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Hydrogeochemical evaluation of the Forsmark site, modelling stage 2.1 – issue report

Svensk Kärnbränslehantering AB

May 2007

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the authors and do not necessarily coincide with those of the client.

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Preface

This work forms part of the initial site investigation stage of the hydrogeochemical evaluation carried out at the Forsmark site leading to a Hydrogeochemical Site Descriptive Model version 2.1. SKB's ChemNet, consisting of independent consultants and university personnel, carried out the modelling during the period October 2005 to December 2006. The INSITE and SIERG review comments on the earlier model versions of Forsmark were considered in this work. Several groups within ChemNet were involved and the evaluation was conducted independently using different approaches ranging from expert knowledge to geochemical and mathematical modelling including also transport modelling. During regular ChemNet meetings the results were presented and discussed. The ChemNet members contributing to this report are (in alphabetic order):

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Summary

This issue report is performed in an interim phase of the project to focus and sort out a few hydrogeochemical key issues for further understanding the site and for improving the site description in time for the 2.2 and 2.3 analyses. The report addresses certain INSITE, SIERG and ChemNet issues (19) related to modelling the 2.1 Forsmark hydrogeochemical data. These issues are associated with explorative analysis, mathematical modelling and conceptualisation of the site. The aim of the work, therefore, is not to update the site descriptive model of Forsmark, but to differentiate those areas or issues that are being adequately addressed, to those requiring more focussed attention in preparation for the 2.2 and 2.3 stages.

Explorative analysis issues: New data have helped to better describe or understand issues related to groundwater origin and evolution, interactions of surface/deep groundwater systems, redox fronts and high U and Mn values, together with microbes, gases and colloids.

Mathematical modelling issues: These issues ranged from modelling or redox conditions, uncertainty analyses of mixing proportions and mass balance deviations, integration of hydrochemical data with mineralogical and microbial data, to the role of monosulphides. M3 issues such as proper selection of end-members and variables in the modelling were addressed. Issues related to drilling impact study (DIS) and the use of electrical conductivity to address the issue of spatial variability.

Conceptual modelling issues: These issues concern 2D and 3D large and small scale conceptualisation approaches and closer and better integration with hydrogeology.

The Forsmark 2.1 data imply relatively small modification to the version 1.2 hydrogeochemical site description, but the overall geochemical understanding of the site has improved. This includes confirmation of previous findings from version 1.2 and also support for the predictions made in version 1.2 based on the limited knowledge at that time. The confidence concerning the three-dimensional variability of processes and properties has also improved due to the addition of both new data in previously drilled boreholes and from new boreholes in specific key areas. By addressing 19 key issues the uncertainties for some of the major processes have been decreased.

The major conclusions and implications for the forthcoming modelling work are:

- New F2.1 data and the modelling applied to address issues related to groundwater origin, evolution and key hydrogeochemical processes have reduced the uncertainties and improved the site understanding. Moreover, additional data needs have been recognised and will be implemented to further this understanding.
- New data from the 2.2 and 2.3 stage require revisions/control/update of the issues related to buffer capacity, compositions and properties of the groundwater relevant to the safety assessment and site understanding.
- The addressed issues can be used as reference cases for the forthcoming final Forsmark and Laxemar modelling. Issues not related to safety assessment or key site understanding can be given a lower priority.
- Further integration between different geoscientific disciplines such as geology, hydrogeology and surface chemistry is required to produce a robust hydrogeochemical site description.

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1 Introduction

1.1 Background and objectives

The Swedish Nuclear Fuel and Waste Management Company (SKB) is undertaking site characterisation at two different locations, the Forsmark and Simpevarp areas, with the objective of siting a geological repository for spent nuclear fuel. The investigations are conducted in campaigns with periodic ‘data freezes’, i.e. dates when no further data are incorporated in the database to allow for interpretation and modelling. After each data freeze, the site data are analysed and site descriptive modelling is carried out with the purpose to develop a Site Descriptive Model (SDM) of the site. A Site Descriptive Model is a synthesis of geology, rock mechanics, thermal properties, hydrogeology, hydrogeochemistry and a surface system description.

So far, two versions of SDM (versions 1.1 and 1.2) have been developed for the Forsmark area. Version 1.1 /SKB 2004/ was completed during 2004 and version 1.2 in June 2005 /SKB 2005a/. Version 1.2 of the SDM concluded the Initial Site Investigation phase (ISI) and formed the basis for a preliminary repository layout (layout D1) as well as for a preliminary safety evaluation (PSE) of the Forsmark site /SKB 2005b/ and a Safety Assessment (SR-Can) of repository layout D1 at Forsmark.

According to present plans, three modelling steps will be carried out during the Complete Site Investigation phase. The scope of the first two modelling steps, 2.1 and is limited, whereas the final step, 2.2 and 2.3, will result in a complete site description. The aim of the 2.1 phase was to give feedback to the site /SKB 2006a/ and to address review issues brought up by various review groups such as INSITE (INdependent Site Investigation Tracking & Evaluation, a review group supported by the authorities such as SKI /e.g. SKI 2005/ SIERG (Site Investigation Expert Review Group, review group supported by SKB) and the ChemNet group itself. This issue report focus and sort out a few key hydrogeochemical issues for understanding the site and for improving the site description in time for the 2.2 and 2.3 analyses. This report describes the work associated with handling of issues based on the Forsmark 2.1 data the aim of the work is not to update the site descriptive model.

1.2 Methodology and organisation of work

Site descriptive modelling comprises the iterative steps of primary data evaluation, descriptive and quantitative modelling and an overall confidence assessment. The applied methodology is described in the methodology report /Smellie et al. 2002/. The analysis and modelling work conducted within modelling step 2.1 has been organised in the same way as the previous modelling version within the discipline specific ChemNet working group. The aim this time was not to update the SDM but rather to address INSITE and SIERG review issues together with issues identified within the ChemNet group (see Chapter 3). The individual modelling contributions are presented in Appendices A–G and the data used in the modelling is presented in Appendix H. Some of the appendices contain details, modelling and approaches that are not described elsewhere in the report. The reader is therefore encouraged to become familiar with the appendices in order to get a complete picture of the work done within the Forsmark 2.1 modelling.

2 Available primary data

2.1 Data freeze 2.1 – investigations performed

The data included in data freeze 2.1 are those that were available for model version 1.2 and new data acquired between data freezes 1.2 and 2.1 (see Figure 2-1). The investigations associated with data collection during the period between the two data freezes comprised both surface and borehole investigations.

Hydrogeochemical logging and characterisation as well as microbial investigations have provided new data from the cored boreholes KFM05A, 06A, 07A and 08A and from the percussion-drilled holes HFM20, 21 and 22. In addition, core samples have been collected from KFM06A for determination of the composition of the rock matrix pore water.

2.2 Databases

The basis for the work conducted in modelling step 2.1 is quality assured field data from Forsmark that were available in the SKB databases SICADA at the time of data freeze 2.1. These data are compiled in tables in Appendix H. The purpose of these tables is to give a reference and account of which data were available and considered in the interpretation and modelling work conducted during step 2.1 of the site descriptive modelling. Primary data used in the analysis and modelling work are described in more detail in the subsection below.



Figure 2-1. Boreholes included in data freeze 1.2 (left) and boreholes included in data freeze 2.1 (right). New boreholes between the two data freezes are named in the right figure.

2.2.1 Available data

The Forsmark 2.1 data freeze included hydrogeochemical data derived from the drilling of three new percussion boreholes (HFM20, 21 and 22) and four new cored boreholes (KFM05A, 6A, 7A and 8A), and sampling from an additional 6 shallow soil pipe installations (SFM0022, 59, 61, 62, 63 and 64).

Surface investigations (lake and stream waters) have been evaluated with respect to demarcating potential recharge/discharge localities and establishing the natural distribution of ¹⁴C and tritium in the Forsmark region (i.e. from primarily a precipitation source). This latter issue is important since there may be some additional effects from the nearby nuclear plant facilities. Borehole investigations have continued to further expand knowledge regarding the vertical and lateral extent of the various identified hydrochemical end members, and the origin and evolution of these end members.

Anomalously high uranium concentrations, often (but not always) coinciding with the Littorina Sea groundwater component, have become a debatable issue to be resolved (see Chapter 3).

Characterisation of additional fractures and their infillings have added further understanding to the spatial extent and origin of specific mineral indicators that can contribute to unravelling the palaeo-evolution of some groundwater types, and also in estimating the depth of redox fronts, etc (Appendix A).

Accessible, interconnected pore water has been extracted successfully by laboratory out-diffusion methods from crystalline rocks using some 20 core samples from borehole KFM06A as part of the Forsmark hydrogeochemical site investigation programme (Appendix A).

The Forsmark 2.1 data extracted from the SICADA database have been screened and reviewed to produce groups of data characterised with respect to being suitable or less suitable for quantitative modelling purposes (Table 2-1).

Table 2-1. The total number of representative samples included in the Forsmark 2.1 data base. Orange = Most representative/suitable (relates to all water types if applicable), Green = Less suitable and to be used with caution (relates to all water types if applicable), Pink = Least suitable and to be used with caution (relates only to surface waters).

		Total number of samples	Representative samples		
			Orange	Green	Pink
Percussion boreholes		107	3	16	
Packed-off sections in cored boreholes	KFM01A	150	2	1	
	KFM02A		2	2	
	KFM03A		4	2	
	KFM04A			2	
	KFM05A				
	KFM06A		1	2	
	KFM07A			1	
Near-surface groundwater		267		231	
Sea water		255		42	106
Lake water		352		80	253
Stream water		341		74	249
Precipitation		23		19	

Percussion boreholes

To gain more insight into the hydrochemical stratification in the upper 100–200 m of bedrock, data have been subdivided into samples collected from: a) percussion borehole sections < 50 m where the groundwater data can be related approximately to a more constrained bedrock level, i.e. dominant water conducting fracture, and b) total percussion borehole lengths which can vary from 100 m to 300 m true depth below the surface. These latter boreholes mostly represent a homogenised mixed groundwater. It is important to know the chemistry of such waters when they are used as a source of flushing water during drilling of the deep cored boreholes, but otherwise such data is of little use in understanding the groundwater stratification in the upper 300 m of bedrock. Table 2-2 provides the approximate depth of major groundwater input to the different percussion boreholes. These data may be used qualitatively to indicate potential hydrochemical stratification in the upper bedrock.

Table 2-2. Locations (vertical depth) indicating points of maximum water flow into the Forsmark percussion boreholes.

Borehole	Sections (vertical depth) with maximum water volume input into the borehole	Borehole	Sections (vertical depth) with maximum water volume input into the borehole
HFM01	~ 38 m	HFM12	~ 93 m
HFM02	~ 43 m	HFM13	~ 140 m
HFM03	~ 21 m	HFM14	Not determined
HFM04	~ 61 m	HFM15	Fairly uniform input along the borehole
HFM05	~ 153 m	HFM16	~ 59 m (some also from 42 m)
HFM06	~ 70 m	HFM17	~ 31 m
HFM07	Not determined	HFM18	~ 30–40 m
HFM08	~ 138 m	HFM19	~ 150 m
HFM09	~ 24 m	HFM20	~ 25 m
HFM10	~ 110 m	HFM21	~ 84–136 m
HFM11	~ 32 m (some also from 83–108 m)	HFM22	~ 53 m

Cored boreholes

Additional boreholes to those evaluated in Forsmark 1.2 are KFM05A, KFM06A, KFM07A and KFM08A; additional sampling of KFM04A is also included. Evaluation of samples from the four new boreholes made use of the published differential flow logs, hydrochemical logs and also hydrochemical characterisation of sampled groundwaters.

The final selection of data which best represents the sampled borehole section is based on identifying as near as possible a complete set of major ion and isotope (particularly tritium, ¹⁸O and deuterium plus carbon isotopes when available) analytical data. This is not always the case, however, and a degree of flexibility is necessary in order to achieve an adequate dataset to work with. For example:

- A charge balance of $\pm 5\%$ was considered acceptable.
- Less or close to 1% drilling water was considered acceptable for suitable (representative) groundwaters. In some cases groundwaters of limited suitability were chosen when exceeding 1% (but < 5%) to provide a wider selection of groundwater data to work with. These groundwaters should be treated with caution if used quantitatively.
- In borehole KFM03A, sections 803.20–804.20 m and 939.50–956.62 m indicate drilling water contents of 16.5% and 11.2% respectively. These have been highlighted in green although strictly speaking they should have been omitted because of high drilling water content. However, because of the general lack of deep groundwater chemistry data at Forsmark, they have been included at this juncture, but should be treated with great care when used quantitatively.

Resulting from this assessment, two groundwater sample types are highlighted in the SICADA database; one type considered representative or suitable (in orange), the other type less representative or of limited suitability (in green) and should be used with caution.

Open-hole tube sampling has been carried out in the cored boreholes. Whilst this approach can be very useful in evaluating borehole groundwater circulation pathways and groundwater budgets (e.g. water in and water out between the borehole and surrounding bedrock), the fact is that these groundwaters may be mixed to varying degrees due to: a) borehole hydraulics, b) borehole activities prior to sampling, and c) perturbation during lowering of the tube system into the borehole, and so their representativeness (or suitability) to describe the bedrock formation waters is questionable.

Consequently, groundwater samples relating to the SICADA tube sampling data contained in the Forsmark 2.1 data freeze are considered unsuitable for use.

Wells, springs and trenches (PFM-series)

Most of these surface waters have a time series of data (most were sampled on 3 occasions over the period of a year) covering autumn and spring. Some have been sampled on two occasions and some only on one occasion, but all these data still can be incorporated to some limited extent since they represent at least one season. Future data freezes should provide additional seasonal values plus outstanding ^{14}C data.

All samples have been highlighted in green to indicate:

- satisfactory charge balance ($\pm 5\%$),
- good coverage of major elements,
- several trace elements,
- tritium,
- ^{18}O and D,
- No ^{14}C (exception: the excavated trench).

Because of the complex nature of the near-surface environment being sampled, all samples in Appendix H have been highlighted in green until future interpretative studies and greater understanding of this environment suggest otherwise.

Soil monitoring pipes (SFM-series)

Most of the soil pipe waters have a good seasonal time series spread over a period of 1.5 years, although some are restricted to only one or two sampling occasions within this period. Other locations included in the earlier 1.2 data freeze that are usually restricted to one sampling occasion, have not been, and will not be, further sampled within the hydrochemical programme. However, even if there may be only one sample from a particular location collected at one season, it may have some general use when included with other better-constrained seasonal values, as mentioned with the PFM-series samples above.

All suitable data, i.e. indicating at least:

- satisfactory charge balance ($\pm 5\%$),
- good coverage of major elements,
- several trace elements,
- tritium,
- ^{18}O and D,

have been included and highlighted in green. Many samples also have more complete data, e.g. ^{14}C (plus boron and chlorine isotopes), REEs and the U/radium/radon group. These samples with more complete analytical data could have been highlighted in orange, but because of the complex nature of the near-surface environment being sampled, all samples have been highlighted in green until future interpretative studies and greater understanding of this environment suggest otherwise.

Baltic Sea water

Baltic Sea samples have been collected over a three year period. Evaluation of suitability is based on:

- satisfactory charge balance ($\pm 5\%$),
- good coverage of major elements,
- within 2,500–2,800 mg/L Cl,
- tritium,
- ^{18}O and D,
- $\pm ^{14}\text{C}$.

Samples satisfying these criteria are highlighted in green. Samples based only on the first three criteria (i.e. no isotopic data) are highlighted in pink.

Lake and stream water

Lake and stream samples have been collected over an approximately three year period. Evaluation of suitability is based on:

- satisfactory charge balance ($\pm 5\%$),
- good coverage of major elements,
- tritium,
- ^{18}O and D,
- $\pm ^{14}\text{C}$.

In common with some of the near-surface soil monitoring pipe groundwaters, these surface waters may have been subject to seasonal fluctuations, complex reaction processes in the biosphere and potential discharge influences. Consequently, in the absence of knowing what could be representative or not, all selected samples that conform to the above criteria are recommended at this juncture (highlighted in green). Samples restricted only to major ion analytical data (perhaps due to poor sampling), have also been recommended cautiously for use (highlighted in pink).

Precipitation

Twenty two samples are included, collected during an approximately two year four month period. These waters have not undergone any representativity check *sensu stricto*. On the other hand, the main intention has been to monitor $\delta^{18}\text{O}$, D and tritium, since these parameters are used to identify modern meteoric groundwater components at depth. Disturbances, such as unpredictable annual and seasonal trends and possible evaporation, have not been evaluated in this present representativity check. Because of the difficulty of assessing representativeness, samples with isotopic values are highlighted in green in the Forsmark 2.1 data base.

Data collected during drilling

The drilling event is considered to be the major source for contamination of the formation groundwater. During drilling, large hydraulic pressure differences can occur due to uplifting/lowering of the equipment, pumping and injection of drilling fluids etc. These events can facilitate unwanted mixing and contamination of the groundwater in the fractures, or the cuttings at the drilling head itself can change the hydraulic properties of the borehole fractures. It is therefore of major importance to analyse the drilling events in detail. From this information not only can the uranine-spiked drilling water be traced, but also the major risk of contamination and disturbance from foreign water volumes can be directly identified. Insufficient or excessive extraction of water from a deformation zone prior to sampling can be determined by applying DIS (Drilling Impact Study) modelling (see, Appendix D).

The DIS modelling requires evaluation of data that are not normally included in the hydrogeochemistry data set. The drilling rig records various parameters during the entire drilling event. This so called DMS (Drilling Machine Survey) data is recorded in separate data files that have to be requested from SICADA. In addition, for the DIS study, electrical conductivity (EC) values recorded during the DIFF (Differential flow) measurements are needed. The extraction and compilation of this data has been problematic for the Forsmark 1.2 and 2.1 modelling phases. The problems can be associated with how the data files are organised, missing information concerning the meaning behind variable names, unequal dosing of uranine at times in the flushing water and inaccuracy in recording of the water volumes pumped in and out from the borehole during drilling. This makes DIS difficult or impossible and makes the determination of the disturbances from drilling inaccurate.

3 Addressed hydrogeochemical key issues in understanding the Forsmark site

The INSITE, SIERG and ChemNet issues addressed in this report are listed in Table 3-1. The issues are addressed and summarised in the subsections below and are described in detail in Appendices A–G. The issues are based on explorative analysis, mathematical modelling and conceptualisations and are, therefore, organised according to these categories in the chapters below.

Table 3-1. Hydrogeochemical issues addressed in this report with references to the appendices with comprehensive information. Some of the issue numbers are missing in the list since they were included in the issues listed.

