid och bromid. Det uppnådda jämviktsförhållanden i utdiffusionsexperimenten indikerades genom att studera förändringar i klorid- och bromidkoncentrationerna som funktion av tid. Isotopsammansättningen av porvattnet bestämdes genom diffusiv isotopjämviktsteknik och genom massbalansberäkningar, vilka också ger ett mått på vatteninnehållet.

Trots att borrhållorna KFM22 och KFM23 kommer från betydligt ytligare borrhål än de som togs i samband med platsundersökningarna, stämmer Cl^- och Br^- koncentrationerna samt $\delta^{18}\text{O}$ och $\delta^2\text{H}$ värdena väl överens med de som togs i närliggande borrhål (Waber et al. 2009).

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1 Introduction

This document reports the performance and results related to the Detum Project (Detailed Investigations in Forsmark), pertaining to the 'Methodology comparison for porewater extraction and characterisation techniques'. The activities were performed on drillcore samples from shallow boreholes KFM22 and KFM23 drilled at the Forsmark investigation site during June and July 2011.

Earlier studies have shown that the mass of porewater contained in the low permeable matrix of crystalline rock at Forsmark is significant compared to the mass of groundwater circulating in the fractures, and therefore its influence on the fracture groundwater and a future deep repository needs to be understood. Porewater that resides in the connected pore space of such crystalline rock cannot be sampled by conventional techniques, but must be extracted by indirect methods based on rock material. During SKB's site investigation programme porewater in the rock matrix was successfully characterised by out-diffusion and diffusive isotope exchange techniques (Waber and Smellie 2005, 2007a, 2008, 2009, Waber et al. 2009). During these investigations the question of alternative techniques arose to assess the porewater chemical and isotopic composition. The decision was taken to characterise the porewater in originally saturated rock material of drillcore samples collected adjacent to each other from two boreholes.

This report presents the methodologies employed earlier during SKB's site investigation programme, i.e. out-diffusion and diffusive isotope exchange techniques. It gives a compilation of the resulting analytical data from the various experiments, and the derived porewater data. It does not attempt, however, to compare the elaborated porewater data to data produced by different techniques, or to put the obtained data into a broader palaeohydrogeological context.

2 Hydrogeological setting

Boreholes KFM22 and KFM23 were drilled at Söderviken within the northern part of the Forsmark characterisation site (Figure 2-1). The two boreholes are situated about 100 m to the north and to the southeast of borehole KFM08C, which was characterised for porewater during the site investigation programme (Waber and Smellie 2007a).

Drilling of the two boreholes commenced in late June 2011 and was completed in early July 2011. The boreholes were drilled to a borehole length of 60.26 m (KFM22) and 100.64 m (KFM23) at an average inclination of 86° and 73°, respectively, from the horizontal plane at ground level. The boreholes were core-drilled with a diameter of 76 mm giving rise to a drillcore diameter of 50 mm.

The geology of borehole KFM22 is characterised mainly by metagranite-granodiorite (sampling protocol rock type 101057) and pegmatitic granite (sampling protocol rock type 101061), with this latter unit (~ 37–42 m in thickness) being sandwiched between two sections of the metagranite-granodiorite. In contrast, the drillcore of borehole KFM23 consists entirely of metagranite-granodiorite (sampling protocol rock type 101057).

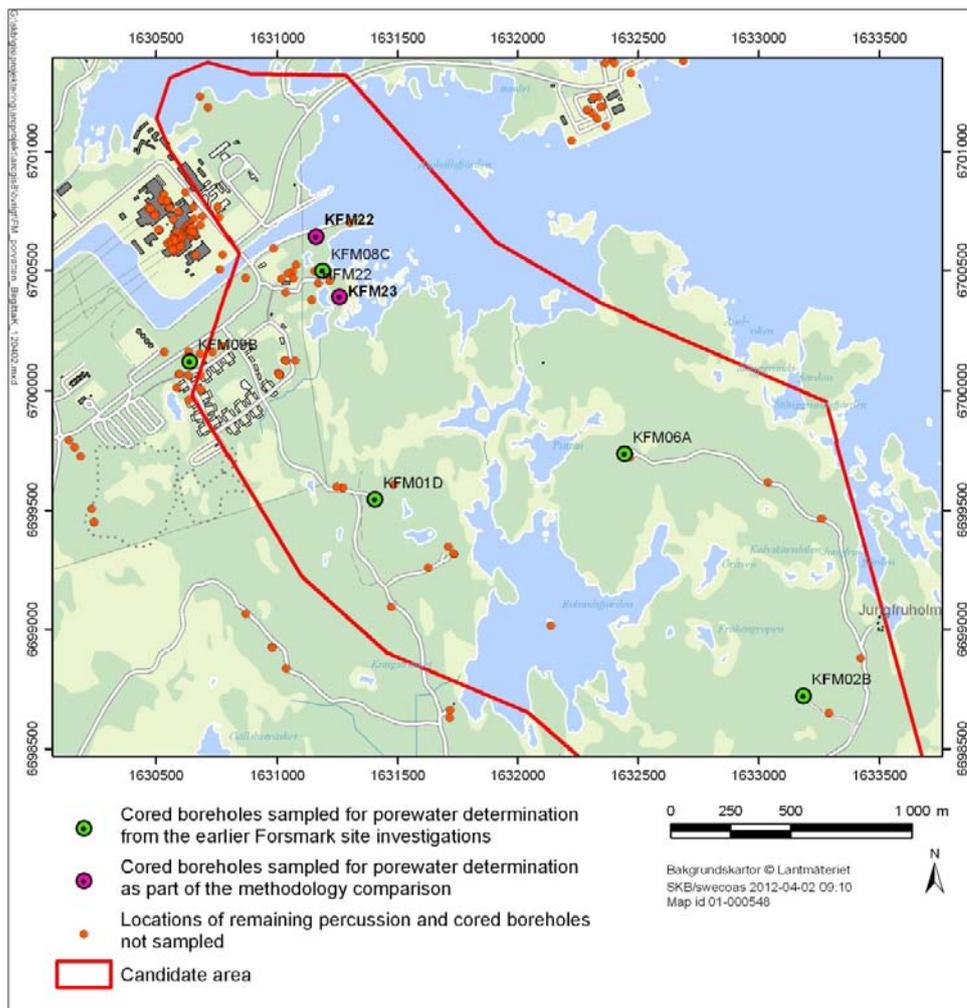


Figure 2-1. Localisation of borehole KFM22 and KFM23 used for porewater characterisation within the Forsmark site investigation area.

3 Materials and methods

3.1 Samples and sample preparation

Between June 30th and July 7th 2011, a total of 6 and 14 samples were collected from boreholes KFM22 and KFM23, respectively, for porewater characterisation at the University of Bern. Drillcore sections of about 20–40 cm in length were taken at regular depth intervals of about 10 metres down to a borehole length of about 85 m and starting at about 6 m (KFM22) and 9 m (KFM23). From borehole KFM23 samples were collected at smaller intervals of 2.5 and 0.3 m from 95.6 m to 99.2 m borehole length.

An important requirement for porewater characterisation using rock samples is the preservation of the fully water-saturated state of the rock material immediately following drilling and sampling and during transportation from the site to the laboratory. This precaution is to inhibit possible water-rock interactions (e.g. caused by evaporation and oxidation) induced by exposure of the rock sample to air. To minimise these potential perturbing effects the samples were immediately wiped clean with a dry towel following drilling and selection, wrapped into a heavy-duty PVC bag, which was repeatedly flushed with nitrogen, evacuated and heat sealed. This procedure was repeated with a second PVC bag and finally sealed in a plastic coated Al-foil. The samples were then air freighted to the laboratory at the University of Bern, Switzerland, where they were immediately stored at 4°C in a cooling room. The 7 samples selected for the method comparison for porewater characterisation techniques were unpacked and prepared for the various measurements and experiments on July 21st, 2011.

For legibility reasons, the sample labelling adopted in this report is a systematic numbering of the samples with depth using the borehole name as prefix; similar labelling was used for the laboratory studies. Table 3-1 gives the list of samples used for porewater characterisation including their SKB number, the sample numbering used in this report, and the experiments and analyses performed on each sample.