Issue to be addressed within the 2.1 work	Issue No. Used within the F2.1 modelling	Report contrib.
Groundwater origin and evolution	1	App#A
Conceptual modelling in 2D and 3D	2	App#A, App#E
Interaction of surface/deep groundwater systems	3	App#A; App#E
Redox front considerations	5	App#A, App#B
Gases	6	App#B
Colloids	7	App#B
Microbes	8	App#B
High manganese values - manganese reducing bacteria	9	App#B, App#C
Redox conditions	10	App#B, App#C
High Uranium content	11	App#A, App#B, App#C, App#F, App#G
Uncertainties analysis (mixing proportions and mass balance deviations)	15	App#C
Revision of conceptual model (role of monosulfides)	16	App#C
Integration of hydrochemical data with mineralogical and microbial data	17	App#C
Investigation of the recharge end-member and its effect on the mixing models and the site understanding	18	App#D
The proper use of Tritium in the models	19	App#D
Test of models including all elements and isotopes versus models with conservative constituents (D, O18, Tr)	20	App#D
Comparison of different models and the number of observations they can describe	21	App#D
Evaluation of suitable data from SICADA and DMS to perform Drilling Impact Study (DIS) calculations	23	App#D
Evaluation of the Electric Conductivity for K boreholes and its use for understanding/validate the GW spatial variability	24	App#D

3.1 Explorative analysis issues

Explorative analysis includes expert judgement and modelling of primary data. The issues related to explorative analysis are addressed in the chapters below.

3.1.1 Groundwater origin and evolution (Issues#1 and #2; App#A)

Explorative analysis in Appendix A has basically updated the Forsmark 1.2 major ion and environmental isotope plots. This has confirmed and strengthened existing hydrochemical trends, and the chemistry and evolution of the various groundwater types. In addition, there are some new data which may suggest that the Forsmark area could be viewed as having two distinct hydrogeochemical systems, i.e. one above and one below the gently-dipping ZFMNE00A2 (i.e. ZFMA2) deformation zone which is a dominant hydrostructural feature in the area. Such gently-dipping deformation zones are regionally common and are known to separate contrasting groundwater types. For example, 'Zone 2' at Finnsjön, sharply separates groundwaters of fresh (< 300 mg/L Cl) and brackish (~ 5,500 mg/L Cl) chemistry /Smellie and Wikberg 1991/.

Differences in salinity gradients

General features

Salinity differences within the Forsmark area are indicated in Figure 3-1 and Figure 3-2 which show the distribution of chloride with depth, and the relationship between chloride and $\delta^{18}\text{O}$, respectively. Figure 3-1 is interesting because of the anomalously high chloride content of 14,400 mg/L which occurs at a slightly shallower depth (KFM07A: 924.77 m vertical depth) than the previously highest value of 9,690 mg/L (KFM03A:990.6 m vertical depth). Although this high value could be explained by groundwater being brought from deeper, fractured levels during sampling, it is also noticeable that this borehole section is located entirely below the gently dipping deformation zone ZFMA2, whilst KFM03A is above. This may suggest simply that groundwaters below zone ZFMA2 achieve greater salinity at shallower depth, or it is an indication of a differently evolved groundwater system as inferred above.

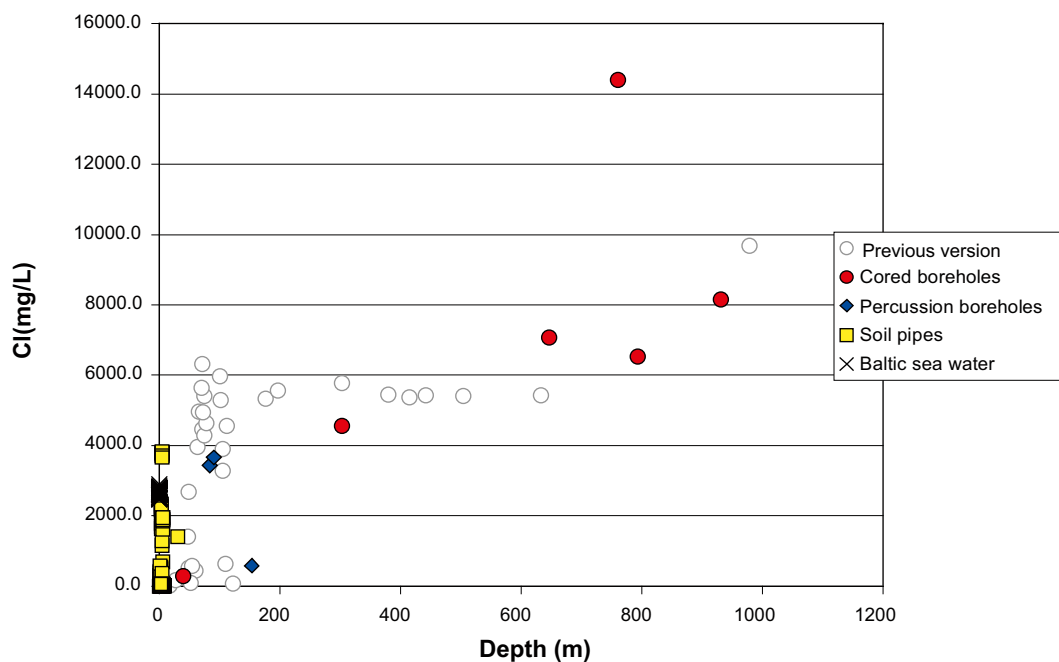


Figure 3-1. Distribution of chloride with increasing depth.

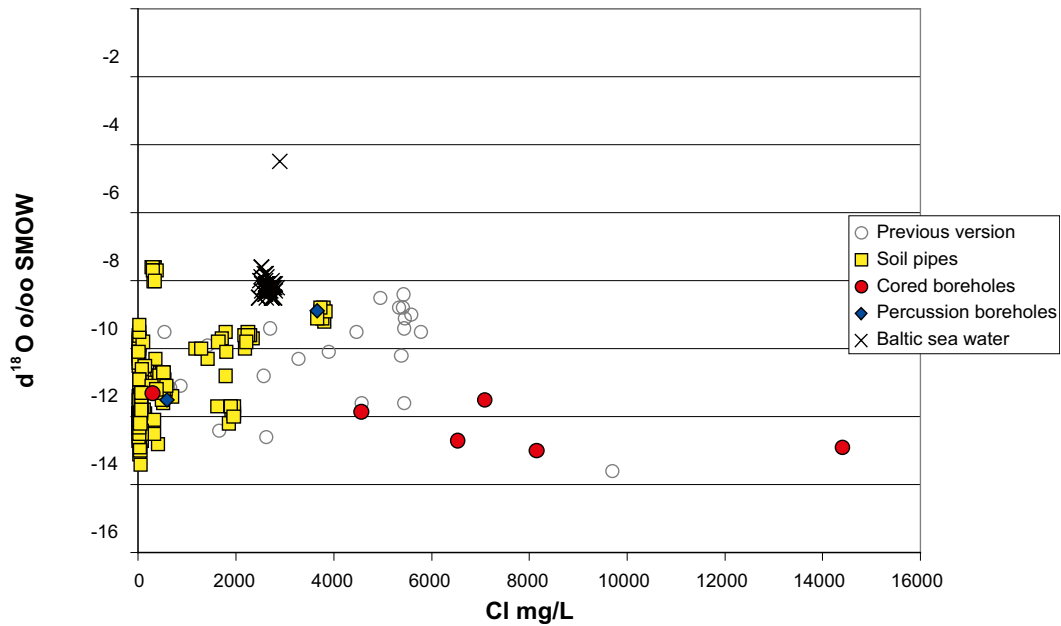


Figure 3-2. Distribution of chloride versus $\delta^{18}\text{O}$.

Figure 3-2 demonstrates four features strengthened by the Forsmark 2.1 data: a) the large spread of $\delta^{18}\text{O}$ values for the fresh soil pipe groundwaters (< 300 mg/L Cl), most likely reflecting seasonal precipitation variations, b) the separate group of soil pipe groundwaters at higher salinity (~ 300–2,500 mg/L Cl), some with a light $\delta^{18}\text{O}$ signature, c) a small cluster of soil pipe (and one percussion borehole) groundwaters of more brackish composition (~ 3,700 mg/L Cl) with heavier $\delta^{18}\text{O}$ signatures plotting close to the Littorina Sea type waters, and d) the continued light $\delta^{18}\text{O}$ values for the deeper, more saline groundwaters (> 8,000 mg/L Cl), indicating a distinct cold climate recharge (glacial) component at the maximum depths sampled. The latter point is interesting in that irrespective of where the deep samples have been taken, i.e. above or under zone ZFMA2, glacial waters have been intruded to considerable depth at some stage in the past.

The influence of structural features

Figure 3-3 shows a NE-SW schematic representation of the Forsmark site with the locations of the boreholes and their relationship to zone ZFMA2 and other gently-dipping deformation zones to the SE /SKB 2006a; modified after Follin et al. 2005/. Note that the demarcated repository area (hatched red line) is at the hanging wall side of zone ZFMA2, which is devoid of important gently-dipping deformation zones.

Figure 3-4 shows the major structural divisions of the area which are referred to as:

- NE Hanging wall of zone ZFMA2 (i.e. FFM03).
- NW Foot wall of zone ZFMA2 subdivided into:
 - surface to depth of ~ 150 m (i.e. FFM02),
 - boundary/border (not indicated, but to the NW),
 - middle (i.e. FFM01).

The structural divisions, and corresponding differences in transmissivity, have been used to present and interpret the updated hydrochemistry data. This is illustrated in Figures 3-5 and 3-6.

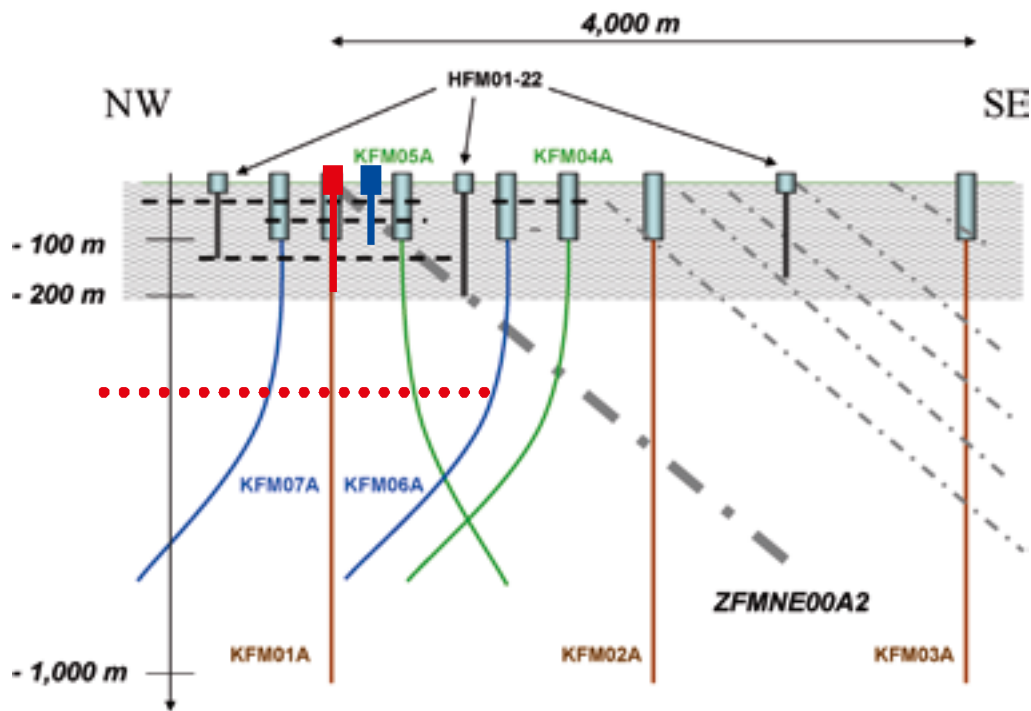
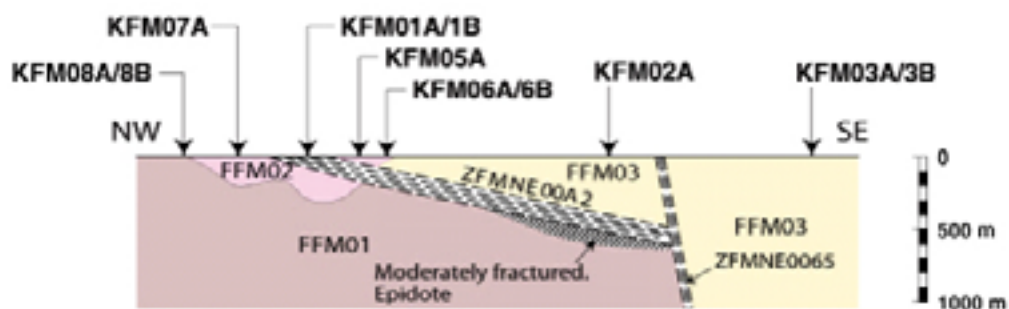


Figure 3-3. Schematic representation of the Forsmark site showing the position, depth and orientation of the boreholes, the position of the gently-dipping ZFMA2 deformation zone and the possible location and depth of a repository construction (red hatched line). The shaded upper 200 m represents bedrock of high transmissivity which contrasts sharply with low transmissive bedrock at increased depth. HFM01–22 represents the lateral extent of these 22 percussion boreholes along the NW-SE transect. /SKB 2006a; modified from Follin et al. 2005/.



Fracture domain (FFM01)

Steeply dipping, minor fault zones with sealed fractures, low fracture frequency between zones, high in situ stress

Fracture domain (FFM02)

High frequency of sub-horizontal fractures with apertures

Fracture domain (FFM03)

High frequency of gently dipping, minor deformation zones containing both sealed fractures and fractures with apertures, low in situ stress relative to FFM01

Figure 3-4. Major structural subdivisions in the Forsmark area. Only two fracture zones, the gently dipping zone ZFMA2 and the steeply dipping zone ZFM65, against which zone ZFMA2 appears to truncate to the SE, are shown /SKB 2006a/.

In Figure 3-5 there are two similar and fairly well defined trends: a) related to the gently-dipping deformation zone ZFMA2, and b) related to the hanging wall of zone ZFMA2 in the Fracture Domain Block (FFM03). Taken together, from the surface to depth, the salinity is seen to rapidly increase from fresh water values close to the surface (< 300 mg/L Cl), through low saline values (300–2,000 mg/L Cl) to brackish values (around 4,300 mg/L Cl) at around 100 m depth. The salinity then evens out forming a plateau at 5,000–6,000 mg/L Cl until around 600 m depth where there is a gradual but consistent increase to just under 10,000 mg/L Cl at 1,000 m depth. At the foot wall of zone ZFMA2, i.e. Fracture Domain Blocks (FFM01+02), there are too few data. However there may be a suggestion of a separate salinity trend with a more restricted brackish groundwater plateau and a more rapid increase in salinity at 600 m to the highest value measured for Forsmark at around 14,800 mg/L Cl at just under 800 m depth.

Figure 3-6, plotting chloride against $\delta^{18}\text{O}$, shows three general groupings: a) shallow, fresh to low saline groundwaters, with values of $\delta^{18}\text{O}$ ranging from -12 to -10 ‰ SMOW, b) brackish groundwaters with a large range in $\delta^{18}\text{O}$ (-14 to -8 ‰ SMOW), and c) high saline groundwaters with values restricted to depleted $\delta^{18}\text{O}$ (-14 to 12.5 ‰ SMOW). The fresh to low saline groundwaters have typical recharge $\delta^{18}\text{O}$ values, and the deep, high saline groundwaters with depleted $\delta^{18}\text{O}$ values signify a cold climate component. The brackish groundwaters are more complex since they are a mixture of an ancient cold climate recharge component (depleted $\delta^{18}\text{O}$ signature), an old Littorina Sea component (enriched $\delta^{18}\text{O}$ signature) and, more recently, of meteoric waters (modern recharge-type $\delta^{18}\text{O}$ signature).

The complexity of the brackish groundwaters is exemplified further in Figure 3-7, where groundwaters with Br/Cl ratios < 0.0045 and Mg values higher than 100 mg/L are shown in a Cl versus $\delta^{18}\text{O}$ plot. It is obvious that the marine water samples in the bedrock at Forsmark and SFR (Final Repository for Radioactive Operational Waste) follow two major trends: a) one indicating mixing between Littorina Sea water and glacial meltwater, and b) the other indicating mixing between Littorina Sea and modern meteoric groundwater. The latter is common for the water sampled in the percussion boreholes whereas the water sampled in the cored boreholes follows the former trend. The mixing of modern Baltic Seawater is evident in a few samples such as percussion boreholes HFM08 and HFM22.

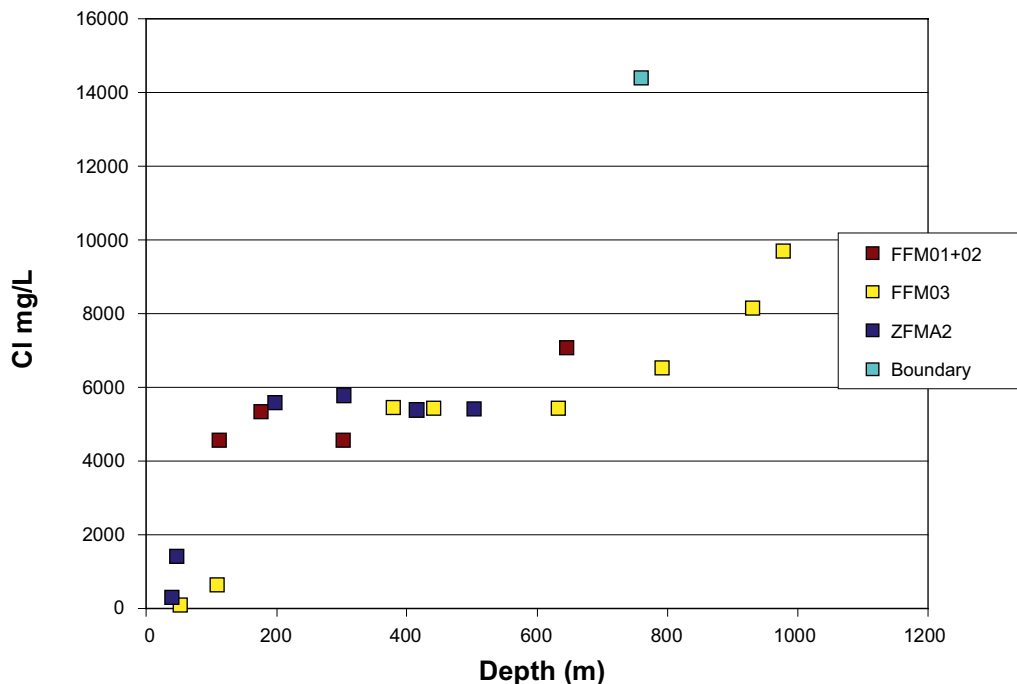


Figure 3-5. Chloride versus depth.