For the experiments, the core sections were cut by dry sawing into full-diameter samples of about 19 cm length to be used specifically for the out-diffusion experiments. For sample KFM23-6 the length of drillcore obtained was too short and this required an adjustment of the experimental set-up to accommodate core pieces of about 12 cm length instead. The remaining material from the top and bottom of the core section was used for the diffusive isotope equilibration method and the determination of the water content. The wet weight of such material was determined immediately after unpacking and preparation (within 3 minutes).

Table 3-1. List of samples received from boreholes KFM22 and KFM23, and the experiments and measurements performed.

Sample No	SKB Sample No	Average bore-hole length (m) ¹⁾	Average Elevation (m a.s.l.) ²⁾	Water Content & Porosity	Density	Isotope equil. method	Out-diffusion experiments Chemistry	Cl, Br timeseries
Borehole KFM22								
22-1	SKB 21200	9.04	-6.26	-	-	-	-	-
22-2	SKB 21201	20.35	-17.55	-	-	-	-	-
22-3	SKB 21202	37.18	-34.34	X	X	X	X	X
22-4	SKB 21203	41.86	-39.00	-	-	-	-	-
22-5	SKB 21204	46.33	-43.37	-	-	-	-	-
22-6	SKB 21205	55.21	-52.23	-	-	-	-	-
Borehole KFM23								
23-1	SKB 21206	6.69	-4.13	-	-	-	-	-
23-2	SKB 21207	17.58	-14.55	-	-	-	-	-
23-3	SKB 21208	31.41	-27.78	-	-	-	-	-
23-4	SKB 21209	37.90	-33.98	X	X	X	X	X
23-5	SKB 21210	47.52	-43.19	-	-	-	-	-
23-6	SKB 21211	57.36	-52.59	X	X	X	X	X
23-7	SKB 21214	65.61	-60.47	X	X	X	X	X
23-8	SKB 21215	76.44	-70.82	X	X	X	X	X
23-9	SKB 21217	83.87	-77.92	X	X	X	X	X
23-10	SKB 21220	95.91	-89.41	X	X	X	X	X
23-11	SKB 21221	98.41	-91.80	-	-	-	-	-
23-12	SKB 21222	98.73	-92.10	-	-	-	-	-
23-13	SKB 21223	98.93	-92.30	-	-	-	-	-
23-14	SKB 21224	99.23	-92.58	-	-	-	-	-

¹⁾ borehole inclination: approx. -86° for KFM22 and -73° for KFM23; X = experiment performed, analytical data available; - = back-up samples with no experiments yet performed.

²⁾ elevation data according to SICADA, 14.05.2012.

3.2 Analytical methods

Most of the analytical work of this study has been conducted at the Institute of Geological Sciences, University of Bern, Switzerland. Thus, if not otherwise stated, the analytics have been performed at this Institution.

3.2.1 Water content and water-loss porosity

The water content was determined by the gravimetric determination of the water loss by drying subsamples at 105°C until stable weight conditions (± 0.002 g). Such subsamples included drillcore material specifically designated to water-content measurements, the material used for the diffusive isotope-exchange method, and the large-sized drillcore sections used for the out-diffusion experiments.

If the material received allowed it, then the weight of the samples specifically designated to water-content measurements was chosen to be as large as possible to minimise possible desaturation effects and to account for variations in the grain size of the rocks. For the same reasons, intact drillcore pieces were used without creating unnecessary new surfaces by cutting and/or breaking. Samples used for the diffusive isotope exchange experiments remained saturated throughout the experiment because they were placed in a vapour-tight vessel at 100% humidity during the equilibration procedure (cf. also below). The mass of samples available for these experiments varied between about 180–300g. The most reliable water-content data are obtained from the large-sized drillcore sections used for the out-diffusion experiments. The mass of these intact core sections ranged between approximately 970–1,050g, except for sample KFM23-6 with a mass of 631g. The difference in mass before (i.e. at the time of receiving the sample in the laboratory) and after (i.e. after more than

100 days of immersion in the test water) the out-diffusion experiment, was less than 0.1 permil for all samples. This indicates that all samples were originally saturated when the experiments commenced.

A measure for the bulk wet density, $\rho_{\text{bulk, wet}}$, of the rocks was obtained from the volume and saturated mass of the core samples used for out-diffusion experiments. The volume was calculated from measurements of height and diameter of the core samples using a Vernier calliper with an error of ± 0.01 mm. Variations in the core diameter along the lengths of the samples was found to be less than 0.05 mm for most samples and a constant diameter was used in the calculation of the volume. For the derived wet bulk density this results in an error of less than 3%.

The water-loss porosity, Φ_{WL} , was calculated using the water content and the bulk wet density according to:

$$\Phi_{\text{WL}} = WC_{\text{wet}} \cdot \frac{\rho_{\text{bulk, wet}}}{\rho_{\text{water}}} \quad (3-1)$$

A density of unity was assumed for the porewater density, ρ_{water} , based on the low to moderate salinity obtained for porewater in shallow rocks of other studied boreholes from the Forsmark site (Waber and Smellie 2009).

3.2.2 Porewater isotope composition ($\delta^{18}\text{O}$ and $\delta^2\text{H}$)

Determination of the water isotope composition of porewater, $\delta^{18}\text{O}$ and $\delta^2\text{H}$, was carried out by the diffusive isotope equilibration technique (cf. Waber and Smellie 2005, 2007a, 2008 for details and references). In this technique, the porewater isotope composition is derived indirectly by isotopic exchange between the porewater and a test water of known composition. The isotope exchange occurs via the vapour phase without any direct contact between the rock sample and the test water. Rock pieces of about 1–2 cm in diameter and a small petri dish filled with test water are stored together in a vapour-tight glass container. The mass and water isotope compositions of the test water are known. Minimisation of test water condensation on the rock fragments and the glass container walls occurred by lowering the vapour pressure above the test-water surface. This was done by lowering the water activity of the test water by adding about 0.3 mol NaCl. The petri dish with the test water and the whole container are weighed before and after the exchange experiment to check that no water is lost from the container and that there occurred negligible or no transfer of test water to the sample by possible sorption on the rock material. Isotopic equilibrium in this system is achieved in about 20 to 30 days at room temperature depending on the size of the rock pieces, the water content and the water diffusivity of the rock. After complete equilibration, the two test waters were removed and analysed by conventional ion-ratio mass spectrometry at Hydroisotop GmbH, Germany. The results of the test solutions are reported relative to the V-SMOW standard with a precision of $\pm 0.15\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 1.5\text{‰}$ for $\delta^2\text{H}$.

The diffusive isotope equilibration method was originally designed for rocks with water contents in the order of several percent (Rübel 2000). Adaption of the diffusive isotope equilibration technique to rocks with water contents of less than 1% requires usage of artificial test water, which is strongly depleted in ^{18}O and strongly enriched in ^2H ($\delta^{18}\text{O}$ around -107‰ and $\delta^2\text{H}$ around -423‰ V-SMOW (cf. Waber and Smellie 2008). In addition, smaller volumes of test water and larger masses of rock were used to reduce the uncertainty of the derived isotope composition.

The diffusive isotope equilibration method delivers the stable isotope composition of porewater and the mass of porewater present in the connected pore space of the rock sample. The mass of porewater can be derived from the relation:

$$m_{\text{PW}} = \frac{m_{\text{TW1}} \cdot (c1_{\text{TW1}}^{\infty} - c1_{\text{TW1}}^0) + m_{\text{TW2}} \cdot (c2_{\text{TW2}}^0 - c2_{\text{TW2}}^{\infty})}{c2_{\text{TW2}}^{\infty} - c1_{\text{TW1}}^{\infty}} \quad (3-2)$$

where m means mass, $c1$ and $c2$ are the concentration of the isotope tracers 1 and 2 in the test waters TW1 and TW2 , and PW is the porewater. The superscripts 0 and ∞ denote the isotope tracer concentrations prior to and after equilibration of the test water with the porewater.

Relating m_{PW} to the rock mass used in the exchange experiments delivers the water content, WC_{IsoEx} . The error of WC_{IsoEx} is determined by applying Gauss's law of error propagation on equation (3-2). This reveals that the error depends essentially on the mass ratio of porewater to test water and a big enough difference in isotopic composition between the two water types. It is minimised when the mass ratio becomes close to unity. For the present samples the average calculated relative error for the water content derived by isotope mass balance, WC_{IsoEx} , is $1.5 \pm 0.3\%$.

The stable isotope composition of the porewater is calculated from mass balance relationship of the experiments according to:

$$c_{PW} = \frac{m_{TW1} \cdot m_{R2} \cdot c2^{\infty} \cdot (c1_{TW1}^{\infty} - c1_{TW1}^0) - m_{TW2} \cdot m_{R1} \cdot c1^{\infty} \cdot (c2_{TW2}^0 - c2_{TW2}^{\infty})}{m_{TW1} \cdot m_{R2} \cdot (c1_{TW1}^{\infty} - c1_{TW1}^0) - m_{TW2} \cdot m_{R1} \cdot (c2_{TW2}^{\infty} - c1_{TW2}^0)} \quad (3-3)$$

where m is the mass, c is the isotope ratio, PW is the porewater, $TW1$ and $TW2$ are the test waters 1 and 2 of the first and second experiment, $R1$ and $R2$ are the rock samples used in the first and second experiment, and the superscripts "0" and " ∞ " are the isotope ratios prior to equilibration ($t = 0$) and after equilibration is achieved ($t = \infty$) in the experiment.

By applying Gauss' law of error propagation on equation (3-3), the average absolute error of the derived porewater isotope composition becomes about $\pm 1.7\%$ for $\delta^{18}O$ and about $\pm 13\%$ for δ^2H (cf. also Section 3.3).

3.2.3 Chemical composition of porewater

The chemical composition of porewater in the core material from boreholes KFM22 and KFM23 was approached by out-diffusion experiments. These were performed on complete core samples of about 120 mm to 190 mm in length by immersion in ultra-pure water (Figure 3-1). To accelerate the out-diffusion, the vapour-tight PVC containers were placed into a water bath with a constant temperature of 45°C. The weight of the core sample, the experiment container, and the artificial test water used was measured before and after the experiment to ensure that no loss of test water occurred during the entire experiment. Weighing of the core before and after the experiment gives additional valuable information about the saturation state of the core at the beginning of the experiment.

At specific time intervals, initially a few days and later a few weeks, 0.5 mL of solution were sampled for the determination of the chloride concentration as a function of time. Based on previous experience (Waber and Smellie 2008, Waber et al. 2009 and references therein) the two reservoirs were allowed to equilibrate for about 140 days. After equilibrium with respect to chloride was achieved, the vessels were removed from the water bath and cooled to room temperature. Subsequently, the core was weighed and the supernatant solution was analysed immediately for pH and total alkalinity and later also for major cation and anion concentrations.

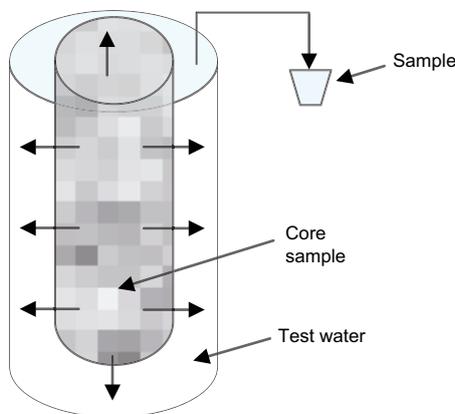


Figure 3-1. Schematic diagram illustrating the out-diffusion experiments performed.

The alkalinity titration and pH measurements were performed using a Metrohm Titrino DMP 785 instrument. Major cations (Na, K, Ca, Mg, Sr) and anions (F, Cl, NO₃, Br, SO₄) of the final test solutions and the 0.5 mL sized time-series samples were analysed by ion chromatography using a Metrohm ProfIC AnCat MCS IC system with automated 5µL and 50µL injection loops. The analytical error of these analyses is ± 5% based on multiple measurements of external check standard solutions.

The chloride and bromide concentrations of the experiment solution can be converted to porewater concentrations using mass balance calculations given that equilibrium conditions in the out-diffusion experiment are attained. At equilibrium, the chloride and bromide concentrations in the connected porosity of the rock sample will be equal to that of the experiment solution. With knowledge of the mass of porewater in the rock sample, the concentration of these chemically conservative compounds in the porewater can be calculated according to:

$$C_{PW} = \frac{(m_{PW} + m_{TWi} - \sum^n m_s) \cdot C_{TW\infty} - (m_{TWi} \cdot C_{TWi}) + \sum^n m_s \cdot C_s}{m_{PW}} \quad (3-4)$$

where C_{PW} = porewater concentration; m_{PW} = mass of porewater; m_{TWi} = initial mass of test water; C_{TWi} = initial Cl-concentration of test water; m_s = mass of subsample used for time series; C_s = Cl concentration of subsample used for time series.

The terms $\sum m_s$ and $\sum m_s \cdot C_s$ in equation (3-4) describe the mass of test water and amount of chloride and bromide removed from the initial experiment solution by the time-series samples. A correction for chloride in the initial experiment solution ($m_{TWi} \times C_{TWi}$) is necessary if this solution is not entirely free of chloride.

It should be noted that the unit of porewater concentrations is given as mg/kg_{H2O} (and not mg/L) because it is derived on a mass basis rather than a volumetric basis. This is because the density of the porewater is not known beforehand. In reality and within the overall uncertainty band, the difference between mg/kg_{H2O} and mg/L becomes only important at an ionic strength of the calculated porewater above that of seawater (~0.7 M).

By applying Gauss' law of error propagation on equation (3-4), the average relative error of the derived porewater Cl⁻ and Br⁻ composition for the present samples becomes $7.8 \pm 0.8\%$ exclusive of the uncertainty induced by drilling fluid contamination (cf. also Chapter 5).

3.3 Nonconformities

Exceptions include the preparation of samples for the diffusive isotope exchange technique. An inappropriate handling of the pipette used for adding test water to the crystallisation dishes resulted in about a 35% increase in the volumes of test water added. This increased test water to porewater ratio resulted in a significantly larger error compared to, for example, in the last porewater investigations performed on rocks from the Forsmark borehole KFM02B (Waber and Smellie 2009) or the Laxemar borehole KLX17A (Waber and Smellie 2007b). In addition, in samples KFM23-7 and KFM23-8 some evaporation and/or condensation of test and porewater occurred on the walls of the vapour-tight container and the replicate isotope analyses for the isotopically modified test water were outside the analytical error. The analysed isotope values of these three samples show a clear deterioration that can no longer be corrected for.

An integration of the porewater data with hydrogeological data (lithology, degree of alteration, fracture type and frequency, hydraulic conductivity etc) was not performed because of the absence of any on-site borehole or drillcore logging data.

4 Petrophysical rock properties

The petrophysical properties determined on the drillcore samples from boreholes KFM22 and KFM23 include the water content derived by different methods, the bulk wet density, and the water-loss porosity. All water content measurements were conducted on originally saturated samples.

4.1 Water content

4.1.1 Gravimetric water content

The wet rock mass of small-sized samples used for gravimetric water content determinations ranged between about 225–329g for samples specifically assigned for these measurements, and between about 180–300g for the samples previously used in the isotope exchange experiments. The water content of the 7 samples varies between 0.15 wt.% and 0.24 wt.% with an average of 0.18 ± 0.05 wt.% (Table 4-1). These water contents compare well with those previously found for granodiorite and pegmatitic granite samples at Forsmark (Waber et al. 2009).

The wet rock mass of large-sized core samples used for out-diffusion experiments and subsequently for gravimetric water content determinations ranged between about 970 g and 1,050 g for 6 samples and was 631 g for one sample (Table 4-1). The difference of the wet weight of the core samples before and after the out-diffusion experiment is $<1\%$. This indicates that no resaturation occurred during the 4.5 months of out-diffusion experiment. Thus, the samples were originally saturated at the start of the out-diffusion experiment.