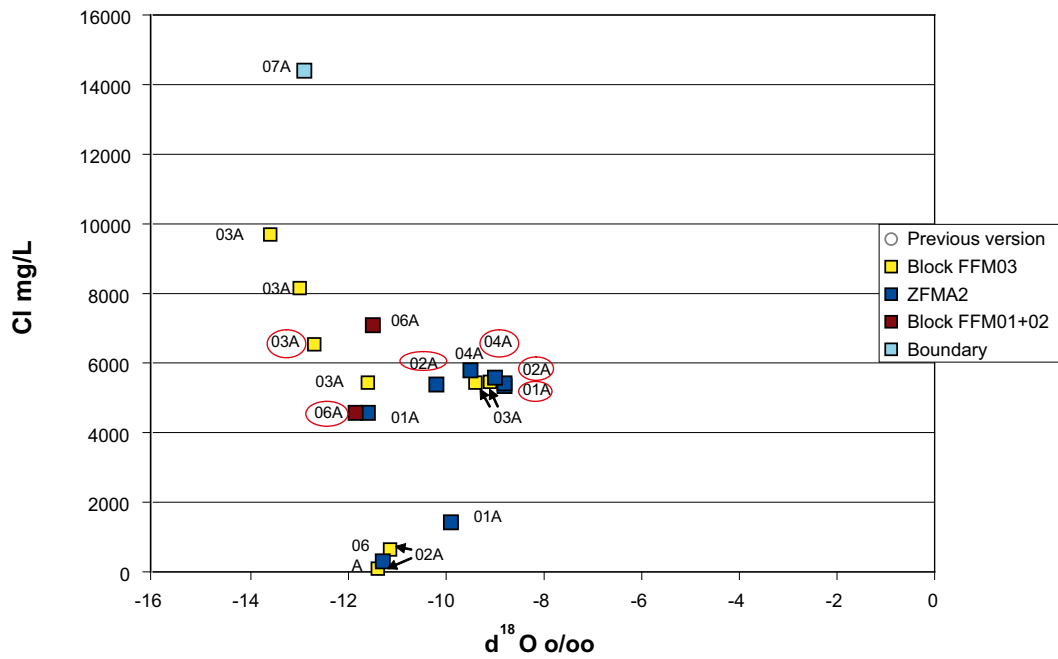


Figure 3-6. Chloride versus $\delta^{18}O$.

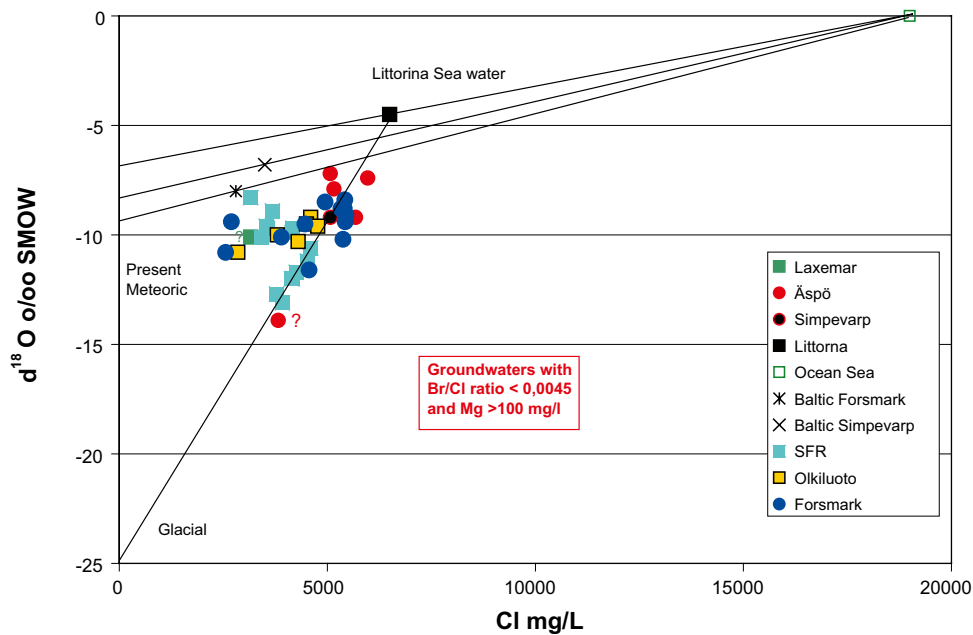


Figure 3-7. Chloride versus $\delta^{18}O$ for groundwater with marine components (identified as $Br/Cl < 0.0045$); all groundwaters show $Mg > 100$ mg/L with two exceptions, one sample from Laxemar and one from Åspö, both denoted with question marks.

Related to the structural subdivisions, zone ZFMA2 is characterised by a more dominant Littorina Sea component and a less cold climate or glacial signature than FFM01+02 (in particular, although data are very limited) and to a lesser extent FFM03. A cold climate recharge component mixed with old saline groundwater dominates at depth in both the FFD01 and FFM01–02 structural domains (see section A2.1.3, Appendix A).

Deformation zone ZFMA2

Because of the importance of the gently dipping deformation zone ZFMA2 in interpreting the hydrogeological and hydrogeochemical evolution of the Forsmark area, some of the hydrochemical issues brought up in section 2.1.3 are further addressed below.

Based on previous understanding of groundwater evolution at Forsmark, the hydrochemical data in ZFMA2 represent approx. 0–100 m of a mixture of fresh to low salinity groundwaters with strong indications of a modern recharge character. Some mixing may be expected from the longer packed-off sections sampled in the five HFM-percussion boreholes which represent the upper 100 m. However the slightly higher than normal salinity so close to the surface, combined with the rapid increase to brackish groundwater at around 150 m, suggest discharge along ZFMA2 from deeper, more saline levels.

The brackish groundwaters from approx. 130–500 m, with a slightly more enriched $\delta^{18}\text{O}$ and a significant increase in Mg, represent typical signatures for a Littorina Sea component in the Forsmark area. In addition to zone ZFMA2, they have also been sampled in other gently-dipping subhorizontal deformation zones such as zone ZFMA7 where it is intersected by KFM03A further to the SE (i.e. Fracture Domain FFM03; Figure 3-4), and also in subvertical zones such as zone ZFMA4, also located to the SE of zone ZFMA2. These zones essentially have preserved groundwaters which reflect the palaeo-evolution of the Forsmark site prior to, and since, the last glaciation some 10,000 years ago. Where Littorina Seawaters have accumulated, mixing with the earlier glacial melt component has undoubtedly occurred, but since the Littorina Sea water originally has had an enriched $\delta^{18}\text{O}$ signature, the glacial component is not that obvious in terms of depleted $\delta^{18}\text{O}$ values. Some exceptions, however, do exist where a glacial signature is more significant (e.g. KFM01A:180 m; $\delta^{18}\text{O} = -11.6\text{‰}$ SMOW; Figure 3-6).

3.1.2 Interaction of surface and deep groundwater systems (Issue #3); App#A; App#E)

The area of interaction of surface/deep groundwater or overburden/geosphere studies has not been well defined in model versions 1.2 and 2.1. The demarcation between SKB net groups such as ChemNet, SurfaceNet and RetNet has not been clear due to the overlap of interests. For example, ChemNet needs to know the recharge groundwater chemistry entering the bedrock from the overburden via the surface environment (i.e. the surface end member used in modelling), and also if there is any evidence of a discharge chemical or isotopic signature from the bedrock to the overburden and eventually to the surface environment. This latter information is required also by SurfaceNet and RetNet in order to characterise the surface environment and locate potential areas of radionuclide uptake and retardation, respectively.

At Forsmark the overburden/bedrock studies are complicated by the hydrogeological conditions. The upper 100 m of bedrock is dominated by one or more shallow, horizontal, highly transmissive zones which effectively channel any recharge water towards the NE of the site close to the Baltic Sea /Follin et al. 2005/. In addition, any discharging groundwater from depth is also flushed away along the same zone, or at least mixed with fresh recharge groundwaters. This hydrological ‘cage-effect’ means that the chances of detecting surface discharge groundwater locations related to specific underlying bedrock fractures is small, and likewise active surface recharge locations directly feeding underlying fractures in bedrock is also small.

To help resolve these issues, the following future strategy is proposed. Before Forsmark model version 2.2 gets under way a series of meetings to better integrate the interests of the three groups are planned. The aim is to demarcate clearly the areas of approach for each group. Detailed descriptions of the surface water chemistry are available /SKB 2005b/ based on a statistical Principal Component Analysis approach, but no attempt has been made to explain the distributions or the main chemical processes which have given rise to such anomalies. Furthermore, little use has been made in modelling the surface water chemistry and less so in model integration with the deeper bedrock system.

For further understanding and integration between the surface and geosphere hydrochemical systems, the main questions to be answered are:

1. What are the chemical and isotopic signatures of deep bedrock groundwaters?
2. What are the characteristic signatures of recharge and discharge groundwaters?
3. What are the redox conditions and the chemical processes that can influence such conditions in the surface water environment?

To help address these questions the following important points have been identified:

- Identification and seasonal variability of chemical and isotopic parameters to describe the surface environment.
- Parameters to include: Temperature, groundwater level, Eh, O₂, DOC, Cl, HCO₃, SO₄, Fe, Mn, U, La, δ¹⁸O, δ²H, ¹³C, ¹⁴C, ³⁴S, and ^{87/86}Sr.
- Model integration (hydrochemical; hydrogeological) between the surface and geosphere environments.

Furthermore, a test to trace influence of deep groundwater signatures is described in section E3.3.2 and in Appendix E.

3.1.3 Redox front (Issue #5; App#A, App#B)

In the Forsmark area, redox changes in recharging waters from oxidising to reducing occur to the largest extent in the overburden (Appendix A and B). Consequently, the majority of all samples from the percussion and cored boreholes are reducing. Of importance, however, for understanding the present-day evolution of the groundwater chemistry and, potentially, modelling of future redox conditions, is to identify any evidence of possible former redox fronts in the bedrock. During periods when the overburden has been much less developed or possibly even absent, the fracture minerals have acted as reducing media in direct contact with the oxygenated water. Furthermore, during glacial activity, in particular, the incursion of dilute, aggressive oxygenated ice melt water to great depths, may also have left its signature with the fracture-filling minerals. Therefore, interpretations based on changes in fracture mineralogy versus depth (e.g. Fe-oxyhydroxides, pyrite and calcite) can help to detect traces of oxidation and, together with the frequency of other Fe(II) containing minerals, confirm the available reducing capacity along the downward penetrating groundwater flow paths. The influence of microorganisms on redox is discussed in section B3.1.6 and in Appendix B.

3.1.4 High Uranium content (Issue#11; App#A, App#B, App#C, App#F, App#G)

The high U content in some groundwaters at Forsmark is discussed in detail in (Appendix A, B, C, F and G). Hypothesis such as effects from e.g. drilling water, complexation, microbes, earth currencies are discussed and tested.

Surface and near-surface waters are characterised by values between 0.05 and 37 µg/L U. Large variations in U content in surface waters are common and are usually ascribed to various redox states (i.e. oxidation will facilitate mobilisation of U) and various contents of complexing agents, normally bicarbonate, which will help maintain the mobility of the U. Plotting U against bicarbonate (Figure 3-8) for deep groundwaters (from cored boreholes) and near-surface groundwaters (from soil pipes) shows no clear trend, although taking only the near-surface groundwaters into account, there is a tendency of higher U contents associated with increasing bicarbonate up to 400 mg/L. At higher bicarbonate contents, however, U tends to decrease, which may be due to very low redox potential in these waters caused by microbial reactions producing the bicarbonate.

For the deep, cored borehole groundwaters it can be concluded that the samples showing U contents greater than 5 µg/L also show greater than 50 mg/L HCO₃. The samples from one section in KFM03A:639–646 m show, however, lower HCO₃ (22–25 mg/L) but still very high U contents (46 to 58 µg/L). Groundwaters from this borehole section indicate a mixed marine and deep saline groundwater origin.

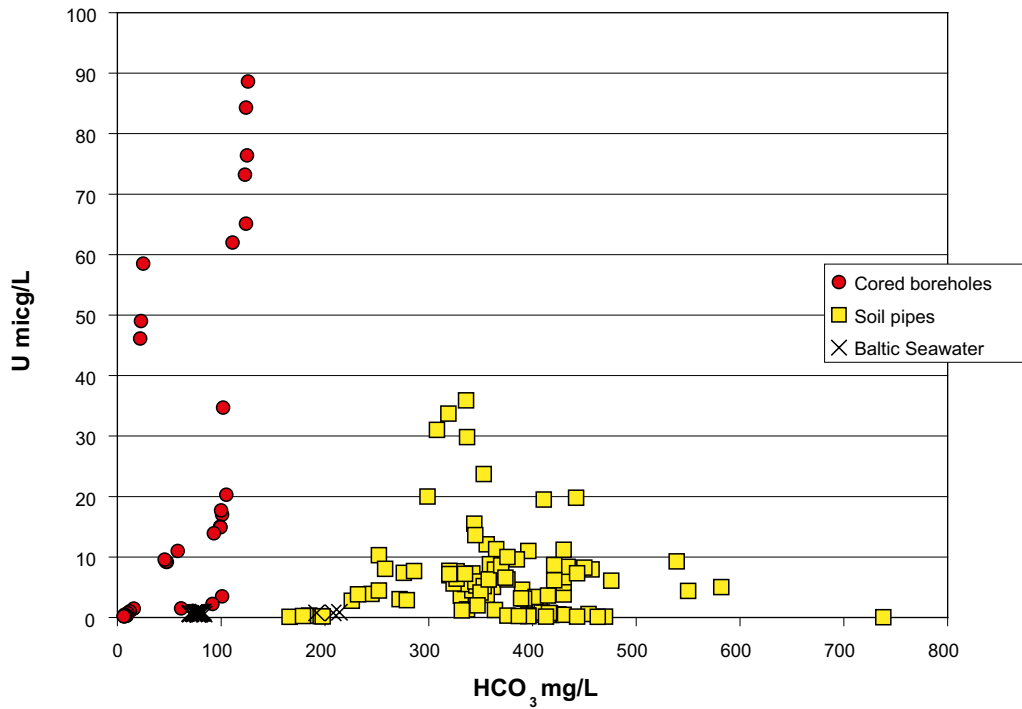


Figure 3-8. Uranium versus HCO_3 in Baltic Sea waters, near-surface groundwaters and groundwaters from the Forsmark area.

The deep saline groundwaters with extremely low HCO_3 contents ($< 10 \text{ mg/L}$) are, however, low in U.

Figure 3-9 shows that groundwater samples between approx. 200 and 650 m depth are all enhanced in U (values $> 5 \text{ } \mu\text{g/L}$) with the exception of two samples close to 400 m depth showing values of 2.2 and 3.5 $\mu\text{g/L}$ respectively.

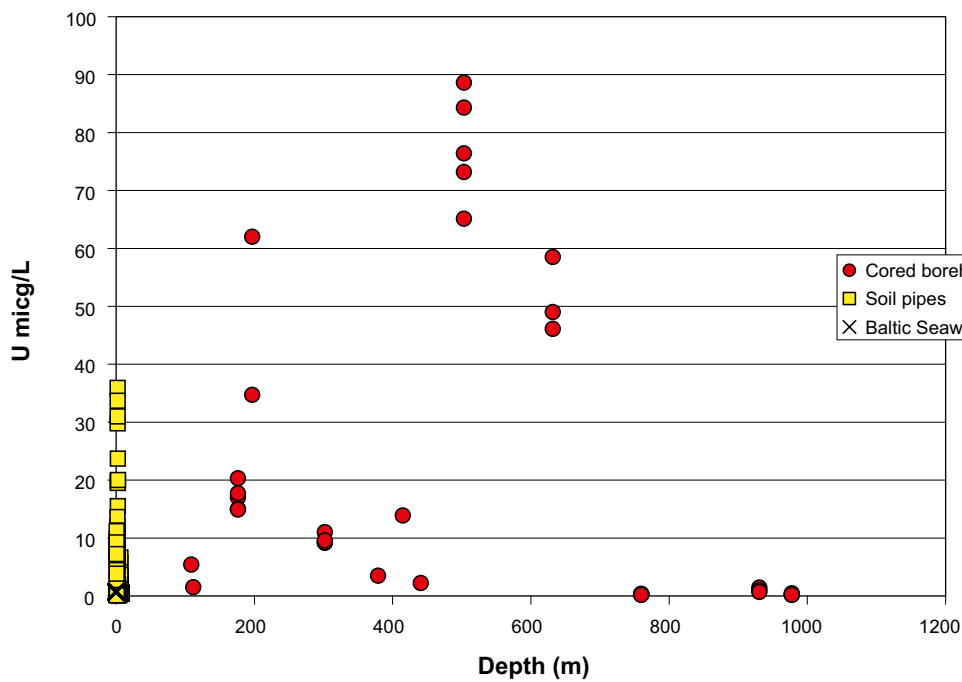


Figure 3-9. Uranium versus depth in surface waters and near-surface and deep groundwaters from the Forsmark area.

Uranium versus chloride (Figure 3-10) shows that in the deeper cored borehole groundwaters the highest U contents are associated with chloride values around 5,000–5,500 mg/L, i.e. the brackish groundwaters dominated by a Littorina Seawater component. However, additional data that will be included in the next model version (F2.2) indicate a more complicated pattern and it is too early to draw leading conclusions concerning high U contents being restricted solely to Littorina Sea-type groundwaters.

In conclusion, it is believed that the reason for high U seems to be a combination of available U, probably at least partly from an amorphous U-phase present in parts of the fracture system, and also groundwater conditions that both mobilise U from this amorphous phase and keep it mobile in solution. Speciation calculations (Appendix C) show how U can remain mobile due to the relatively mildly reducing conditions and to the presence of sufficient HCO_3^- to allow U-carbonate complexation. Microbial activity may have an important influence on U mobilisation (Appendix B); Fe-reducing bacteria may produce strong ligands for complexation and it has even been suggested that U may be microbially oxidised during anaerobic conditions /Andersson and Lovely 2002/. It is also possible that the microbial activity has increased due to mixing of groundwaters of different origins (e.g. related to the drilling fluid content, i.e. Appendix F and G).

The origin of the primary U is probably the result of oxidation and remobilisation of U from mineralisations found at several localities in Uppland, for example pitchblende vein fillings in skarn rocks that have been documented some kilometres from the site /Welin 1964/. The mobilisation/redistribution of the U have probably taken place on several different occasions during the geological history of the region, at least the last 300 000 years as indicated from natural uranium decay series analyses (Appendix A).

The high radium is discussed in Appendix F. Radium is clearly related to groundwater salinity and attains concentrations of 23 Bq/L, well above the drinking water maximum of 0.5 Bq/L. Most of the high Ra concentrations, however, occur in brackish groundwater (salinity $\sim 5\text{--}10$ g/L), and are unlikely to be consumed.

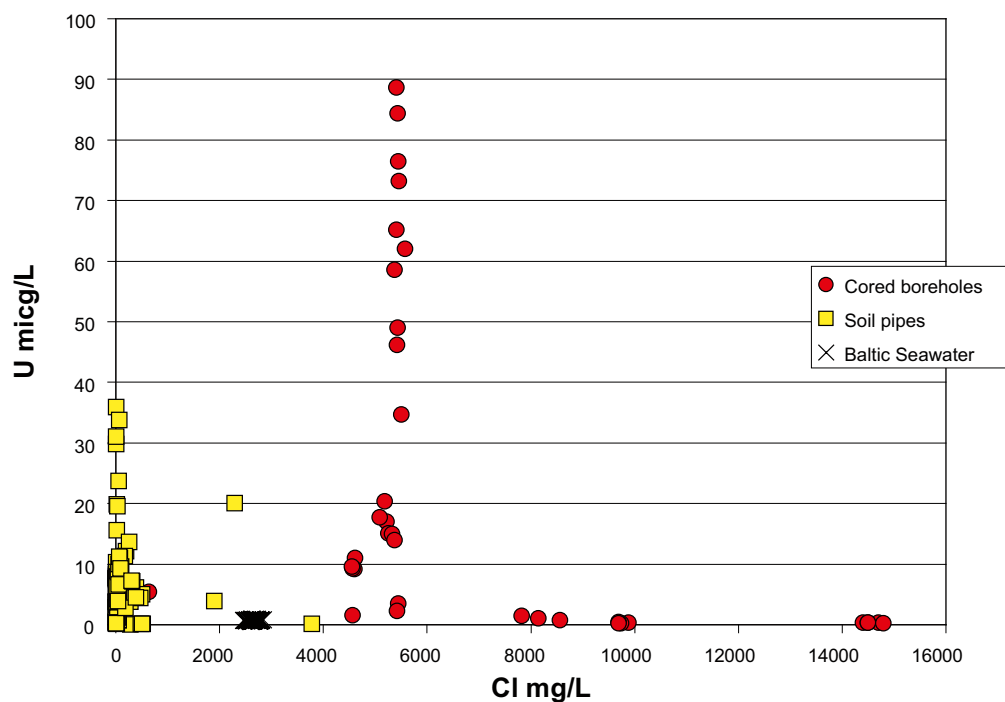


Figure 3-10. Uranium versus Cl in surface waters and near-surface and deep groundwaters from the Forsmark area.