The water content of these large-sized samples varies between 0.17 and 0.23 wt.% with an average of 0.17 ± 0.05 wt.% (Table 4-1). The water content of the large-sized out-diffusion core samples agrees fairly well with that determined on smaller sample aliquots adjacent to the out-diffusion core. The differences are mainly due to heterogeneities in the rock texture and the greater risk of partial desaturation during sample preparation of small-scaled samples. Although within $\pm 10\%$ for most samples, the differences have a notable effect on the back-calculated porewater Cl^- concentrations. In the case of sample KFM23-6, for instance, the difference of more than 10% in water content between the out-diffusion core and adjacent small-sized samples will lead to an unacceptable deviation in the back-calculated porewater Cl^- concentrations.

It should be noted that the time until stable weight conditions (i.e. ± 0.005 g) are attained during drying at 105°C takes almost as long as the attainment of equilibrium conditions for the out-diffusion of chloride (Figure 4-1).

Table 4-1. Gravimetric water content by drying at 105°C (WC_{Grav}) and diffusive isotope exchange (WC_{IsoEx}) of drillcore samples.

Laboratory sample No	Borehole length (m)	Small-sized samples			Large-sized samples		Isotope exchange	
		No of samples	WC_{Grav} aver. (wt.%)	error 1σ (wt.%)	Mass (g)	WC_{Grav} ¹⁾ (wt.%)	WC_{IsoEx} aver. (wt.%)	Relative error ²⁾ (%)
Borehole KFM22								
22-3	37.18	3	0.21	0.04	1,053.128	0.23	0.21	1.2
Borehole KFM23								
23-4	37.90	3	0.15	0.03	1,029.580	0.17	0.15	1.6
23-6	57.36	3	0.24	0.04	973.081	0.18	0.17	1.3
23-7	65.61	2	0.13	0.02	631.137	0.12	– ³⁾	–
23-8	76.44	2	0.12	0.01	1,028.733	0.11	–	–
23-9	83.87	2	0.22	0.01	989.251	0.18	0.19	1.3
23-10	95.91	2	0.21	0.04	1,014.877	0.22	0.14	1.4

¹⁾ – = error assumed to be $\pm 10\%$, ²⁾ error calculated with Gauss' law of error propagation; ³⁾ – = experiment failed.

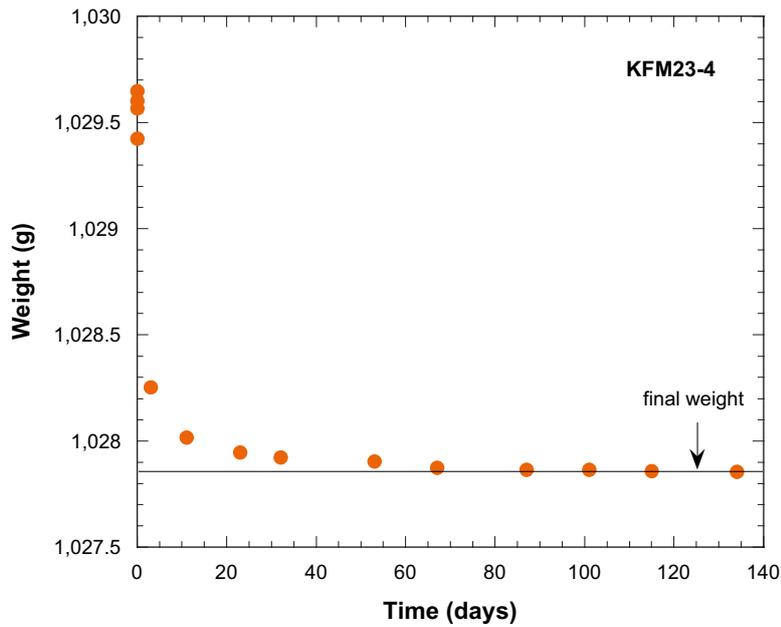


Figure 4-1. Example of weight loss of an out-diffusion core sample (size about 190×50 mm) upon drying at 105°C to stable weight conditions, which are attained after about 100 days (sample KFM23-4).

4.1.2 Water content by diffusive isotope exchange

The water content derived by the diffusive isotope exchange method via isotope mass balance varies in the same range between 0.14 wt.% and 0.21 wt.% and in the same range as the gravimetrically determined water content (Table 4-1). For all samples the water content derived by isotope mass balance agrees within about ± 10% to the gravimetrically determined water content of the same samples, except for sample KFM23-10. The reason for this larger difference is not clearly known, but appears to be attributed to a slightly erroneous $\delta^{18}\text{O}$ value determined in the exchange experiment with test water strongly depleted in $\delta^{18}\text{O}$. Whereas this has a strong impact on the calculated water content, its impact on the calculated porewater $\delta^{18}\text{O}$ value is less than 0.3 ‰ (cf. Chapter 5).

4.2 Bulk density

The bulk wet density of the rock samples was derived from the wet mass and the volume of the large-sized drillcore samples used for the out-diffusion experiments. Although the volumetric measurement might not be as accurate as other techniques, the large size and the well-shaped drillcores allowed reasonable estimates of the bulk wet density. For the present granodiorite and pegmatitic granite samples the bulk wet density varies between 2.60–2.65 g/cm³ (Table 4-2). It compares well with other samples used for porewater characterisation (Waber et al. 2009) and with bulk density values derived by other methods for the predominantly metagranite to metagranodiorite type rocks (e.g. Liedberg 2006).

4.3 Water-loss porosity

As will be shown in Chapter 5, the salinity of the porewater is far below that of seawater in all samples. Therefore, the assumption of a density for the porewater of one is justified, and the calculation of the water-loss porosity from the water content according to equation (3-1) becomes essentially a scaling with the rock density. Because of small variation in the rock density of all samples, the water-loss porosity of the different samples shows the same dependencies and trends described for the water content (Table 4-2).

Table 4-2. Water-loss porosity (WL-P) determined by gravimetry and isotope exchange and bulk density of drillcore samples.

Laboratory Sample No	Borehole Length (m)	Small-sized Samples			Out-Diffusion Samples		Isotope Exchange	
		No of samples	WL-P _{Grav} (Vol.%)	error 1 σ (Vol.%)	Bulk Density ¹⁾ (g/cm ³)	WL-P _{Grav} ²⁾ (Vol.%)	WL-P _{IsoEx} (Vol.%)	error (Vol.%)
Borehole KFM22								
22-3	37.18	3	0.54	0.10	2.60	0.61	0.61	0.02
Borehole KFM23								
23-4	37.90	3	0.40	0.08	2.63	0.44	0.42	0.02
23-6	57.36	3	0.63	0.12	2.64	0.49	0.51	0.02
23-7	65.61	2	0.34	0.04	2.65	0.31	– ³⁾	–
23-8	76.44	2	0.31	0.01	2.64	0.30	–	–
23-9	83.87	2	0.58	0.02	2.64	0.43	0.50	0.02
23-10	95.91	2	0.54	0.09	2.65	0.57	0.41	0.02

¹⁾ calculated from volume and mass, ²⁾ error assumed to be 10%, ³⁾ experiment not performed or experiment failed.

5 Porewater composition

5.1 Out-diffusion experiments

Out-diffusion experiments have been performed on seven core samples from boreholes KFM22 and KFM23. All samples originate from shallow depth down to about 100 m below surface. From this depth interval no previous porewater data exist for the Forsmark site.

5.1.1 Equilibrium control in the out-diffusion experiment

The monitoring of equilibrium conditions in the out-diffusion experiments was performed using extracting small-sized samples of 0.5 mL at regular intervals and analysed for their chemical composition. Equilibrium conditions were attained for the chemically conservative Cl^- and Br^- after about 50–60 days independent of the rock type, sample mass, porosity or depth of sampling (Figure 5-1). To allow a complete equilibration, the experiment time was 137 days for all samples and based on previous experience.

Deviations from the general concentration curves towards higher concentrations of Cl^- and Br^- observed for a few individual subsamples are explained by evaporation of the sample during storage (e.g. subsample 8 of sample KFM23-4 and subsample 5 of sample KFM23-8 in Figure 5-1).

5.1.2. Chemical composition of experiment solutions

The chemical composition of the supernatant solutions after termination of the out-diffusion experiments is given in Table 5-1. The quality of the chemical analyses is excellent as can be seen from the charge balance between dissolved cations and anions, which is better than $\pm 5\%$ and averages at $2.7 \pm 0.7\%$.

The pH of the experiment solutions varied between 6.92 and 7.53 and the total mineralisation ranged from 153 mg/L to 311 mg/L. These values are within the range given by previous out-diffusion experiments performed with rocks from the Forsmark site. It should be noted that the total mineralisation obtained for the experiment solutions is dependent on the water content of the sample and the water/rock ratio used in the experiment (Tables 4-1 and Table 5-1) and does not directly reflect differences in porewater salinity. Furthermore, mineral dissolution that occurs during the experiment obviously affects to a certain degree the concentrations of reactive compounds, pH and total mineralisation, so that these are not representative for *in situ* porewater. Major reactions that affect measured elemental concentrations in the experiment solutions involve the dissolution of plagioclase (Ca, Na), K-feldspar (K), biotite (K, Mg), muscovite (K), chlorite (Mg) and possibly fluorite (F), pyrite (SO_4) and calcite (Ca, CO_3). The dissolution of Al-silicate minerals consumes carbonic acid present in the initial test water and will also change the total alkalinity. Because the general rock mineralogy is rather constant for all investigated samples, mineral dissolution during the experiments is expected to be similarly uniform.

The contribution of mineral dissolution during the out-diffusion experiment is of special interest with respect to the Mg^{2+} concentration as this concentration might give some indication of a Littorina and/or Baltic Sea water component being present in the porewater of the low-permeability rocks. Geochemical scoping calculations revealed that weathering reactions during the out-diffusion experiment appear to contribute only little (in the order of 0.03 mmol/L) to the total cation concentrations in the final experiment solution (Waber et al. 2009). For Mg^{2+} , for instance, this converts to a contribution from weathering of less than about 0.7 mg/L during the experiment.

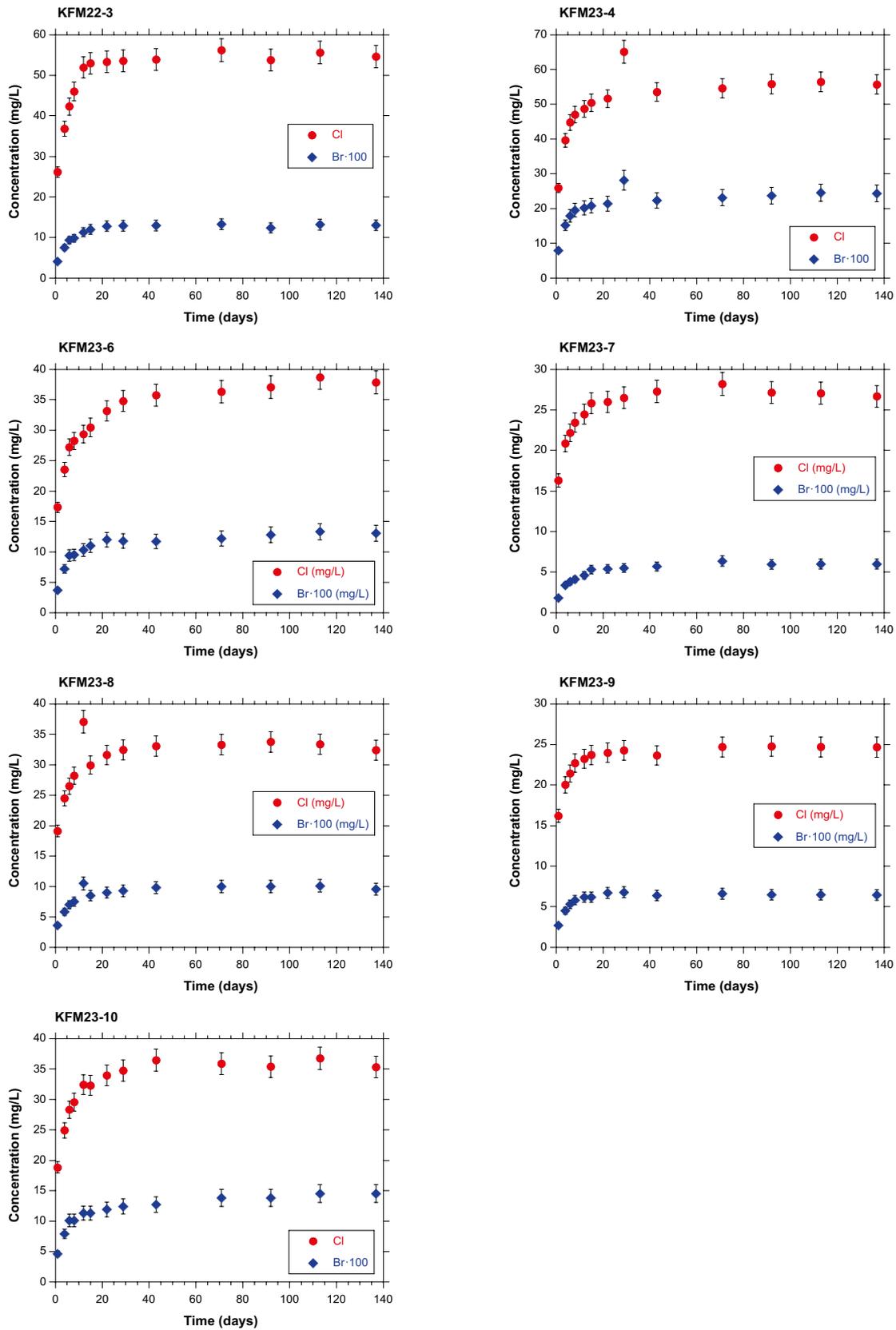


Figure 5-1. Time series of Cl^- and Br^- concentrations during equilibration of the porewater with the test water in the out-diffusion experiments of samples KFM22-3 and KFM23-4, -6, -7, -8, -9 and -10.

Table 5-1. Chemical composition of solutions from out-diffusion experiments at equilibrium conditions.

Out-Diffusion Experiment Solution	Units	KFM22-3	KFM23-4	KFM02B-6	KFM23-7	KFM23-8	KFM23-9	KFM02B-10
SAMPLE DESCRIPTION								
Borehole Length	m	41.86	37.90	57.36	65.61	76.61	83.87	95.61
Rock Type		pegm. granite	granodiorite	granodiorite	granodiorite	granodiorite	granodiorite	granodiorite
Water-Rock Ratio		0.098	0.100	0.068	0.154	0.098	0.107	0.100
Experiment Temperature	°C	45	45	45	45	45	45	45
Experiment Time	days	137	137	137	137	137	137	137
MISC. PROPERTIES								
Chemical Type								
pH (lab)	-log(H ⁺)	7.35	7.41	7.40	6.92	7.08	7.34	7.53
Sample Temperature	°C	20	20	20	20	20	20	20
CATIONS								
Sodium (Na ⁺)	mg/L	63.41	69.91	71.57	45.42	46.52	56.60	68.84
Potassium (K ⁺)	mg/L	5.31	4.65	2.60	2.42	2.76	2.37	2.67
Magnesium (Mg ²⁺)	mg/L	2.08	1.53	0.65	0.44	0.68	0.75	0.91
Calcium (Ca ²⁺)	mg/L	19.02	14.91	5.94	2.31	4.75	8.19	16.84
Strontium (Sr ²⁺)	mg/L	0.09	0.11	0.04	0.00	0.05	0.07	0.16
ANIONS								
Fluoride (F ⁻)	mg/L	3.57	5.73	5.14	6.11	6.41	6.43	4.75
Chloride (Cl ⁻)	mg/L	54.55	55.67	37.81	26.64	32.39	24.66	35.29
Bromide (Br ⁻)	mg/L	0.12	0.23	0.13	0.07	0.09	0.06	0.15
Sulphate (SO ₄ ²⁻)	mg/L	12.91	11.67	13.54	9.42	7.17	4.87	2.95
Nitrate (NO ₃ ⁻)	mg/L	6.44	1.66	1.45	2.68	1.18	5.98	0.79
Total Alkalinity	meq/L	2.22	2.11	2.1	0.95	1.09	1.88	2.92
CALC. PARAMETERS								
Total dissolved solids	mg/L	303	295	267	153	168	225	311
Charge Balance	%	-3.65	-2.67	-2.93	-1.67	-2.50	-1.94	-3.15

The concentration of Mg²⁺ in the final out-diffusion experiments solutions is 2.1 mg/L and 1.5 mg/L for the two shallowest samples (KFM-22-3 and KFM23-4) and then drops below a concentration of 0.9 mg/L for the remaining samples (Table 5-1). It thus appears that at least in the two shallowest samples a component of Littorina and/or Baltic Sea water is present.