3.1.5 High manganese values – manganese reducing bacteria (Issue#9; App#B, App#C)

Low Mn contents and undersaturation with respect to rhodochrosite in deep (> 700 m) saline Forsmark groundwaters is the common situation, in parallel with many other granitic groundwater systems (Appendix C). However, brackish groundwaters with a significant Littorina contribution show high Mn concentrations and reach equilibrium with respect to rhodochrosite. This is a very uncommon condition in most other granitic systems in the Scandinavian Shield, unless the Littorina proportion happens to be in the same range. All this suggests that Mn content and equilibrium with rhodochrosite in brackish groundwaters are characteristics imposed by the superficial marine environment prevailing during the Littorina stage. Authigenesis of Mn-carbonates is an active process in the Baltic Sea since 7,000–8,000 year ago /Kulik et al. 2000, Neumann et al. 2002 and references therein/.

Logically, the observation of this signature in Forsmark groundwaters requires the presence of waters with high Littorina proportions (higher than 40%) and has been probably favoured by the isolated character (pockets) of the analysed samples and by the lack of manganese reducing bacteria (MRB) (Appendix B). Groundwaters with less (although relatively high) Littorina proportion (20–30%) seem to have lost this characteristic as they are undersaturated with respect to rhodochrosite. If an active presence of MRB would have been detected in these Littorina-rich groundwaters, the equilibrium with rhodochrosite could have been related with this activity at present instead of with an inherited character.

Therefore, the hypothesis suggested here (rhodochrosite equilibrium imposed by the superficial marine environment prevailing during the Littorina stage) is consistent with these singular hydrogeological and microbiological characteristics of Forsmark groundwaters (presence of pockets and absence of MRB). Nevertheless, it would be interesting to explore in more detail its applicability to other analogous granitic systems like Finnsjön or Olkiluoto.

The simultaneous presence of high U and high Mn contents in some Forsmark groundwaters seems to be fortuitous. High Mn contents are related to high Littorina proportions, but all other systems with high Littorina proportions (e.g. Olkiluoto), do not have an associated high U content (on the contrary, U levels are very low).

The anthropic perturbations to the system (oxygen intrusion, high drilling water proportion, etc), already mentioned in previous sections, could have introduced modifications in the concentration of dissolved Mn²⁺. But, if this is indeed the case, they have not been strong enough to alter the equilibrium state with respect to rhodochrosite, a state that seems to be the “natural” one in other groundwater systems with high proportions of Littorina that have not suffer anthropic perturbations.

3.1.6 Microbes (Issue#8; App#B)

In their energy harvesting reactions, microbes use available energy-rich compounds as electron donors and various electron acceptors from groundwater and fracture minerals. This means that they are intimately coupled to the redox conditions in the groundwater system (Appendix B). Redox pair analyses described in the Forsmark 1.2 report /SKB 2005a/ and the present work in Appendix B and B coincides very well with the microbial data, i.e. the physiological groups of microorganisms that are present at the different sampling sites.

Figure 3-3 shows the results from sampling in Forsmark. Data to the right of the vertical line in the figure are new for the 2.1 data freeze; this also includes a duplicate sampling at 302 m depth in KFM06A. The data from this sampling verified the Most Probable Number (MPN) method to be both confident and reproducible, and that the sampling method was accurate. In the last sampling, nitrate-reducing bacteria were included in the MPN analyses. Figure 3-4 shows microbial data together with the reduction potential in groundwater at the sampled depths.

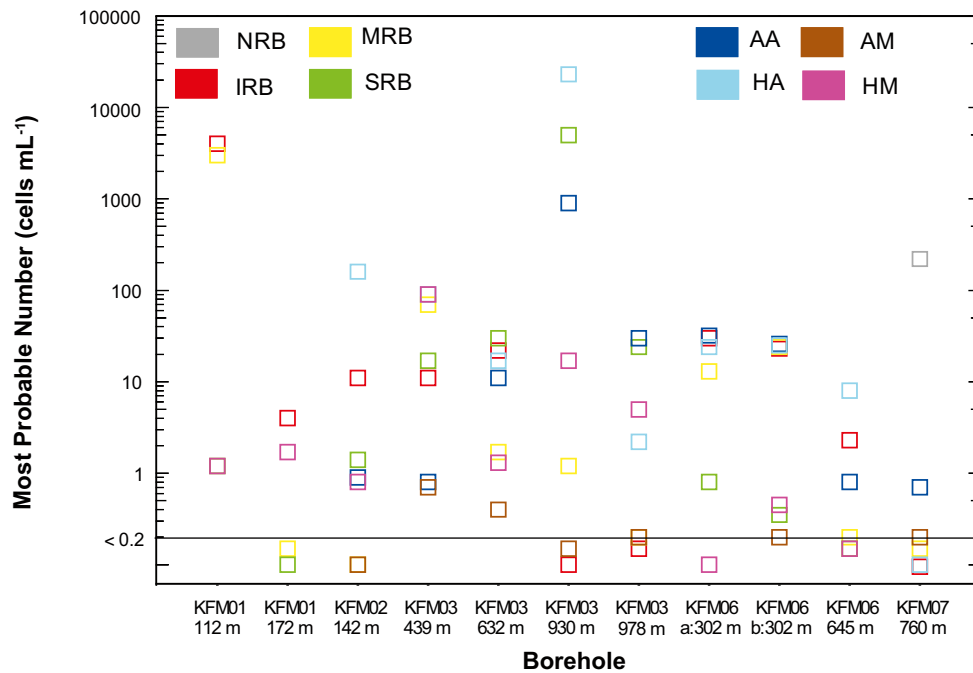


Figure 3-11. The most probable numbers of different physiological groups of microorganisms in the Forsmark area. The data to the right of the vertical line are new in the 2.1 data freeze. NRB; nitrate-reducing bacteria, IRB; iron-reducing bacteria, MRB; Manganese-reducing bacteria, SRB; sulphate-reducing bacteria, AA; autotrophic acetogens, HA; heterotrophic acetogens, AM; autotrophic methanogens, HM; heterotrophic methanogens.

Figure 3-12 shows that when iron- and manganese-reducing bacteria dominate at 111 m depth, the redox values are below -150 mV. When the sulphate-reducing bacteria increase in numbers at 632 m and even more at 930 m, the redox values decrease to -175 and -250 mV. At depths between 200–600 m the values increase due to a low number of microbes and few redox lowering reactions. The conclusions in Appendix B are:

- Microbes are the poisoning agents for REDOX in groundwater. Their enzymes catalyze reactions that are energetically most favourable for the geochemical system they inhabit.
- The microbial oxidation of organic carbon and/or hydrogen will lower the REDOX in the groundwater system.

The data so far give a good overview of possible microbial processes and important microbial redox control mechanisms in the depth interval from 100–1,000 m (Appendix B). However, several of the SIERG and INSITE reviewers have asked also for data and models of the processes which dominate in the region between the surface and 100 m, in particular, information about the oxygen penetration depth. Figure 3-2 and Figure 3-4 show that there is a lack of data from the surface down to 100 m in Forsmark. The lack of data is problematical since this region is very important with respect to microbial processes. It is at this depth interval that the main inflow of meteoric water containing oxygen and organic material occurs. The importance of organic matter input to the subsurface is that it effectively blocks oxygen intrusion by microbial consumption of the organics with oxygen, and by that governs the redox conditions at depth. This lack of data will be handled by using experiences from other measurements such as oxygen measurements in shallow boreholes (see Appendix B) and from investigations of microbial populations at shallow locations at other sites.

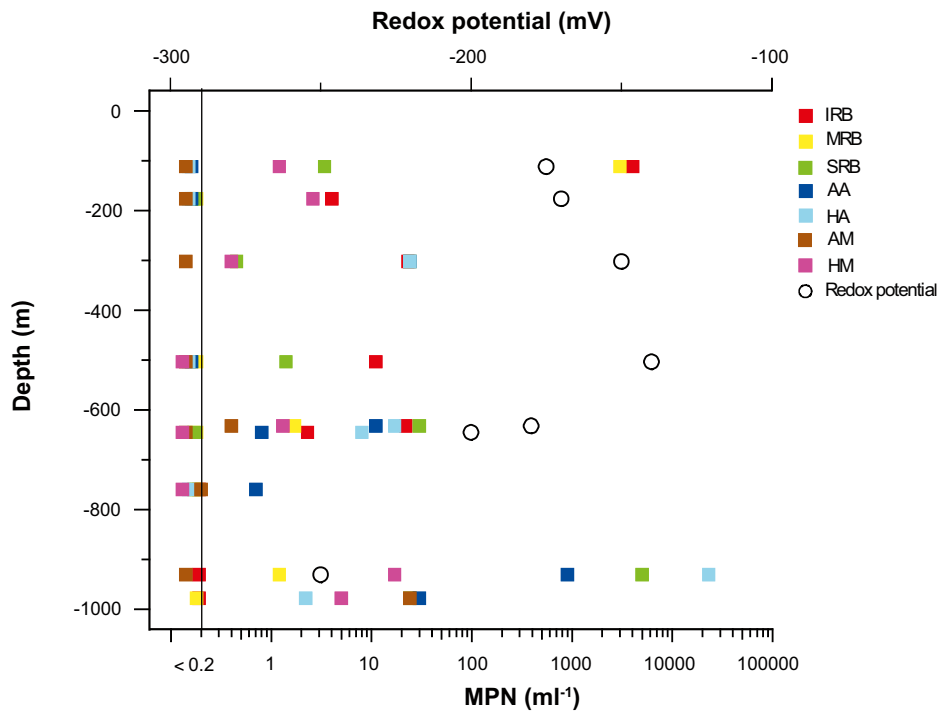


Figure 3-12. Most probable numbers of different physiological groups of microorganisms and redox potential plotted against depth, in the Forsmark area. NRB; nitrate-reducing bacteria, IRB; iron-reducing bacteria, MRB; Manganese-reducing bacteria, SRB; sulphate-reducing bacteria, AA; autotrophic acetogens, HA; heterotrophic acetogens, AM; autotrophic methanogens, HM; heterotrophic methanogens.

3.1.7 Gases (Issue#6; App#B)

Several dissolved gases are important components in microbial redox processes and in the understanding of the origin of the gas phases in the groundwater. The F2.1 data freeze provided more data to be used in the models and further modelling and evaluation was possible (see Appendix B). Figure 3-1 shows the total volume of gas for all groundwater samples. The volume of gas in samples from Forsmark follows the common trend for groundwater in the Fennoscandian Shield, i.e. it increases with depth. This pattern can be seen in Olkiluoto in Finland /Pitkänen et al. 2004/ and in the Laxemar area in Sweden /SKB 2006b/. The only exception to this trend is the gas volume in one sample from KFM07A that is greater than the deeper samples from KFM03A (Figure 3-13). The conclusion in Appendix B is:

- Nitrogen gas is the dominant gas at all depths.
- Helium increases with depth – its presence indicates groundwater of deep origin.
- Methane, carbon dioxide and hydrogen decrease with depth.
- Difficulties with the detection limit of hydrogen could possibly give to low values for this gas.

3.1.8 Colloids (Issue#7; App#B)

Measuring the number of colloid particles has been investigated in Appendix B. Knowledge of the colloid composition is important in the transport modelling and ultimately in the safety assessment modelling. The amount of colloids in the Forsmark area groundwater is low (approximately $20 \mu\text{g l}^{-1}$ or lower). The colloid values obtained from the Forsmark area agreed well with data from colloid studies in Switzerland, i.e. 30 ± 10 and $10 \pm 5 \mu\text{g l}^{-1}$ /Degueudre 1994/, but are approximately ten times lower than those reported from Canada, i.e. $300 \pm 300 \mu\text{g l}^{-1}$ /Vilks et al. 1991, Laaksoharju et al. 1995/. Although the colloid data set is still limited, it will increase in the sampling campaigns for the 2.2 and 2.3 model stages.

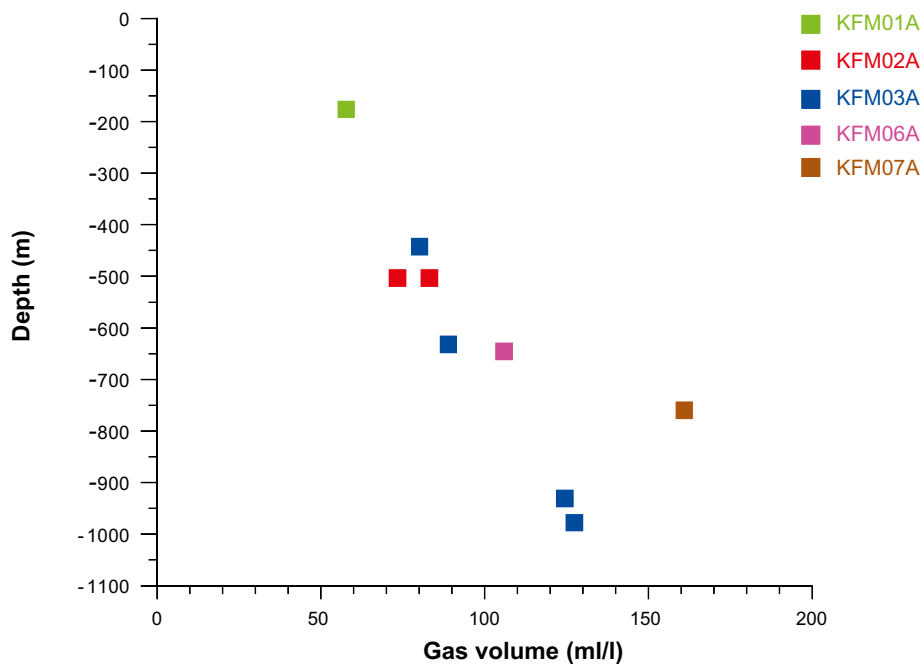


Figure 3-13. Total volume of gas in samples from the Forsmark area.

3.2 Mathematical modelling issues

Mathematical modelling of hydrogeochemical data includes involves the applying of a modelling tool code together with the use of expert judgement and knowledge on of the primary data. The issues of mathematical modelling are addressed in the chapters below.

3.2.1 Redox conditions (Issue#10; App#B, App#C)

The redox potential measured in the deepest groundwaters in Forsmark (Appendix C), has only one data point (KFM03, at 930 m depth, Table 3) but is the most reducing in the system and is in agreement with the value obtained in the calibration by /Grenthe et al. 1992/. This suggests that the Eh value of these groundwaters is in equilibrium with a crystalline iron oxyhydroxide such as goethite or, more probably, hematite. This is consistent with the reducing character and long residence times of these groundwaters, where low crystallinity phases are not expected /SKB 2004 and references therein/.

The remainder of the Eh values have been determined in brackish groundwaters at depths between 110 and 646 m. These seem to be controlled by the occurrence of an iron phase with an intermediate crystallinity (Figure 3-14) such as the one considered by /Banwart 1999/ in the Äspö large-scale redox experiment. This finding has important consequences.

The natural occurrence of an iron oxyhydroxide with this degree of crystallinity is difficult to justify in groundwaters with a long residence time. The brackish groundwaters with a high percentage of the Littorina end member may indicate the existence of pockets isolated from the hydrogeological system and, therefore, with an estimated residence time of, at least, thousands of years. The recrystallization kinetics of poorly crystalline ferric oxides, towards the more crystalline and stable phases, can be very fast, in the order of days to years, when the groundwaters are alkaline, reducing /Houben 2003, Schwertmann and Murad 1983, Stipp et al. 2002/ and have high contents of Fe²⁺ /Pedersen et al. 2005/.

However, oxygen intrusion in reducing media usually induces the precipitation of amorphous phases (ferrihydrites or hydrous ferric oxides, /Langmuir 1997/), with a pK between 37 and 39 (Figure 3-14). As it has previously been pointed out, these phases quickly recrystallize to less soluble and more stable phases when the reducing conditions return.

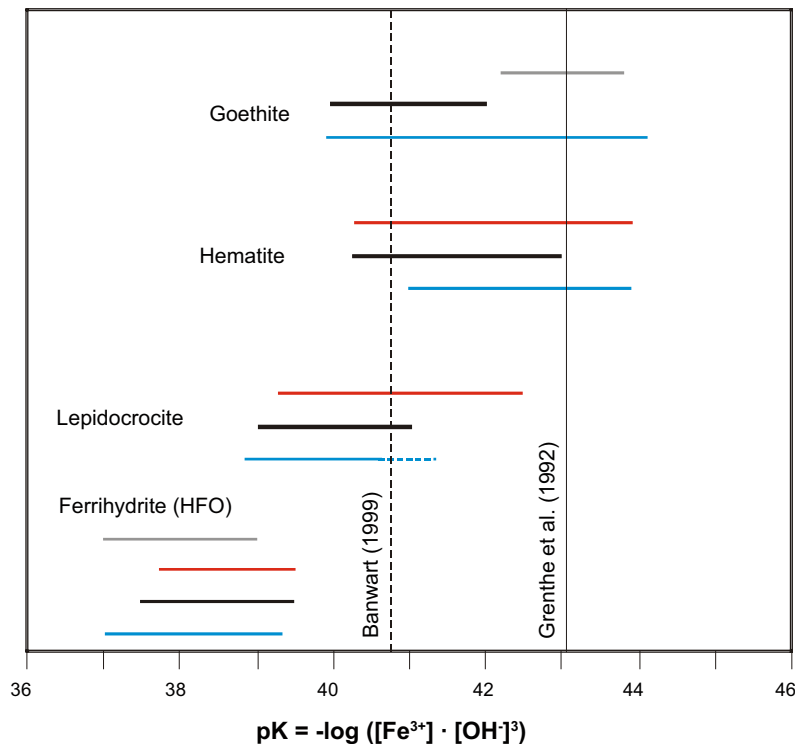


Figure 3-14. Reported solubility ranges at 25°C for the main ferric oxyhydroxides. Blue lines represent the ranges obtained by /Langmuir 1969, 1997/; black lines correspond to the values suggested by /Appelo and Postma 2005/ from an analysis of /Cornell and Schwertmann 2003/ data; red lines represent the ranges reported in /Bonneville et al. 2004/; and grey lines represent the range of values proposed by /Nordstrom et al. 1990/. The most recent solubility ranges obtained by /Majzlan et al. 2004/ for 2-line and 6-line ferrihydrite (HFO: hydrous ferric oxyhydroxides; values between 37.5 and 39.5) coincide with the ranges shown in the plot for this phase. The values reported by /Macalady et al. 1990/ for goethite (pK=44.15) and hematite (pK=44.0) are in agreement with the less soluble extreme of the range shown in the plot for these minerals. Empirical values deduced by /Grenthe et al. 1992/ (pK=43.1) and /Banwart 1999/ (pK = 40.8) for different Swedish groundwaters are also indicated.