The chemical character of the experiment solutions is fairly similar and represents a Na-Ca-HCO₃-Cl type for the shallow samples and a Na-HCO₃-Cl type for the deeper samples (Figure 5-2). Compositional differences between the two shallowest samples (KFM22-3 and KFM23-4) and the other samples are mainly relate to difference in the ratios of alkaline earth elements (Ca²⁺, Mg²⁺, Sr²⁺) to the total alkalinity, Na⁺ and Cl⁻ (Figure 5-2).

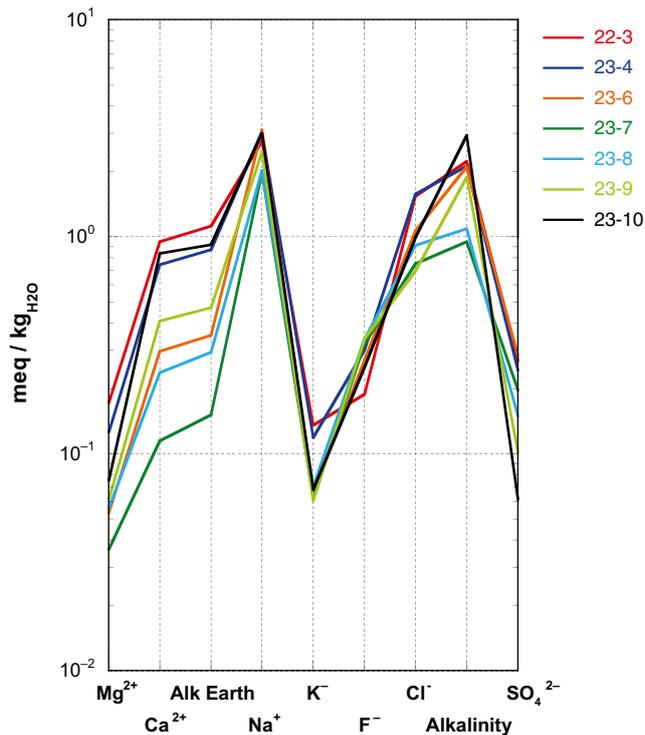


Figure 5-2. Schoeller diagram of out-diffusion experiment solutions from drillcores of borehole KFM22 and KFM23.

5.2 Chloride and bromide composition of porewater

Porewater Cl^- concentrations calculated according to equation (3-4) from the water content out-diffusion cores (Table 4-1), and the Cl^- concentration in the out-diffusion experiment solution at equilibrium of the out-diffusion process, range between 1,410 $\text{mg}/\text{kg}_{\text{H}_2\text{O}}$ and 3,546 $\text{mg}/\text{kg}_{\text{H}_2\text{O}}$ (Table 5-2). Associated porewater Br^- concentrations cover the range between 4 $\text{mg}/\text{kg}_{\text{H}_2\text{O}}$ and 15 $\text{mg}/\text{kg}_{\text{H}_2\text{O}}$.

The relative experimental error associated with these porewater concentrations can be calculated by applying Gauss' law of error propagation on equation (3-4) and the measured parameters used there. For the present samples this relative error varies between 7.1% and 9.4% (Table 5-2) and is thus below the conservatively estimated error used in previous Forsmark porewater studies ($\pm 10\%$); in this error the uncertainty induced by drilling fluid contamination is not included. For drillcore samples collected from the Forsmark borehole KFM02B at about 540 m depth below surface, the impact of drilling fluid on the porewater composition was shown to be less than 1% (Waber et al. 2011). This value can be taken as a maximum for the present samples collected at shallow depth, as the effect of stress release will be lower. In absence of the chemical composition of the drilling fluid used to drill boreholes KFM22 and KFM23, the total uncertainty cannot be quantified.

The Cl^- and Br^- when available, and the concentrations of porewater in rocks from boreholes KFM22 and KFM23, cover the range given by porewater samples from nearby boreholes KFM08C and KFM01D earlier investigated (Figure 5-3). The highest porewater Cl^- concentrations exhibited by samples KFM23-4 and KFM23-7 are almost identical to those observed in groundwater of borehole KFM01D at greater depth. In contrast, the lowest Cl^- concentrations of about 1,410–1,670 $\text{mg}/\text{kg}_{\text{H}_2\text{O}}$ (samples KFM23-6, KFM23-9 and KFM23-10) are below those observed in boreholes KFM08C and KFM01D, but similar to those observed in the Hanging Wall Bedrock Section of borehole KFM06A (Figure 5-3).

Table 5-2. Porewater Cl⁻ and Br⁻ concentrations and isotope composition (δ¹⁸O and δ²H).

Laboratory sample No	Borehole Length (m)	Lithology	Porewater Cl [mg/kg _{H2O}]	Error ¹⁾ [mg/kg _{H2O}]	Porewater Br [mg/kg _{H2O}]	Error ¹⁾ [mg/kg _{H2O}]	Porewater δ ¹⁸ O [‰ VSMOW]	Error ¹⁾ [‰]	Porewater δ ² H [‰ VSMOW]	Error ¹⁾ [‰]
Borehole KFM22										
22-3	37.18	pegmatitic granite	2,343	176	5.1	0.4	-3.3	1.4	-47.6	11.1
Borehole KFM23										
23-4	37.90	granodiorite	3,371	238	14.1	1.0	-4.2	2.1	-43.2	15.8
23-6	57.36	granodiorite	1,410	113	4.7	0.4	-6.8	1.6	-65.0	12.0
23-7	65.61	granodiorite	3,546	268	9.0	0.7	-	-	-	-
23-8	76.44	granodiorite	2,845	236	8.2	0.7	-	-	-	-
23-9	83.87	granodiorite	1,643	116	4.2	0.3	-7.5	1.5	-64.0	13.3
23-10	95.91	granodiorite	1,666	157	7.1	0.7	-9.1	1.8	-79.8	13.8

¹⁾ errors calculated with Gauss' law of error propagation.

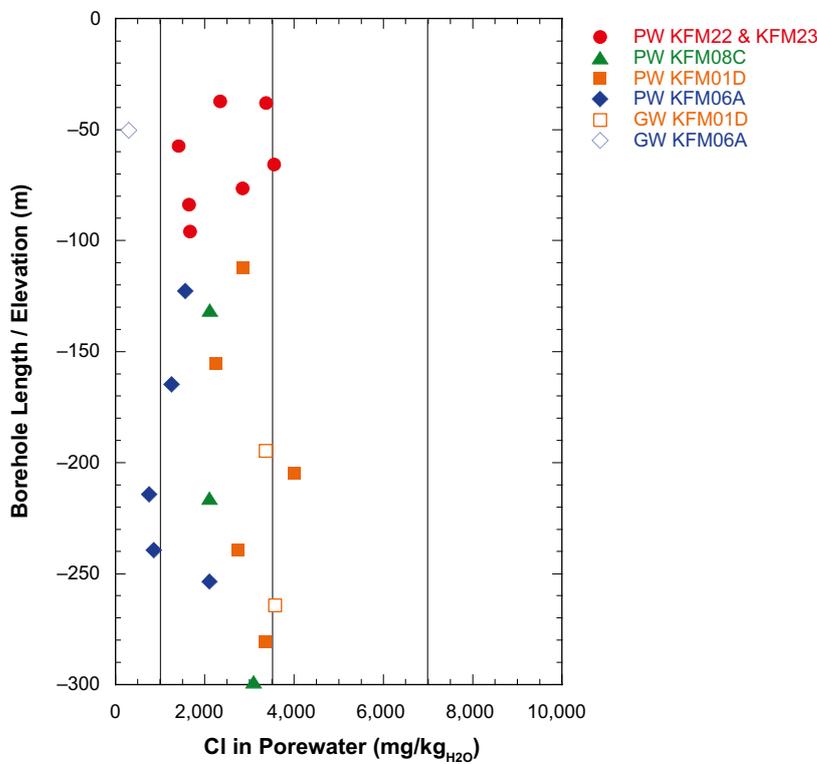


Figure 5-3. Chloride concentration of porewater from boreholes KFM22 and KFM23 as a function of sampling depth and compared to porewater and groundwater Cl⁻ concentrations from nearby boreholes KFM08C and KFM01D (data from Waber et al. 2009).

5.3 Porewater $\delta^{18}\text{O}$ and $\delta^2\text{H}$

The water isotope compositions of the porewater, expressed as $\delta^{18}\text{O}$ and $\delta^2\text{H}$ relative to VSMOW, were derived by the diffusive isotope exchange technique.

The oxygen and hydrogen isotope composition of porewater in rock samples from boreholes KFM22 and KFM23 cover the range from -3.3 to -9.1‰ VSMOW in $\delta^{18}\text{O}$ and from -43.2 to -79.8‰ VSMOW in $\delta^2\text{H}$ (Table 5-2). They plot mainly parallel to the Global Meteoric Water Line, GMWL, along a line given by the proposed end-member fracture water compositions (Figure 5-4). The KFM22 and KFM23 samples have porewater isotope compositions between that of the end-member compositions of Littorina seawater and present day infiltration. All samples have a porewater isotope composition within the range given by porewater down to 300 m depth in near-by boreholes KFM08C, KFM1D and the Hanging Wall Bedrock Section of borehole KFM06A (Figure 5-4).

As a function of depth the isotope composition of porewater appears to become more depleted in ^{18}O and ^2H from about 40 m to 95 m depth (Figure 5-5). Samples from below about 60 m depth agree well with those of porewater between 100 m and 300 m in nearby boreholes. It has been recognised that the field sampling protocol could not be completely fulfilled for the shallowest samples because of a vacuum pump failure (Åkerström K, 2011, personal communication). Therefore, in how far the two shallowest samples (KFM22-3 and KFM23-4) represent *in situ* conditions would need to be confirmed with additional samples collected from similar depths.

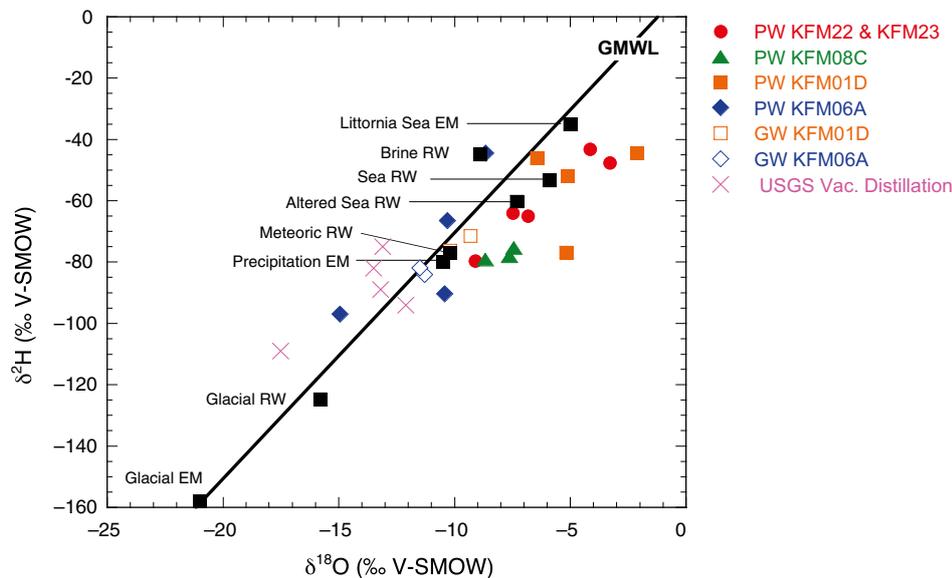


Figure 5-4. $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of porewater from boreholes KFM22 and KFM23 compared to porewater and groundwater from nearby boreholes down to 300 m depth, and also related to proposed end member (EM) and reference water (RW) compositions of various Swedish groundwaters (data from SKB 2007; see Figure 5-5 and Table 5-2 for errors).

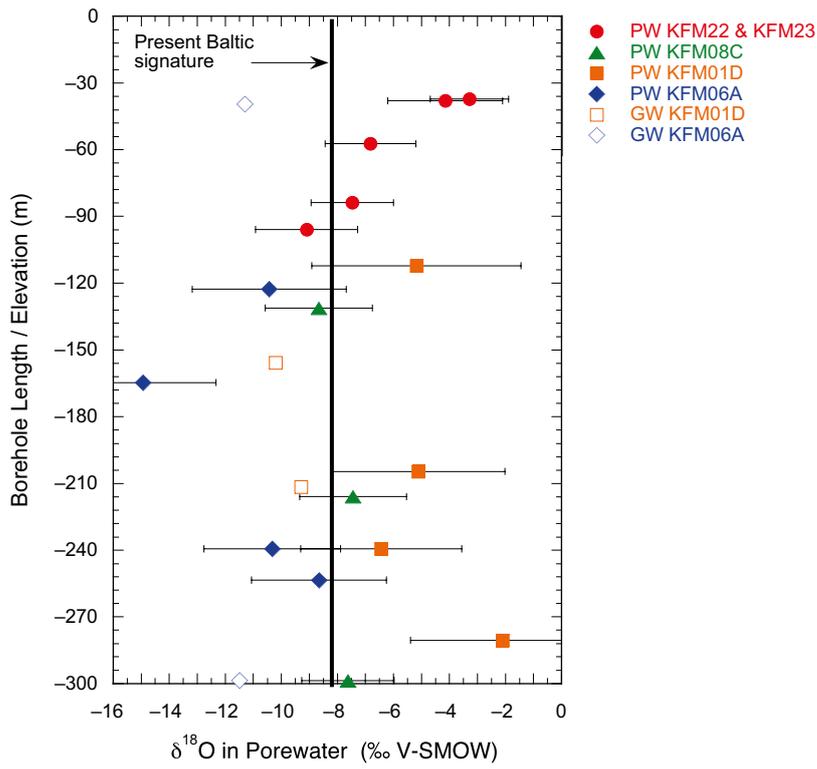


Figure 5-5. $\delta^{18}\text{O}$ values of porewater from boreholes KFM22 and KFM23 versus depth compared to porewater and groundwater from nearby boreholes down to 300 m depth (data from Waber et al. 2009).

6 Acknowledgements

We would like to thank Kenneth Åkerström (SKB) for the on-site logistics and sample selection, packaging and rapid dispatching of the drillcore samples to the University of Bern. The analytical support of P. Bähler (solution chemistry) at the Institute of Geological Sciences, University of Bern, is much appreciated.

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Memorandum on the interlaboratory porewater methodology comparison.

John Smellie (Conterra AB) and Nick Waber (University of Bern).

Within the Detum Project (Detailed Investigations in Forsmark) a ‘Methodology comparison for porewater extraction and characterisation techniques’ was initiated (cf. Activity Plan: 2011-08-30). This has involved Niklaus Waber of the University of Bern, Institute of Geological Sciences, and Zell Peterman of the United States Geological Survey (USGS) in Denver. The objective of the exercise was to compare the extraction of porewater from low porosity crystalline rocks using the tested out-diffusion method at Bern with the hitherto untested method of ultracentrifugation at the USGS. Of the two methods, ultracentrifugation would appear to offer the best option as it avoids potential chemical changes (e.g. water-rock interaction) which may be involved in the out-diffusion process of Bern. In both cases, the very small volumes of expected porewater (approx. 1–3 ml per kg rock based on out-diffusion) require highly sophisticated micro-analytical techniques with the inevitability of associated errors.