Therefore, as /Banwart et al. 1994/ reported in the Äspö large-scale redox experiment, the presence of an intermediate iron oxyhydroxide with higher solubility than a crystalline phase is possible in these brackish groundwaters if there is a brief oxidizing disturbance.

All this would support the occurrence of oxygen intrusion, already suspected in some of the P-reports on the borehole hydrochemical characterization /e.g. KFM03A; Wacker et al. 2004b/ in spite of the absence of measurable oxygen concentrations in the Chemmac loggings. Moreover, the occurrence of an oxyhydroxide of intermediate crystallinity would indicate that the system is still evolving and compensating for the effects of the intrusion of oxygen.

There is no clear and systematic relationship between high drilling water contents in the brackish groundwater samples and the Eh control by intermediate-crystallinity oxyhydroxides (Appendix C). Therefore, the perturbation of the system could be also related to atmospheric air contamination. However, independent to the mechanism, this perturbation seems to affect only the brackish groundwaters. This fact suggests that the original conditions of these waters and/or the lithological-hydrogeological system with which they are associated, must have some characteristic that makes them more susceptible.

In summary, it is difficult to assess the effects that oxygen contamination could have had on the redox system which, moreover, seems to be re-equilibrating and compensating for its effects. Dissolved sulphide could have also been affected; in fact, its contents in most of the Forsmark groundwaters are very low, notwithstanding the good results obtained with sulphur redox pairs (Appendix C).

3.2.2 Uncertainties analysis of mixing proportions and mass balance deviations (Issue#15; App#C)

In Appendix C, the special characteristics of the group of brackish groundwaters with a similar chloride content of $5,500 \pm 300$ mg/L (0.15 ± 0.01 mol/kg) was investigated in terms of mixing. This group are located between 150 and 650 m depth in the Forsmark area and are characterised by an important Littorina signature (Figure 3-15). In spite of this constant chloride content, most of the other elements have a fairly broad range of values for this same depth interval. In other words, Cl content is constant but the concentrations of the other elements are not. This is especially the case for the redox elements (Appendix C).

The question is if this is due to mixing or reaction or both. The hypothesis in Appendix C proposes that this behaviour could be the result of pure mixing of different proportions of Littorina waters (with a chloride content of 6,500 mg/L) in a volume of rock where a previous mixture of Glacial + Brine (giving a similar Cl concentration) already existed.

Figure 3-16 plots those mixtures of Brine (Br), Glacial (Gl), Dilute Groundwater (DGw) and Littorina (Lit) that give a total Cl concentration of 5,500 mg/L. In the plot, the horizontal axis describes the proportion of Gl+DGw, and the vertical axis, the proportion of Brine. Black dotted lines give the proportion of Littorina and the continuous red line gives the combinations of Brine, Dilute Groundwater and Glacial that provide a Cl concentration of 5,500 mg/L.

As the fraction of Littorina in Forsmark groundwaters at 150 to 650 m depth varies from 20 to 60% (the dark blue rectangle with rounded corners enclosing the red line in Figure 3-16), that means that the expected values of the ratio (Gl+DGw)/Br compatible with this mixing hypothesis are between 8.5 (for 20% Litt) and 10 (for 60% Litt). These values are obtained from the plot as the ratio of the abscissa to the ordinate (light blue lines).

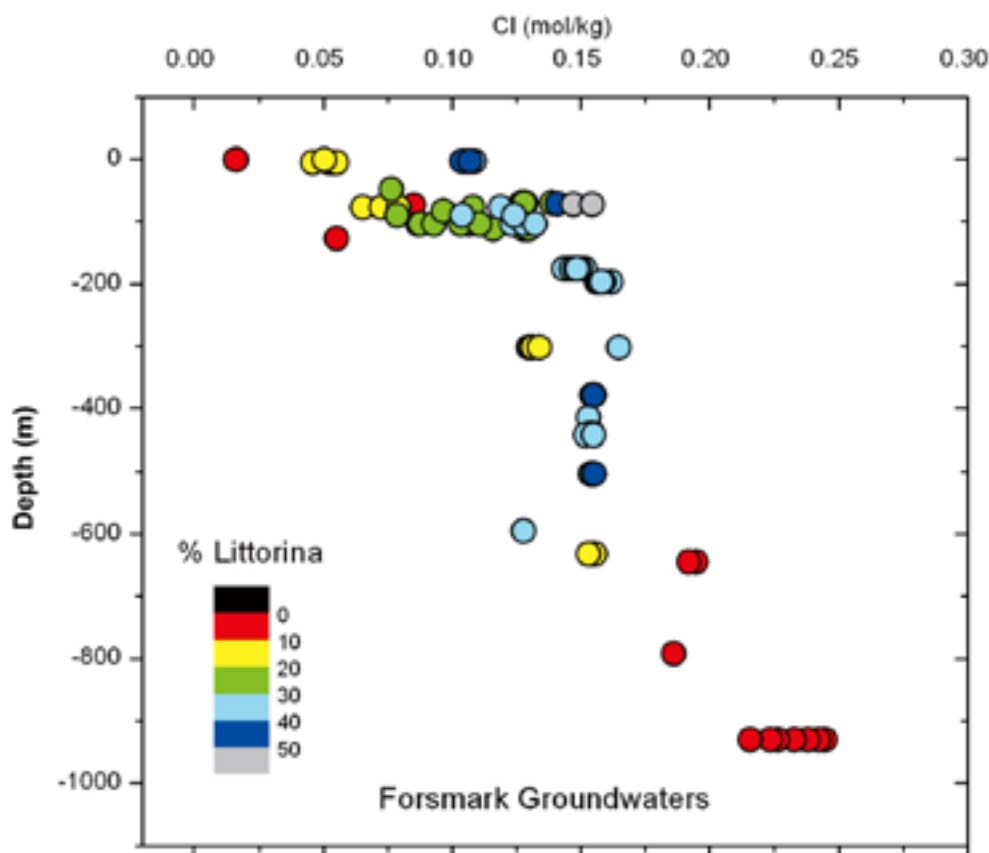


Figure 3-15. Chloride-depth distribution in the Forsmark groundwaters. The colour coding gives the percentage of Littorina in the mixture, and between 150 to 650 m depth varies from 20 to 60%.

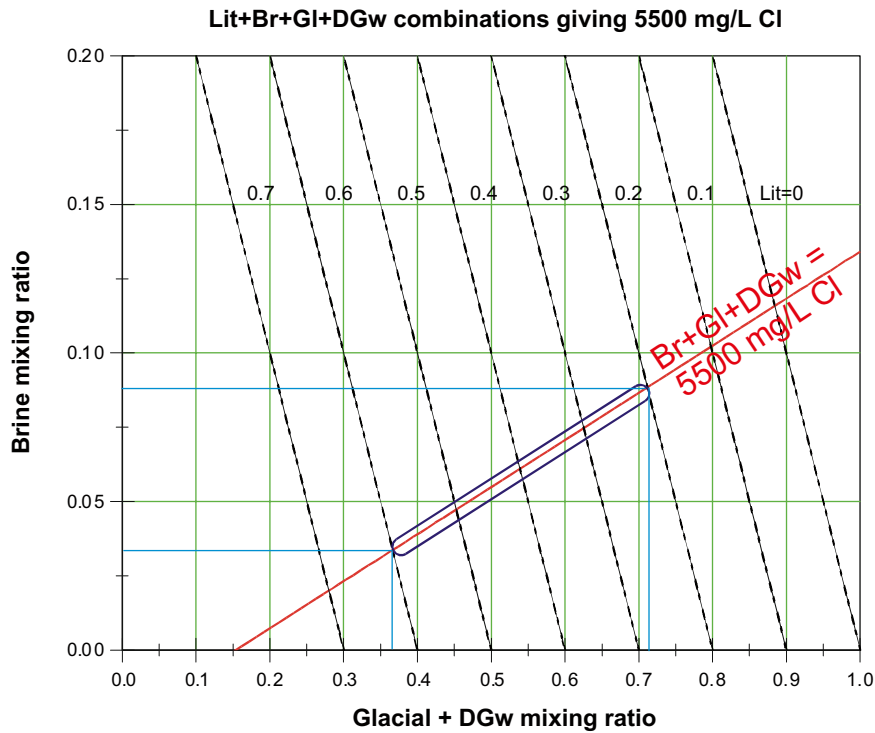


Figure 3-16. Mixtures of end-member waters Brine, Glacial, Dilute groundwater and Littorina that gives a final chloride content of 5,500 mg/L.

Figure 3-17 shows that this is indeed the case. In this figure, depth increases to the right. Open black circles represent the chloride content in Forsmark groundwaters with the scale on the right. On the left, the ratio $(GI+DGw)/Br$ of each sample is plotted as coloured squares, the colour giving the percentage of Littorina in the mixture.

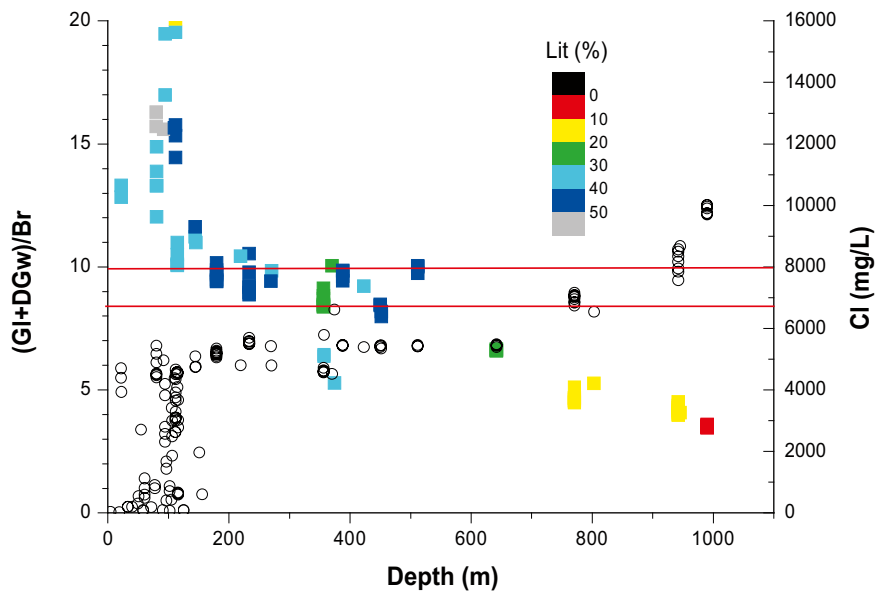


Figure 3-17. Ratio of Glacial+Dilute groundwater to Brine in waters between 0 and 1,000 m depth in the Forsmark area. Samples between 150 and 650 m depth have a constant Cl content of $5,500 \pm 300$ mg/L, a $(GI+DGw)/Br$ ratio of 8.5–10 and a fraction of Littorina of 20–50%.

The two horizontal red lines show the (GI+DGw)/Br ratio between 8.5 and 10, as the above analysis indicates. It can be seen that samples between 150 and 650 m depth correspond to Littorina proportions of 20–50% and (GI+DGw)/Br ratios that fall inside the expected bracket.

The intrusion of variable amounts of Littorina (from 20% to around a maximum of 60%) with its $5,500 \pm 300$ mg/L of Cl, does not modify the Cl concentration of the previous Br+GI+DGw mixture, *but* it does modify the concentrations of all remaining elements.

To further investigate if the concentration of the other elements can also be explained by the mixing-only hypothesis, PHREEQC mixing calculations was carried out (Appendix C). Littorina mixing fractions of 20 to 60% (as computed by M3, n-PC algorithm for Forsmark samples) in steps of 10% were used to calculate the concentration of selected elements in waters composed of different mixtures of Lit+Br+GI+DGw, all with a chloride content of $5,500 \pm 300$ mg/L and a (GI+DGw)/Br ratio of 9. The results are summarised in Figure 3-18 for some major ions Na, Mg and SO_4^{2-} .

As can be readily observed, the calculations closely reproduce the observed ranges of these elements between 150 and 650 m depth. Black spheres are the result of the simulations, and coloured dots are the actual samples. The horizontal axis gives the chlorine content in mol/kg ($5,500 \text{ mg/L} = 0.15 \text{ mol/kg}$). In all cases the range of values of the synthetic samples matches the observed range, confirming that a simple mixing hypothesis can explain the geochemical behaviour of the constant-Cl depth range in Forsmark area.

3.2.3 Integration of hydrochemical data with mineralogical and microbial data (Issue#17; App#C)

for examples of integration of hydrogeochemical data with mineralogical and microbial data (see, e.g. sections 3.1.3; 3.1.4; 3.2.1; 3.2.4 and Appendix C). This issue will be further addressed in the F2.2 and F2.3 stage when more data is available to facilitate further integration.

3.2.4 Revision of conceptual model the role of monosulphides (Issue#16; App#C)

The number of groundwater samples with sulphidic character is lower in Forsmark than in Laxemar (Appendix C). The same is valid for sulphide concentrations, lower in Forsmark than in Laxemar. This fact could be a simple question of sampling bias as there are important differences in the number of available samples in the two areas. This issue will probably be clarified when more samples are available in the 2.2 and 2.3 modelling phases. In fact, some of the samples from the 2.2 phase indicate a even more marked sulphidic character in Forsmark area.

With the data available up to now, the agreement between geochemical and microbiological results on the presence or absence of SRB activity is very successful (Appendix B). Both sets of data indicate the active occurrence of these bacteria at depths between 900 and 1,000 m in Forsmark, which is in agreement with the maximum depth with bacterial activity of this type in Laxemar (Appendix C).

The same agreement between geochemical and microbiological data is found for the brackish groundwaters at depths between 100 and 600 m; waters undersaturated with respect to iron monosulphides have very low concentrations of SRB. However, new data from datafreeze 2.2 suggest the presence of a slightly more intensive SRB activity in some waters that are in equilibrium with mackinawite. In any case, all the brackish samples show a lower SRB activity than found deeper in Forsmark or in general in the Laxemar area. Therefore, brackish groundwaters in this depth range (waters that are characterised by having an important Littorina proportion) should correspond more or less, to isolated pockets with a very low nutrients supply (Appendix B).

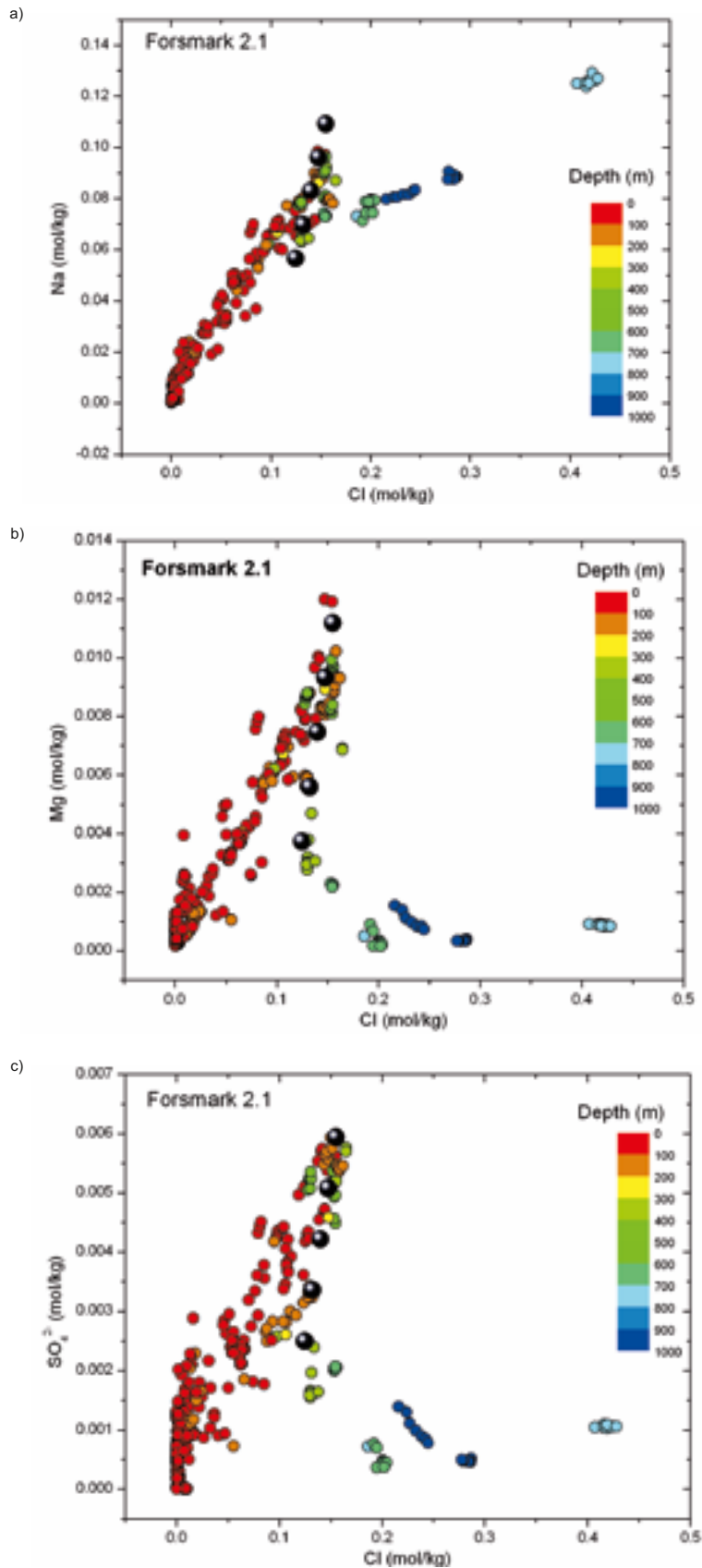


Figure 3-18. Computed concentrations (black spheres) of selected major ions (a: Na, b: Mg and c: SO_4^{2-}) in synthetic mixtures of Lit+Br+Gl+DGW with a Cl content of $5,500 \pm 300$ mg/L ($=0.15 \pm 0.01$ mol/kg). The different mixing proportions plotted as black spheres correspond to :3.2B+36.8(G+DGW)+60L, 4.0B+46.0(G+DGW)+50L, 4.8B+55.2(G+DGW)+40L, 5.6B+64.4(G+DGW)+30L and 6.4B+73.6(G+DGW)+20L. The computed range matches the observed range (coloured dots) in the 0.15 ± 0.01 mol/kg Cl interval. Real samples are colour coded according to depth. Note how all depths from 150 to 650 m (orange to green) are found around a Cl content of 0.15 mol/kg.

A result that may be significant is the equilibrium with respect to amorphous iron monosulphides found in sample 12001 (data freeze 2.2) one of the deepest brackish groundwater sampled up to now (at 630 m depth). This could indicate the active precipitation of amorphous iron monosulphides and, although not available yet, the presence of an important SRB activity at shallower depths than previously believed. Moreover, this depth is especially important as many other redox elements undergo severe modifications in their concentrations (Appendix C). On the other hand, this fact suggests that some high-Littorina waters have indeed a supply of nutrients and therefore, that not all of them occupy isolated pockets.

Sampling problems (oxygen intrusion, high contents of drilling water, etc) could have modified the original Fe^{2+} and S^{2-} groundwater contents and, consequently, some of the results of their saturation state with respect to the iron monosulphides. However, new data from the 2.2 data freeze do not change the conclusion of a very low SRB activity in the brackish groundwaters between 100 and 600 m depth.

3.2.5 Investigation of recharge end-member: its effect on mixing models, site understanding and the proper use of tritium (Issues# 18 and 19; App#D)

In Appendix D, the testing of different compositions for the recharge end-member to be used in the M3 modelling shows that different end-member options for Meteoric (rain60, with tritium age corrected to 168TU) together with the reference waters Brine, Glacial, Littorina and Sea sediment can explain most of the water compositions obtained from Forsmark and Laxemar (see also section 3.2.6) and is therefore the suggested set of end-members when modelling these sites.

3.2.6 Test of models including all elements and isotopes versus models with conservative constituents such as D, ^{18}O , ^3H (Issue#20, App#D)

Testing different end-members and compositional options showed that the PCA analysis in M3, employing all groundwater samples with major elements (Na, K, Ca, Mg, SO_4 , HCO_3 , Cl) and isotopes H^2 , O^{18} and ^3H (non-corrected) and employing the end members Littorina, Brine, Glacial, Meteoric (rain60 age-corrected), give the most robust characterization of the Forsmark 2.1 and Laxemar 2.1 dataset (Appendix D). The reasons are:

- robust calculations and most samples can be included in the PCA
- the use of only conservative variables cannot provide a unique solution when employing 4 end-members, therefore, non-conservative elements have also to be included in the calculation despite increasing the uncertainty in the calculations
- the same end members used by the hydrogeologists are included; this helps the model comparison and integration.

3.2.7 Comparison of different models and the number of observations described (Issue#21; App#D)

The updated version of M3 was tested in Appendix D. The old version of M3 and the new version M3-2D return the same calculated results. This was an important verification test that the new version works properly. The new option in M3, the n-PC /Gomez et al. 2006/, which calculates the mixing proportion in multivariate space, gives similar trends with the calculation in 2D but for some observations (e.g. high HCO_3 samples), the differences can be considerable. When using the n-PC, fewer samples are included in the polyhedron but the results are generally more accurate than calculating using the 2D option.

3.2.8 Evaluation of suitable data from SICADA and DMS to perform Drilling Impact Study (DIS) calculations (Issue#23; App#D)

Drilling Impact Study issues is discussed in Appendix D. In order to perform a drilling impact study, a water balance of the drilling water flushed in and out from the borehole is performed. The water pumped out is usually higher than the volume in since the water volume is mixed with formation water and this can make the correct calculations difficult. If the uranium is correctly monitored, the return water can be calculated based on the percentage of uranium, and a water balance and DIS calculations can be performed for the borehole. The field data is such that a simplified methodology for DIS has to be employed and this development is done in a separate pilot study (Gascoyne and Gurban, pers. comm.).

3.2.9 Evaluation of the Electric Conductivity for K boreholes and its use in understanding/validating the GW spatial variability (Issue#24; App#D)

The measured electrical conductivity from core boreholes can be used to support the spatial variability description of Cl in the bedrock as described in Appendix D.

3.3 Conceptual modelling issues

Conceptual modelling for the site descriptive model (SDM) includes evaluation, simplification or modelling to synthesise the information from primary data. The issues concerning conceptual modelling are addressed in the chapters below.

3.3.1 Conceptual modelling in 2D and 3D (App#A, App#E)

Large-scale conceptualisation approach

The updated Forsmark 2.1 SICADA database has served to confirm the 2D conceptual modelling presented for Forsmark 1.2 (for details see Appendix A).

For the Forsmark 2.2 and 2.3 model versions, several improvements will be attempted to further quantify model version 1.2. These will include: a) a closer integration of hydrochemistry and hydrogeology based on 2D and 3D mathematical modelling, and b) use a modified version of the hydrogeological conceptual model as a framework to integrate the hydrochemistry.

For improved hydrogeological and hydrochemical integration a 3D model will be produced showing the locations of the general lithological units, the major fracture zones, and the cored boreholes sampled for hydrochemical characterisation (see tests based on Forsmark 2.1 data, in Appendix E). Based on this 3D model, strategic 2D cutting planes will be selected to best illustrate from the Forsmark site: a) the vertical and lateral spatial distribution of the groundwater chemistry, and b) where possible to illustrate the variation of groundwater chemistry along chosen fracture planes (e.g. zone ZFMA2) and, if possible, to integrate hydraulic flow properties from head measurements. To further embellish these cutting planes with additional hydrogeochemical information, manually-based 2.2 versions will also be produced, for example, illustrating the major groundwater types, isotopic data, main geochemical reactions etc.

Small-scale conceptualisation approach

To widen the scope for Forsmark 2.2, effort will be put into small-scale conceptualisation of specific issues such as: a) pore water chemistry, b) fracture mineralogy, and c) redox front evolution. Preliminary examples are given in Appendix A for the matrix pore water studies. Similar approaches are also planned for the fracture mineralogy and redox front evolution studies.

3.3.2 Better integration with hydrogeology (Issue#25; App#E).

Hydrochemical observations are used to support the hydrogeological modelling, e.g. to understand the interplay between surface water, near-surface groundwater and deep groundwater (see, Appendix E).

Figure 3-19 shows a plot of tritium (^3H) versus chloride (Cl^-) in the soil pipe samples (near-surface groundwater in the Quaternary deposits) located at potential discharge zones (selected on the basis of topography). It can be seen that the lowest tritium contents are measured in soil pipes under three lakes (Lake Bolundsfjärden, a small lake named Lake Gällsboträsket (SFM12) and Lake Eckarfjärden, cf. the map in Figure 2-1). However, the near-surface groundwater compositions under these three lakes shows very different salinities:

- The near-surface groundwater under Lake Bolundsfjärden shows chloride concentration values higher than the present Baltic Sea water.
- The near-surface groundwater under Lake Eckarfjärden shows much lower chloride concentration values than the present Baltic Sea water.
- The near-surface groundwater under Lake Gällsboträsket (SFM12) shows intermediate chloride concentration values.

It is worth noting that groundwater sampled beneath the Baltic Sea shows chloride concentrations lower than the present sea water, which is consistent with the occurrence of local discharge of fresh groundwater under the sea.

Figure 3-20 shows a plot of oxygen 18 isotope values ($\delta^{18}\text{O}$) versus chloride (Cl^-) concentration values from soil pipe samples gathered (selected on the basis of topography at potential discharge zones (selected on the basis of topography). Littorina Sea and average Baltic Sea values have been included in the plot. It can be seen that near-surface groundwater plot along a hypothetical mixing line between Littorina Sea water and fresh water, with the exception of groundwater sampled below Lake Eckarfjärden, which shows a clear absence of Littorina Sea influence.

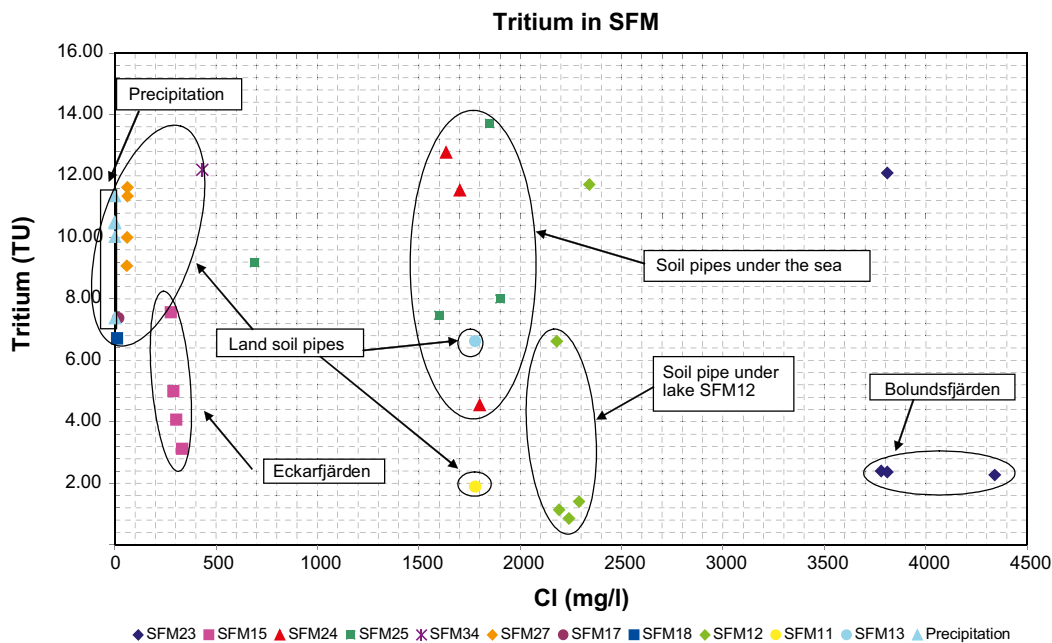


Figure 3-19. Tritium versus chloride (Cl^-) in soil pipe samples (near-surface groundwater) located in potential discharge zones (selected on the basis of topography).

In conclusion, the hydrochemical and isotopic patterns of near-surface waters collected under three lakes in Forsmark show differences between them. The occurrence of brackish near-surface groundwater with a low content of tritium under Lake Bolundsfjärden, together with hydrogeological observations exclude the possibility of deep saline groundwater discharge in this area and suggests that “trapped” marine water not yet flushed out, i.e. Littorina Sea water, is the most likely hypothesis to explain the current salinity of these near-surface waters at Bolundsfjärden. The low salinity groundwater with a slightly higher tritium content under Lake Eckarfjärden indicates flushed conditions by sub-modern groundwater. The conditions under Lake Gällsboträsket are intermediate in this regard.

Based on the findings it may be questioned if all of the potential discharge zones may be acting as such. Here the upcoming feedback from the ongoing hydrogeological monitoring is important.

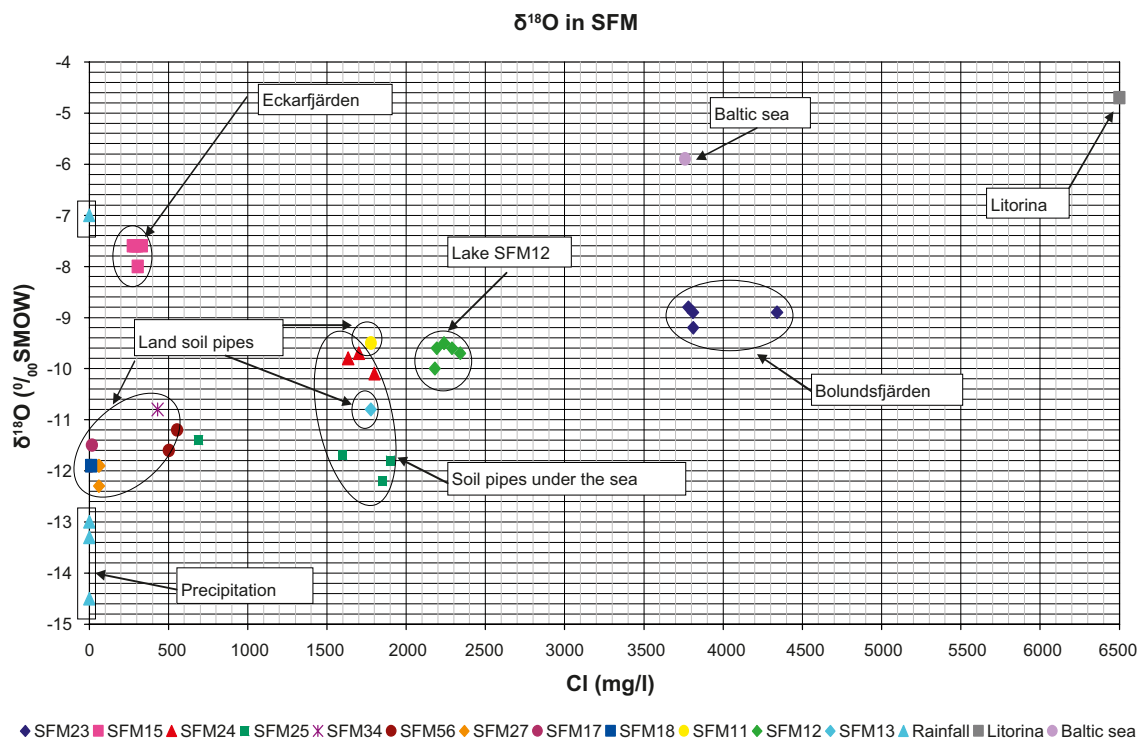


Figure 3-20. ^{18}O versus Cl in soil pipe samples (near-surface groundwater) located at the presumed discharge zones. The ^{18}O variation for precipitation are due to seasonal fluctuations.

4 Summary of current knowledge

4.3.1 Hydrogeochemistry

The Forsmark 2.1 datafreeze has resulted in relatively small modifications to the version 1.2 hydrogeochemical site description /SKB 2005ab/, but the overall geochemical understanding of the site has improved /SKB 2006a/. This includes confirmation of previous findings from version 1.2 and also support for the predictions made in version 1.2 based on the limited knowledge at that time. Confidence in the three-dimensional variability of processes and properties has also improved due to the addition of both new data in previously drilled boreholes and from new boreholes in specific key areas.

Figure 4-1 shows the spatial distribution of chloride concentration values (only representative values) available in bedrock water samples (Appendix E). It can be seen that there is a strong salinity contrast between the groundwaters in the upper 100 m of the bedrock and those below this depth; moreover, there are very few representative samples available below the gently dipping deformation zone ZFMA2. This fact is related to the lower hydraulic conductivity of the bedrock below this deformation zone which hinders normal hydrochemical sampling. Therefore, it should be borne in mind that the hydrochemical evaluation provides a biased “picture”, representing information only from the most conductive part of the bedrock. In this respect, the results of the matrix fluid characterisation programme (Appendix A) is expected to be an extremely useful tool to approach a proper (“unbiased”) conceptualisation of the hydrogeochemical system.

The most conductive part of the upper 100 m in the bedrock is supported by the tritium contents measured in groundwater samples (Figure 4-2). Samples taken above 100 m show high tritium contents typical of modern water; available data show that these decrease to below 4 TU at around the 100 m depth. It can be stated, therefore, that even in the most conductive zones of the bedrock, groundwater deeper than 100 m is, at least, sub-modern.

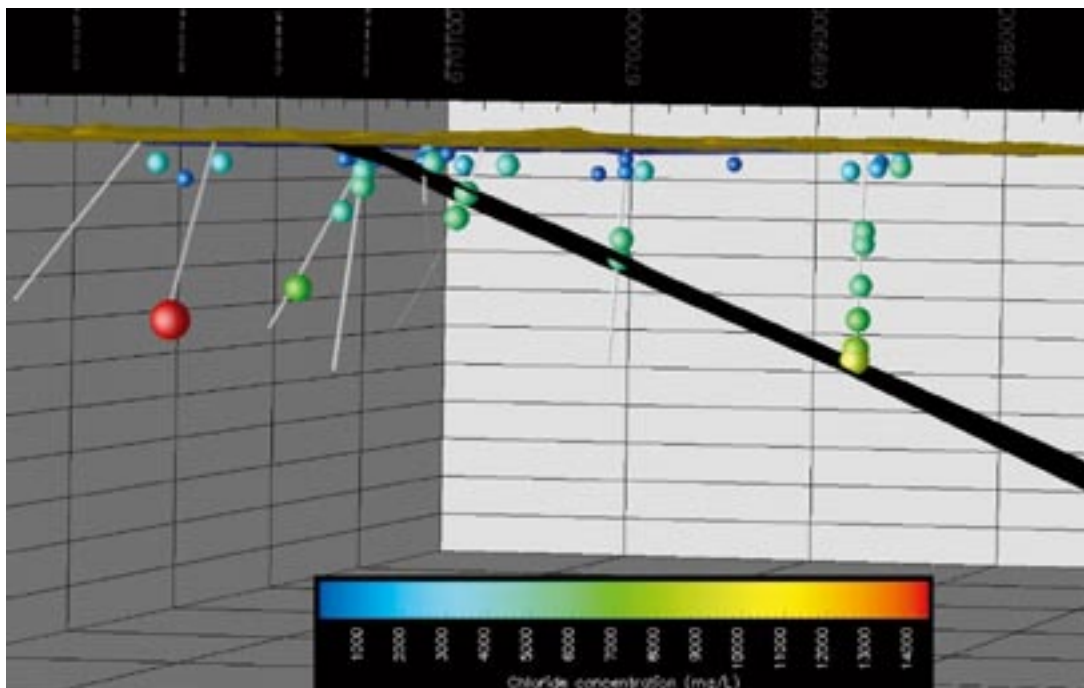


Figure 4-1. Spatial distribution of Cl concentrations in bedrock groundwater samples available in Forsmark, and its relationship with the gently dipping deformation zone ZFMNE002A. The vertical depth scale division is for every 200 m.

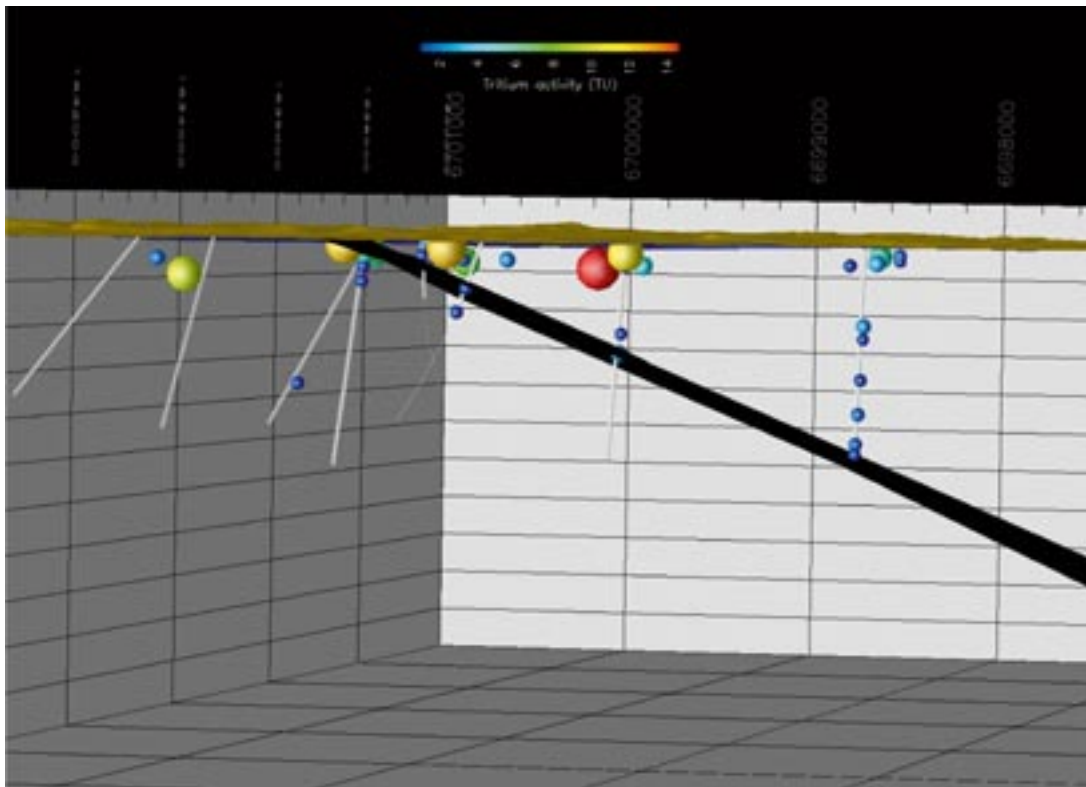


Figure 4-2. Spatial distribution of the tritium activities in the bedrock groundwater samples available in Forsmark, and its relationship with the gently dipping deformation zone ZFMNE002A. The vertical depth scale division is for every 200 m.