For the methodology comparison, two shallow boreholes from the upper 100 m of bedrock were sampled from the northern part of the Forsmark investigation site. Care was taken to select geologically homogeneous rock cores and to avoid section lengths containing open fractures which may be water conducting. Sample splits were taken as soon as possible after the core was brought to the surface. The exposed samples were quickly wiped to remove surplus drilling water, then packed and vacuum sealed following flushing with nitrogen to avoid any atmospheric contact and reaction, and one set of splits was immediately dispatched to the University of Bern. Based on Bern’s previous geological and mineralogical experience from the Forsmark site (Waber et al. 2009), five samples were selected quickly for study and the remaining splits to these samples were then dispatched subsequently from Sweden to the USGS laboratory.

Bern applied the same procedures of preparation, extraction and analyses based on earlier experience from both the Swedish and Finnish investigation sites (Waber and Smellie 2008, Waber et al. 2011). Extracted porewater analyses from the five splits included the conservative species Cl and Br and the stable isotopes (^{18}O and ^2H), and also a suite of non-conservative major ions subsequently corrected for any water/rock reactions incurred during the out-diffusion extraction process. Petrophysical parameters, such as measured water content, bulk density, and water-loss porosity determined by both gravimetry and isotope exchange, were also determined.

Unfortunately, the USGS laboratory was not able to extract any porewater; the water contents were very low (<0.15 percent by weight) despite spinning 150 to 200 grammes of each sample for 24 hours at 15,000 rpm. Because the core samples were well packaged, water loss was not considered an issue. In conclusion, for crystalline rock samples of low porosity (<0.5 Vol.%) it appears that porewaters cannot be extracted by ultracentrifugation with presently available equipment.

However, the USGS analysed the five sample splits for initial moisture/water content (0.09–0.14 wt.%) and bulk density (2.62–2.67 g/cm³), and also the stable isotopes on porewater extracted by the **vacuum distillation** technique. Oxygen isotopes were analysed using the CO₂ equilibration method and hydrogen isotopes by the zinc reduction method. Both methods were calibrated by analysing isotopically-heavy and isotopically-light standards and reproducibility is $\pm 0.2\%$ or better for $\delta^{18}\text{O}$ and $\pm 2\%$ or better for $\delta^2\text{H}$. The results showed that from about 58–84 m borehole length there was little stable isotope variation (–13.5 to –12.1‰ for $\delta^{18}\text{O}$ VSMOW and –94 to –75‰ for $\delta^2\text{H}$ VSMOW) but at 95.91m borehole length there was a marked depletion to –17.5‰ $\delta^{18}\text{O}$ VSMOW and –109‰ $\delta^2\text{H}$ VSMOW.

The University of Bern data for initial moisture/water content (0.15–0.24 wt.% with an average of 0.18 ± 0.05 wt.%) are systematically greater than that recorded by the USGS, but the bulk density data (2.60–2.65 g/cm³) show a similar range. With respect to the porewater stable isotopes, Bern used the **diffusive isotope equilibration** technique with a precision of $\pm 0.15\%$ for $\delta^{18}\text{O}$ and $\pm 1.5\%$ for $\delta^2\text{H}$. Data from the five sample splits ranged from –9.1 to –3.3‰ $\delta^{18}\text{O}$ VSMOW and –79.8 to –43.2‰ $\delta^2\text{H}$ VSMOW, which contrast with the more depleted USGS values. Furthermore, the Bern data show a

clear systematic increase in $\delta^{18}\text{O}$ depletion with increasing depth which is not reflected by the USGS data. Nevertheless, both sets of data show a shift to a maximum $\delta^{18}\text{O}$ depletion at the greatest depth sampled (95.91 m borehole length).

The disparity in the porewater stable isotope values from the two laboratories may reflect to some extent the complexity of the two contrasting analytical approaches used, i.e. possible fractionation effects in both cases. However, there is the additional possibility that the greater moisture/water content extracted by Bern may indicate that the USGS have not been as successful in this respect. There is little reason to assume that the sample splits studied at each laboratory are not closely compatible. Furthermore, although there was a time gap of one month between transporting the sample splits to Bern and later the USGS laboratory, in both cases the samples on arrival were well packed with no indication of atmospheric contact. However, unlikely as it may seem, it cannot be ignored that some evaporation may have been a factor contributing to the lower moisture/water contents measured by the USGS.

Assuming inadequate extraction of the moisture/water content by the USGS, this may explain the lighter isotope values measured as lighter isotope waters are preferentially removed in the initial stages of extraction. This certainly would support the difference in stable isotope values observed between the two laboratories. Furthermore, less depleted stable isotope values for the porewaters from Bern are more in line with present palaeohydrogeological interpretation of the Forsmark area.

While this interlaboratory comparison has been a very useful exercise, especially in confirming that ultracentrifugation is not an option at the moment, future comparisons involving at least two additional laboratories should focus now on replicating the Bern approach of out-diffusion (or other approaches) to ensure or otherwise its reliability, in particular the confidence in the stable isotope values both with respect to the analytical approach used and confidence in that the maximum moisture/water content has been extracted for analysis. Lastly, although it is thought that the delay of one month in shipping the samples to the USGS laboratory (mostly due to administrative/customs problems at the USGS) did not contribute significantly to the results, there still remains a question mark and future effort should be made to shorten as much as possible the time gap in transporting sample splits to different laboratories.

June 25, 2012

Comments on USGS results for water extraction and stable isotope measurements for core from Borehole KFM23 (SKB Memorandum of 12-06-25)

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Isotopic and chemical characterization of pore water in low porosity and low permeability matrices of rocks such as gneisses and granites continues to be pose challenges even after decades of study. Core samples from KFM23 are no exception.

To reiterate the measurements by the USGS on SKB core from KFM23, initial moisture measurements were made on 100 to 150 grams of core broken into pieces of 3 cm on edge or less. These samples were heated in a drying oven at 120°C for 5 to 7 days. Water for the stable isotope measurements was extracted from approximately 100-gram samples of core broken into large pieces and heated to 105°C for 48 hours in a vacuum system. The water sample was collected in a cold finger, and the core pieces were returned to the drying oven where they were heated at 120°C for an additional 2 to 3 days. Further weight loss (water loss) was small (less than 0.01 weight percent). However, because of the small initial water content of the samples, this post-extraction loss could have composed as much as 10 to 15 percent of the total water present in the core.

Two issues are assessed in the Smellie and Waber memorandum of 12-06-25: (1) the differences in measured moisture contents between the USGS and the RWI (Rock Water Interaction) group and Bern, and (2) the differences in the stable isotope compositions measured by the different techniques. Smellie and Waber attributed the lower water contents of the USGS measurements to (1) water loss during holding and transport time or (2) subsequent incomplete water extraction in the laboratory. We agree that water loss during the holding and shipping time is unlikely (this would have fractionated oxygen and hydrogen compositions of the residual water to heavier values), whereas incomplete water extraction seems likely. The time-weight loss curve of Waber and Smellie for a temperature of 105°C (2012, Figure 5) for a core sample from KFM23 at a depth of 37.90 meters indicates extraction of 80 to 85 percent over 2 to 7 days of heating. Thus, incomplete moisture extraction in the USGS experiments is likely.

Given the incomplete water extraction, the oxygen and hydrogen isotopic differences between the RWI and the USGS measurements can be explained by Raleigh fractionation during the vacuum distillation extraction. Therefore, the USGS approach did not test the validity of the RWI diffusion approach for determining the isotopic composition of pore water.

The physical processes involved in vacuum distillation and diffusive isotope equilibration methods may not be well understood, but such an understanding is immaterial if complete isotopic equilibration or complete water extraction is attained. The small amount of water in these rocks is likely held in microfractures within and between grains, in grain boundaries and triple-point intersections of different grains. Chemically bound water in high-temperature hydrous minerals and primary fluid inclusions would not be accessed by either method.

The USGS still maintains confidence in the vacuum distillation approach providing that complete or nearly complete extraction can be obtained and demonstrated. Time (as shown by RWI) is the fundamental parameter controlling moisture release regardless of the physical disposition of the porosity. If SKB is interested, the USGS could conduct a study of one of the KFM23 core samples using much longer periods of extraction such as 30 days and 60 days. After the initial sampling, the core samples were resealed and are currently stored in a refrigerator to preserve moisture.

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