Stable isotopes indicate that glacial signatures can be recognised in the bedrock, in general at depths greater than 500–600 m. Figure 4-3 shows the spatial distribution of $\delta^{18}\text{O}$ values.

It is worth noting that there are two main exceptions to the low stable isotope values (potentially indicative of glacial signatures) in shallow groundwater samples. They correspond to groundwater samples collected in percussion boreholes, located between Bolundsfjärden and Fiskarfjärden. The boreholes HFM11 and HFM12 will be resampled and modelled to exclude possible input from recent snow melt. In general, the new Forsmark 2.1 data have allowed for a more detailed geochemical process modelling and redox description (Appendices A–G).

4.3.2 Groundwater composition

Data on groundwater composition in the bedrock shows a fairly low salinity in the uppermost 100–150 m and rather distinct increase in salinity down to a depth of about 200 m. This combined with the finding that ^3H data show no input of modern water at depths greater than 200 m indicates that groundwater in the uppermost parts of the bedrock is influenced by meteoric water (precipitation). At depths between 200 and 800 m, the salinity remains fairly constant at a level between 5,000 and 6,000 $\text{mg}\cdot\text{L}^{-1}$, which together with high Mg concentrations indicate input of Littorina Sea water at these depths (Appendix A, C, D and E). At depths between 600 and 1,000 m, the salinity steadily increases to high values and there are some weak indications that the salinity is higher at great depths in the rock in the north-western part of the candidate area (i.e. in the target area) as compared to the south-eastern part.

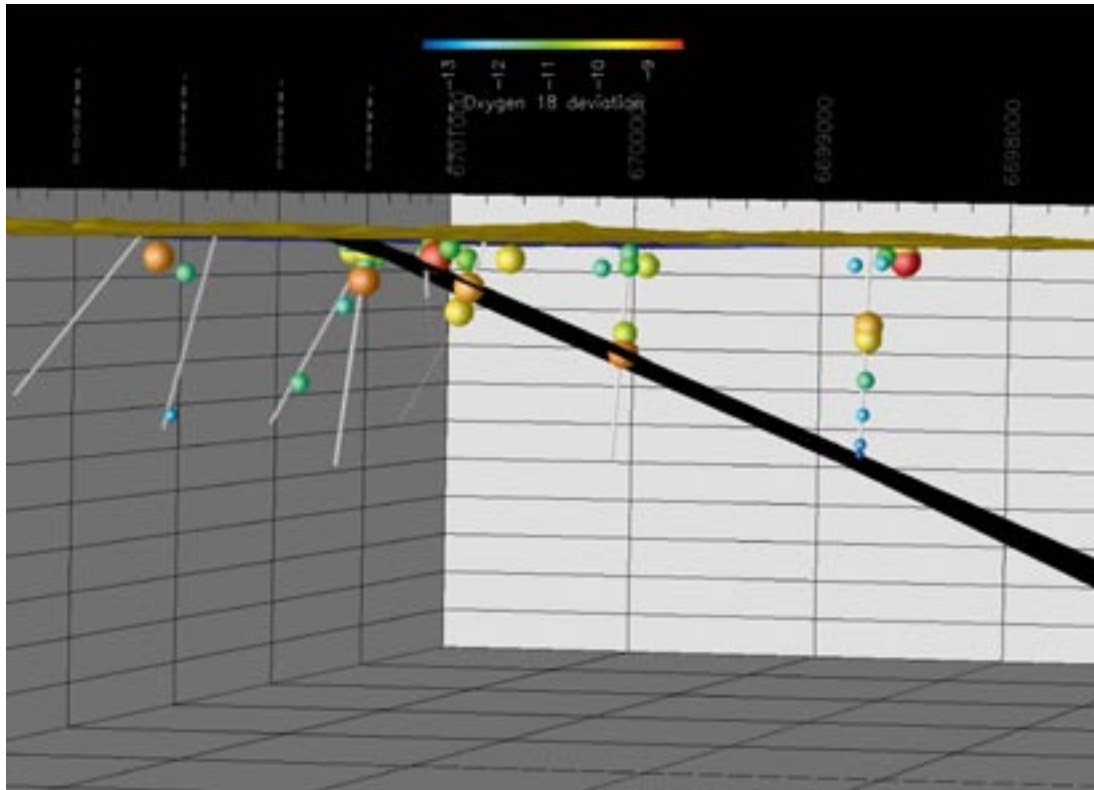


Figure 4-3. Spatial distribution of the $\delta^{18}\text{O}$ deviations in the bedrock groundwater samples available in Forsmark and its relationship with the gently dipping deformation zone ZFMNE002A. The vertical depth scale division is for every 200 m.

Analyses of groundwater chemistry data have also revealed an anomaly in U concentration. Large variations in U content in surface waters are common and are usually ascribed to various redox states (oxidation will facilitate mobilisation of U) and various contents of complexing agents, normally bicarbonate (which will keep the U mobile). Lower U content with depth is expected due to decreasing redox potential and decreasing bicarbonate content. This trend is not seen in the data collected so far at Forsmark. Instead, most of the data indicate high values at depths between 200 and 600 m. The conclusion is that the reason for high U seems to be a combination of available U, probably at least partly, from an amorphous U-phase present in parts of the fracture system, and also groundwater conditions that both mobilise U from this amorphous phase and keep it mobile in solution. Speciation calculations show that U can remain mobile due to the relatively mildly reducing conditions and presence of sufficient HCO_3^- to allow U-carbonate complexation. Microbial activity may have an important influence on U mobilisation.

The hydrogeochemical data evaluation and modelling has revealed that the main compositional changes in groundwater composition at Forsmark is caused by mixing of water with various origin, and microbial processes and rock-water interactions are important in controlling certain parameters such as redox, pH and certain trace elements.

Hydrogeological simulations of the past evolution of groundwater composition conducted in model version 1.2 show good agreement between simulated and measured hydrogeochemical data at depth, whereas poorer matches were obtained in the upper 100 m of the rock /SKB 2005a/. In model version 2.1 /SKB 2006a/ it is envisaged that a reasonable explanation to the poor match in the upper part of the rock can be that the uppermost part of the bedrock is much more anisotropic and hydraulically heterogeneous than accounted for in the hydrogeological model. Different strands of evidence for a 'hydraulic cage' concept is suggested, see /SKB 2006a/.

5 Conclusions

The aim of this report is to address certain INSITE, SIERG and ChemNet issues by modelling the 2.1 Forsmark hydrogeochemical data. The issues are associated to with explorative analysis, mathematical modelling and conceptualisation of the site.

Explorative analysis issues: New data have helped to better describe or understand issues related to groundwater origin and evolution, interactions of surface/deep groundwater systems, redox front, high uranium U and manganese Mn values together with microbes, gases and colloids.

The new groundwater data have confirmed and strengthened existing hydrochemical trends, and the chemistry and evolution of the various groundwater types. In addition there are some new data which may suggest that the Forsmark area could be viewed as representing two distinct hydrogeochemical systems, i.e. one above and one below the gently-dipping ZFMNE00A2 (i.e. Zone A2) deformation zone which is a dominant hydrostructural feature in the area.

A strategy for better description of the interaction between surface and deep groundwater has been established; this will include ^{36}Cl isotopic data from strategically selected shallow, intermediate and deep groundwater types. A proper redox front description requires more detailed fracture mineralogical data before this evaluation and modelling can be performed.

The reason for high U values in some groundwaters seems to be a combination of available U in fracture minerals and rock and also groundwater conditions that both mobilise U and keep it mobile in solution. Uranium can remain mobile due to the relatively mildly reducing conditions and presence of sufficient HCO_3^- to allow U-carbonate complexation. Microbial activity may have an important influence on U mobilisation. Perturbation from, for example drilling, may also explain some of the high U values. The simultaneous presence of high U and high Mn contents in some Forsmark groundwaters seems to be fortuitous. Brackish groundwaters with an important Littorina contribution show high Mn concentrations and reach equilibrium with respect to rhodochrosite. This is a very uncommon condition in most other granitic systems in the Scandinavian Shield and suggests that the high Mn content and equilibrium with rhodochrosite in brackish groundwaters are characteristics imposed by the superficial marine environment prevailing during the Littorina stage.

The microbial evaluation and modelling shows that when iron- and manganese-reducing bacteria dominate at 111 m depth, the redox values are below -150 mV. When sulphate-reducing bacteria increase in numbers at 632 m and even more at 930 m, the redox values decrease to -175 and -250 mV. At depths between 200–600 m the values increase due to a low abundance of microbes and few redox-lowering reactions. The gas data showed that the volume of gas increases with depth in samples from Forsmark and follow the common trend for groundwater found in the Fennoscandian Shield. Nitrogen is the dominant gas at all depths, helium increases but methane, carbon dioxide and hydrogen all decrease with depth. The colloid values obtained from the Forsmark are low and in the range of $10\text{--}30 \mu\text{g l}^{-1}$.

Mathematical modelling issues: These issues ranged from modelling of redox conditions, uncertainty analyses of mixing proportions and mass balance deviations, integration of hydrochemical data with mineralogical and microbial data to the role of monosulphides. M3 issues such as proper selection of end-members and variables in the modelling was addressed. Issues related to drilling impact study (DIS) and the use of electrical conductivity to address the issue of spatial variability.

The conclusion for redox modelling is that it is very difficult to determine the effects of oxygen contamination on the redox system which, moreover, seems to constantly be re-equilibrating and compensating for various effects. Dissolved sulphide could have also been affected; in fact, its contents in most of the Forsmark groundwaters are very low, notwithstanding the good results obtained with sulphur redox pairs.

The uncertainty analyses of mixing proportions and mass balance deviations focused on the modelling of the origin of brackish water with a Littorina signature. The hypothesis is that the result of pure mixing of different proportions of Littorina waters in a volume of rock where various mixtures of Glacial + Brine (giving around 5,500 mg/L of Cl) already existed. In all cases, the range of values of the calculated samples matches the observed range, confirming that a simple mixing hypothesis can explain the geochemical behaviour of the constant-Cl depth range in Forsmark area.

The importance to integrate hydrochemical data with mineralogical and microbial data was addressed in several issues. A probable, significant result is the equilibrium with respect to the amorphous iron monosulphides found in a sample at 630 m depth. This could indicate the active precipitation of amorphous iron monosulphides and also the presence of an important SRB activity at shallower depths than thought before. Moreover, this depth is especially important as many other redox elements undergo severe modifications here. This fact suggests that some high-Littorina waters have indeed a supply of nutrients and therefore, that not all of them occupy isolated pockets. Sampling problems (oxygen intrusion, high contents of drilling water, etc) could have modified the original Fe^{2+} and S^{2-} groundwater contents and, consequently, also some of the results on their saturation state with respect to the iron monosulphides. However, new data from the 2.2 data freeze do not change the conclusion of a very low SRB activity in the brackish groundwaters between 100 and 600 m depth.

The conclusion of testing different end-member and compositional options showed that the PCA analysis in M3 employing all groundwater samples with major elements (Na, K, Ca, Mg, SO_4 , HCO_3 , Cl) and isotopes the H^2 , O^{18} and ^3H (non corrected) and employing the end members: Littorina, Brine, Glacial, Meteoric (rain60 age-corrected) give the most robust characterization of the Forsmark 2.1 and Laxemar 2.1 datasets.

The field data is such that a simplified methodology for DIS has to be employed and this development is ongoing. The measured electrical conductivity from core boreholes can be used to support the spatial variability description of the salinity of the bedrock.

Conceptual modelling issues: These issues concerns 2D and 3D large and small scale conceptualisation and better integration with hydrogeology needed for the site descriptive model (SDM).

For the Forsmark 2.2 and 2.3 model version, several improvements will be attempted to further quantify the conceptual model version 1.2. This will include: a) a closer integration of hydrochemistry and hydrogeology based on 2D and 3D mathematical modelling, and b) use a modified version of the hydrogeological conceptual model as a framework to integrate the hydrochemistry. Effort will be put into small-scale conceptualisation of specific issues such as: a) pore water chemistry, b) fracture mineralogy, and c) redox front evolution.

Hydrochemistry observations are used to support the hydrogeochemical modelling and can be used to indicate interaction between surface and deep groundwater. The occurrence of brackish near-surface groundwater under Bolundsfjärden points towards the discharge of older groundwater, and/or the presence of “trapped” relict water not yet flushed out. On the contrary, the low tritium contents under Eckarfjärden indicate the influence of sub-modern groundwater close to the surface, but with no signature of older marine or non-marine deep saline components.

In general it has been possible to test more quantitatively several chemical hypotheses by the 2.1 issue analysis. This has resulted in additional understanding such as:

- The major reason for high U concentrations can be attributed mostly to U-complexation in the groundwaters, with the uranium source probably present as a mineral phase in the fracture systems. At least the influence of drilling activities can be excluded now as the major mechanism to enhanced U in the groundwaters. However, further information (e.g. redox state of U; mineralogical data etc) is required.

- The complex origin of the groundwater under the lakes in Forsmark (specifically Bolundsfjärden) had initially been conceptualised as resulting from direct discharge effects from deeper in the bedrock. Now, with an updated hydrogeological model of the area, this explanation has been changed. This is a good example of integrated hydrogeological/hydrogeochemical interpretation.
- The redox description is more robust thanks to more measurements, improved data and better microbial understanding, all contributing to greater modelling confidence.
- The difference in the groundwater origin in Forsmark compared with Laxemar (e.g. seawater influences) necessitated an update of the M3 code thus providing a more quantitative modelling approach with less associated uncertainties.
- Greater focus for future interpretation and visualisation has been achieved. For example, the possible implications of structural domains on hydrochemical evolution etc at Forsmark. This will require, however, further data and closer integration with hydrogeological progress before any final decision can be made.

Where greater focus has not been possible is due mostly to a lack of data and/or requires greater integration with output from other disciplines which is not yet available.

The present conceptual understanding of the Forsmark site is that the groundwater composition shows an increase in salinity down to a depth of about 200 m in combination with ^3H data showing no input of modern water at depths greater than 200 m. This indicates that groundwaters in the uppermost parts of the rock are of meteoric origin. At depths between approx. 200 and 600 m, the salinity remains fairly constant at a level between 5,000 and 6,000 $\text{mg}\cdot\text{L}^{-1}$, which together with high Mg concentrations indicate input of Littorina waters at these depths. At depths between 600 and 1,000 m, the salinity increases to high values with a glacial and deep water signature and there are some weak indications that the salinity is higher at large depths in the rock in the north-western part of the candidate area (i.e. in the target area) as compared to the south-eastern part.

In conclusion, the Forsmark 2.1 data imply relatively small modifications to the version 1.2 hydrogeochemical site description, but the overall geochemical understanding of the site has improved. This includes confirmation of previous findings from version 1.2 and also support for the predictions made in version 1.2 based on the limited knowledge at that time. The confidence concerning the three-dimensional variability of processes and properties has also improved due to the addition of both new data in previously drilled boreholes and from new boreholes in specific key areas. By addressing 19 key issues the uncertainties for some of the major processes have been reduced.

The major conclusions and implications for the forthcoming modelling work are:

- New F2.1 data and the modelling applied to address issues related to groundwater origin, evolution and key hydrogeochemical processes have reduced the uncertainties and improved the site understanding. Moreover, additional data needs have been recognised and will be implemented to further this understanding.
- New data from the 2.2 and 2.3 stage require revisions/control/update of the issues related to buffer capacity, compositions and properties of the groundwater relevant to the safety assessment and site understanding.
- The addressed issues can be used as reference cases for the forthcoming final Forsmark and Laxemar modelling. Issues not related to safety assessment or key site understanding can be given a lower priority.
- Further integration between different geoscientific disciplines such as geology, hydrogeology and surface chemistry is required to produce a robust hydrogeochemical site description.

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Forsmark 2.1 Hypothesis/issues identified within the hydrogeochemical programme

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A1 Introduction

A.1 Background

Based on outstanding hydrogeochemical hypotheses/issues to be addressed, identified from the Forsmark 1.2 hydrogeochemical evaluation /SKB 2005a/, the following issues are described and discussed in this report:

1. Groundwater origin and evolution.
 - Differences in salinity and salinity gradients between different sites.
 - Hydrochemistry of transmissive deformation zones.
2. Conceptual modelling in 2D and 3D.
3. Interaction of surface/deep groundwater systems.
 - Depth of active modern groundwater circulation.
 - Location of groundwater discharge zones.
4. Uranium, radium and radon.
5. Redox front considerations.

One of the main objectives is to propose a practical strategy to address these issues, for example: a) identify the need for supplementary groundwater and fracture mineral analysis, b) provide a last opportunity to propose specific isotopic analyses such as groundwater chlorine-36 dating, c) facilitate greater integration with other disciplines (geology, hydrogeology) now that respective conceptual models are nearing completion, and d) to produce alternative 2D and 3D models integrating hydrogeology and hydrogeochemistry.

A2 Groundwater origin and evolution (Issue #1)

The Forsmark 2.1 hydrogeochemical explorative analysis input has basically focussed on updating the Forsmark 1.2 major ion and environmental isotope plots by integrating new data. This has confirmed and strengthened existing hydrochemical trends, and further supports the chemistry and evolution of the various groundwater types. In addition there are some new data which may suggest that the Forsmark area could be viewed as representing two distinct hydrogeochemical systems, i.e. one above and one below the gently-dipping ZFMNE00A2 deformation zone (ZFMA2) which is a dominant hydrostructural feature in the area. Such gently-dipping deformation zones are regionally common and are known to separate contrasting groundwater types, for example ‘Zone 2’ at Finnsjön which sharply separates groundwaters of fresh (< 300 mg/L Cl) and brackish (~ 5,500 mg/L Cl) chemistry /Smellie and Wikberg 1991/.

A2.1 Differences in salinity gradients between different sites

A2.1.1 General features

Salinity differences within the Forsmark area are exemplified in Figure A2-1 and Figure A2-2 which show the distribution of chloride with depth, and the relationship between chloride and $\delta^{18}\text{O}$, respectively. Figure A2-1 is interesting because of the anomalously high chloride content of 14,400 mg/L which occurs at a slightly shallower depth (KFM07A: 924.77 m) than the previously highest value of 9,690 mg/L (KFM03A:990.6 m). Although this high value could be explained by groundwater being brought from deeper, fractured levels during sampling, it is also noticeable that this borehole section is located entirely below the gently-dipping deformation ZFMA2, whilst KFM03A is above. Maybe this suggests simply that groundwaters below ZFMA2 achieve greater salinity at shallower depth, or it is an indication of a differently evolved groundwater system as inferred above.

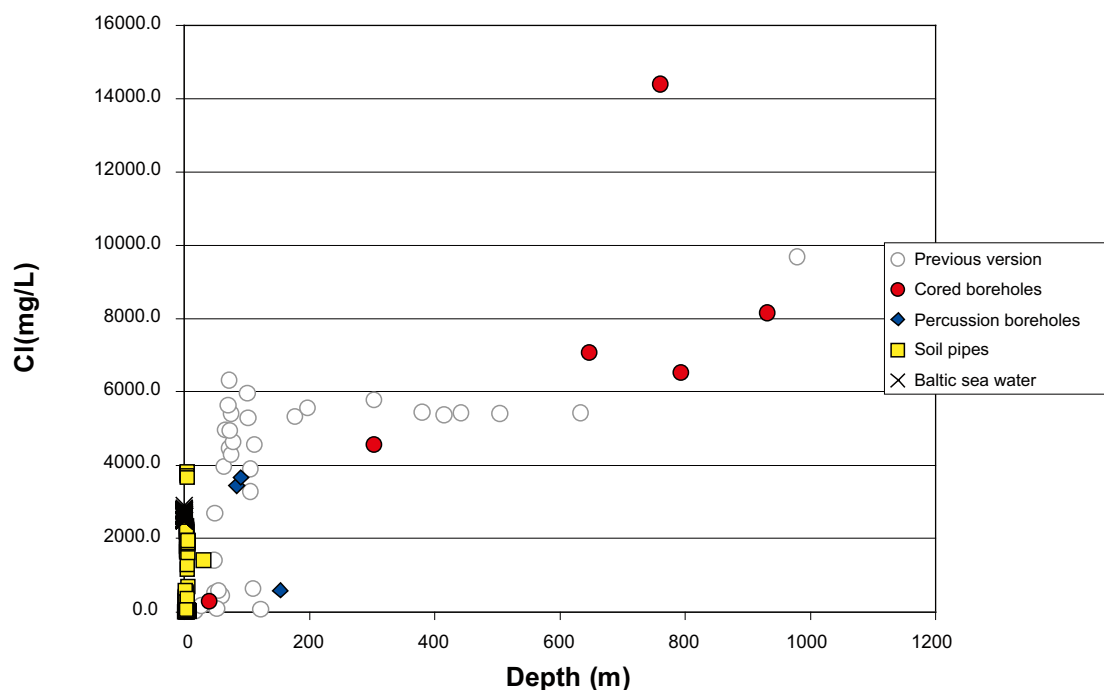


Figure A2-1. Distribution of chloride with increasing depth.

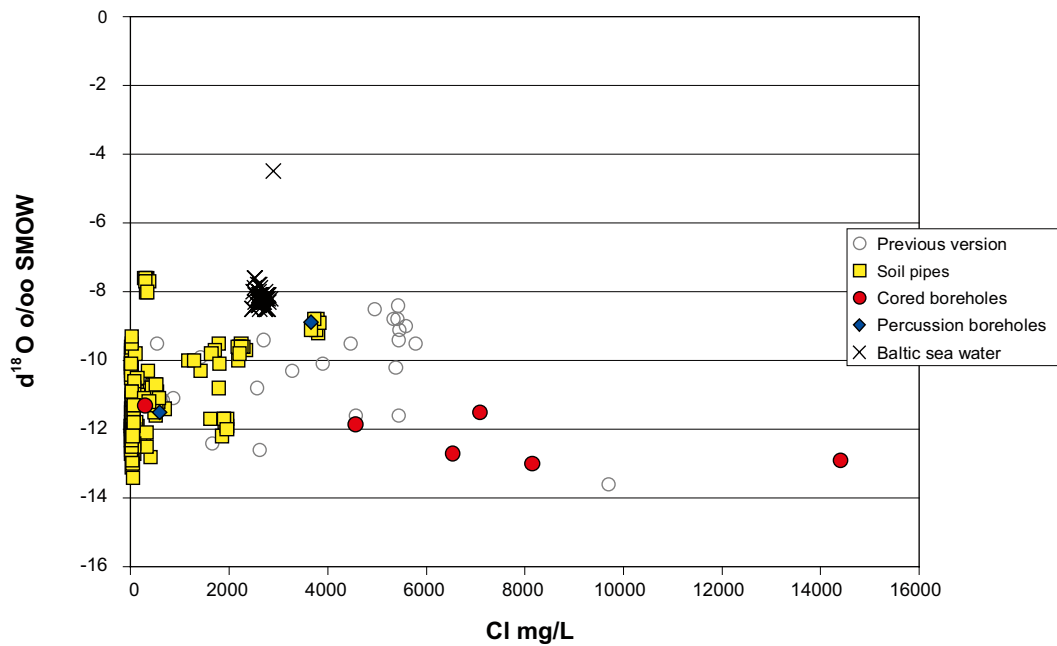


Figure A2-2. Distribution of chloride versus $\delta^{18}\text{O}$.

Figure A2-2 demonstrates four features strengthened by the Forsmark 2.1 data: a) the large spread of $\delta^{18}\text{O}$ values for the fresh soil pipe groundwaters (< 300 mg/L Cl), most likely reflecting seasonal precipitation variations, b) the separate group of soil pipe groundwaters at higher salinity (~ 300–2,500 mg/L Cl), some with a light $\delta^{18}\text{O}$ signature, c) a small cluster of soil pipe (and one percussion borehole) groundwaters of more brackish composition (~ 3,700 mg/L Cl) with heavier $\delta^{18}\text{O}$ signatures plotting close to the Littorina Sea type waters, and d) the continued light $\delta^{18}\text{O}$ values for the deeper, more saline groundwaters (> 8,000 mg/L Cl), indicating a distinct cold climate recharge (glacial) component at the maximum depths sampled. The final point is interesting in that irrespective of where the deep samples have been taken, i.e. over or under ZFMA2, glacial waters have been intruded to considerable depth at some stage in the past.

A2.1.2 The influence of structural features

The Forsmark site is traversed by local steeply-dipping deformation zones mainly trending NE-SW and ENE-WSW with a weaker fracture group mostly trending approximately N-S and NW-SE (Figure A2-3).

The Eckarfjärden and Singö deformation zones effectively truncate these former fracture zones and form the regional NW-SE-trending boundaries to the candidate site; the Forsmark deformation zone, of similar strike, is located parallel and south of the Eckarfjärden zone (Figure A2-4).

Gently-dipping subhorizontal deformation zones also exist, but since their presence can only be confirmed by a systematic drilling campaign, they tend to be under-represented from surface bedrock investigations. The most important gently-dipping deformation zone in the Forsmark site is ZFMA2 which is highly transmissive with hydraulic connections over a distance of 2 km.

Figure A2-5 shows a NE-SW schematic representation of the Forsmark site with the locations of the boreholes and their relationship to ZFMA2 and other gently-dipping deformation zones to the SE. Note that the demarcated repository area (hatched red line) is at the foot wall side of ZFMA2, which is devoid of important subhorizontal deformation zones below around 150 m depth.

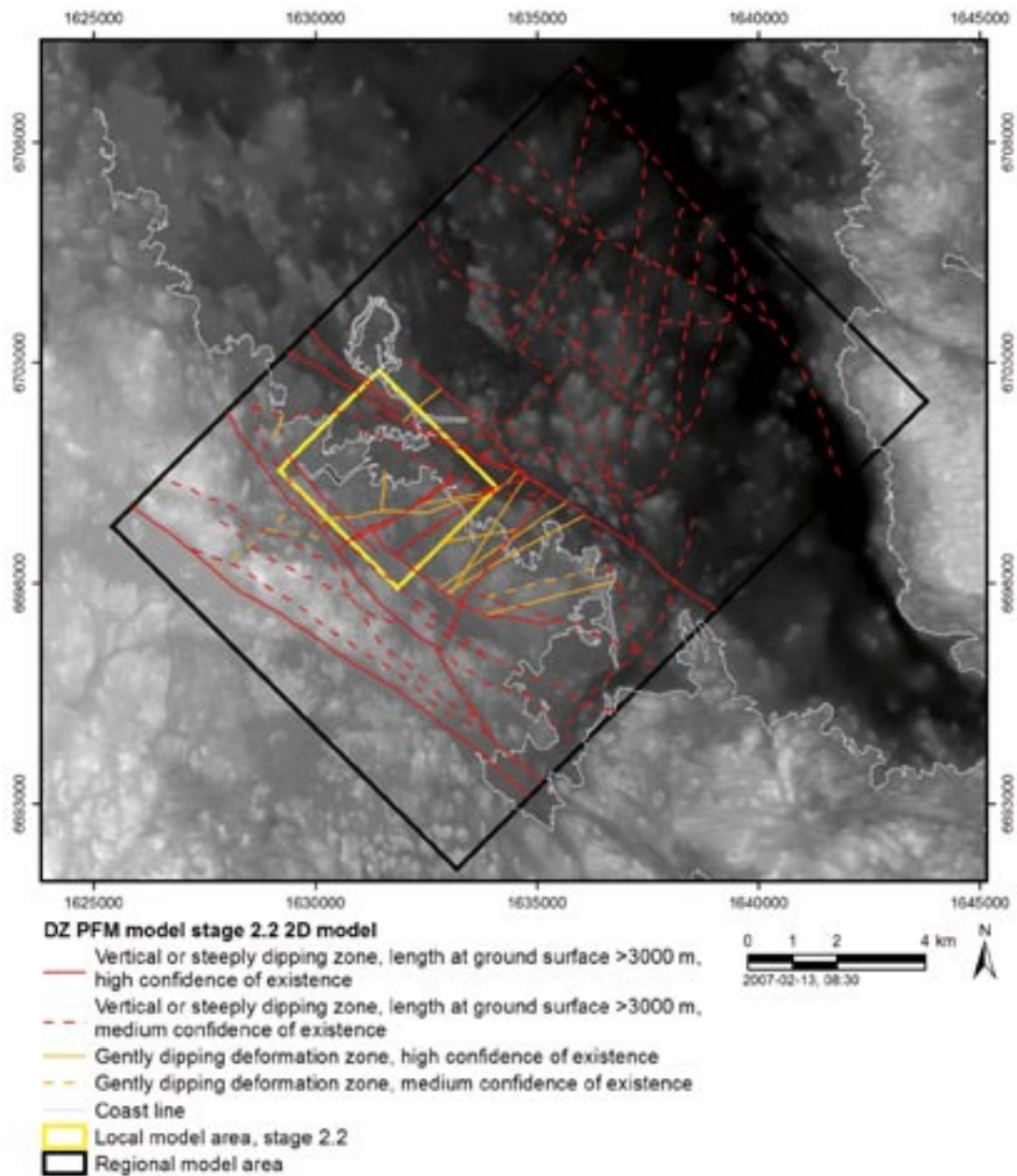


Figure A2-3. Structural patterns in the Forsmark area (version 2.2). The deformation zones (steeply dipping and gently dipping varieties) are subdivided on the basis of high, medium and low confidence (modified from v. 2.1 in /SKB 2005b/).

Figure A2-6 shows the major structural divisions of the area which are referred to as:

- NE Hanging wall of zone ZFMA2 (i.e. FFM03).
- NW Foot wall of zone ZFMA2 subdivided into:
 - surface to depth of ~ 150 m (i.e. FFM02),
 - boundary/border (not indicated, but to the NW),
 - middle (i.e. FFM01).

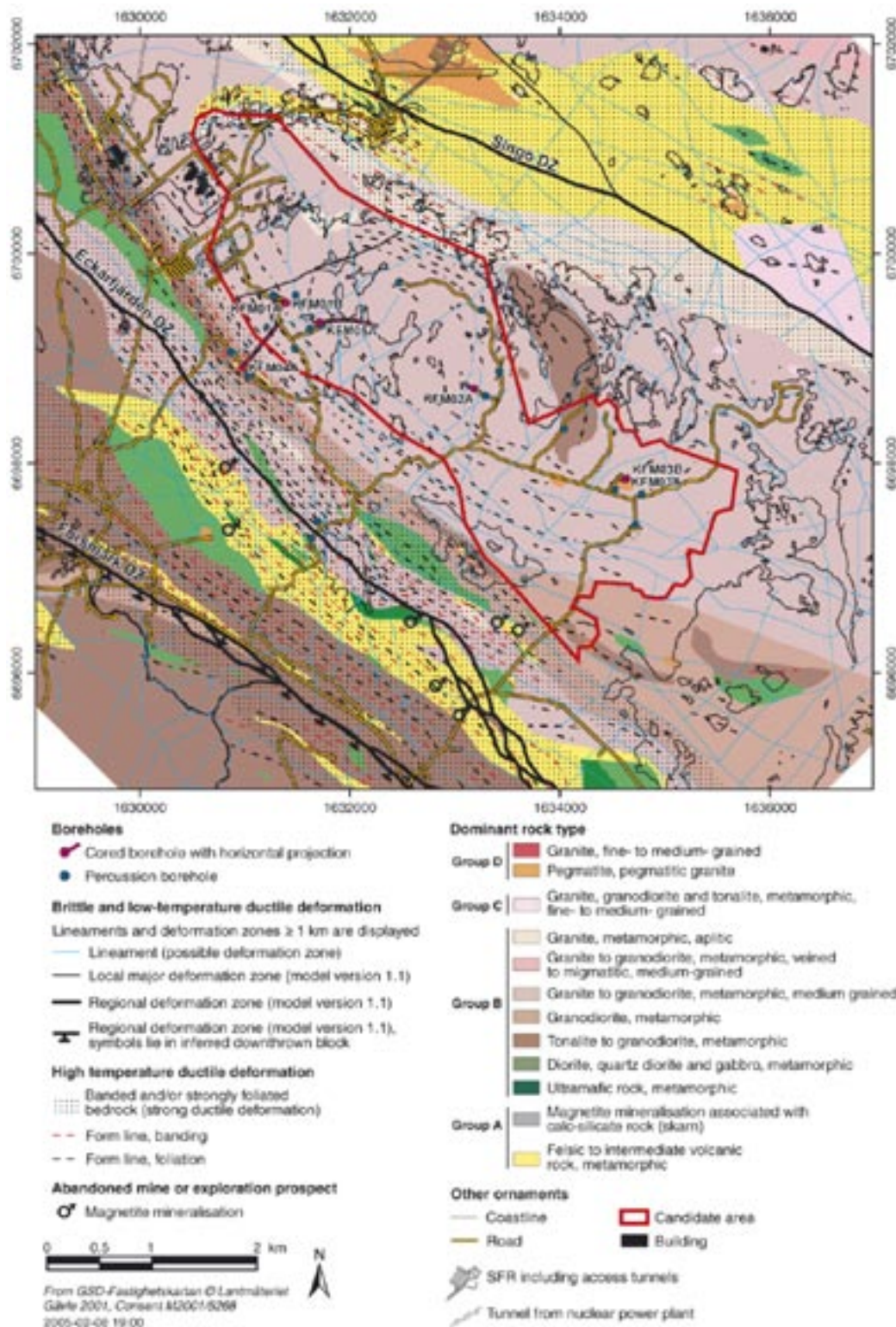


Figure A2-4. Detailed geology of the Forsmark area. Plastic deformation zones are indicated by hatched lines along and beyond the west (strongly deformed) and east (less deformed) boundaries of the demarcated candidate site (red line) /from SKB 2005b/.

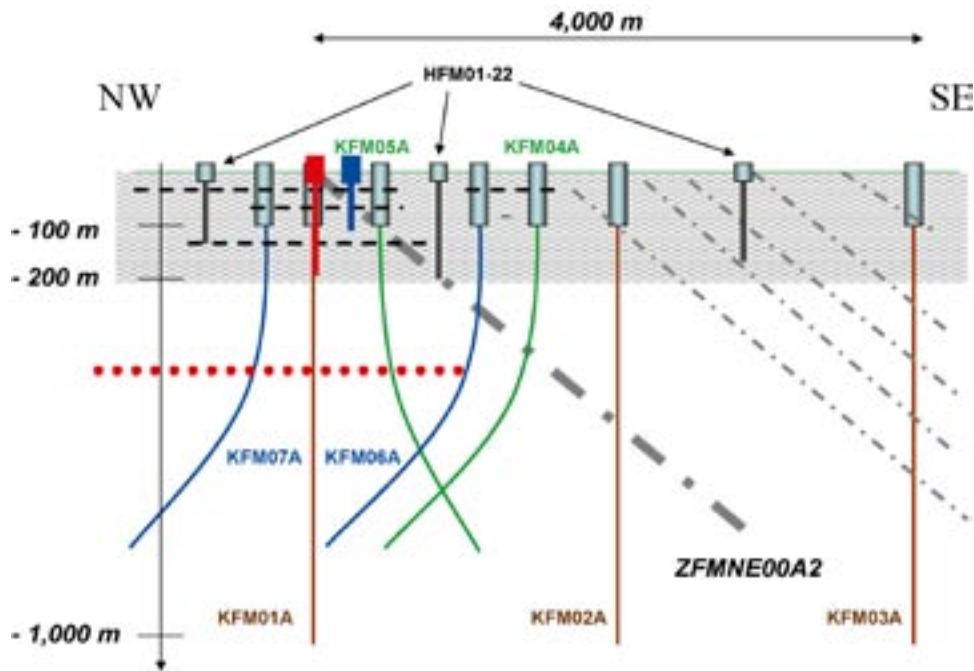
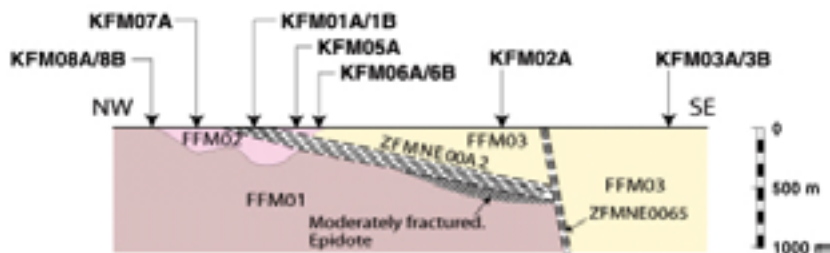


Figure A2-5. Schematic representation of the Forsmark site showing the position, depth and orientation of the boreholes, the position of the gently-dipping ZFMA2 deformation zone and the possible location and depth of a repository construction (red hatched line). The shaded upper 200 m represents bedrock of high transmissivity which contrasts sharply with low transmissive bedrock at increased depth /SKB 2006a, modified from Follin et al. 2005/.



Fracture domain (FFM01)

Steeply dipping, minor fault zones with sealed fractures, low fracture frequency between zones, high in situ stress

Fracture domain (FFM02)

High frequency of sub-horizontal fractures with apertures

Fracture domain (FFM03)

High frequency of gently dipping, minor deformation zones containing both sealed fractures and fractures with apertures, low in situ stress relative to FFM01

Figure A2-6. Major structural subdivisions in the Forsmark area. Only two fracture zones, the gently dipping zone ZFMA2 and the steeply dipping zone ZFM65, against which zone ZFMA2 appears to truncate to the SE, are shown /SKB 2006a/.

The boundary/border area (i.e. outside the target area and the demarcated candidate site) is shown in Figure A2-7 where boreholes KFM04A, 6A, 7A and 8A are indicated to have intersected.

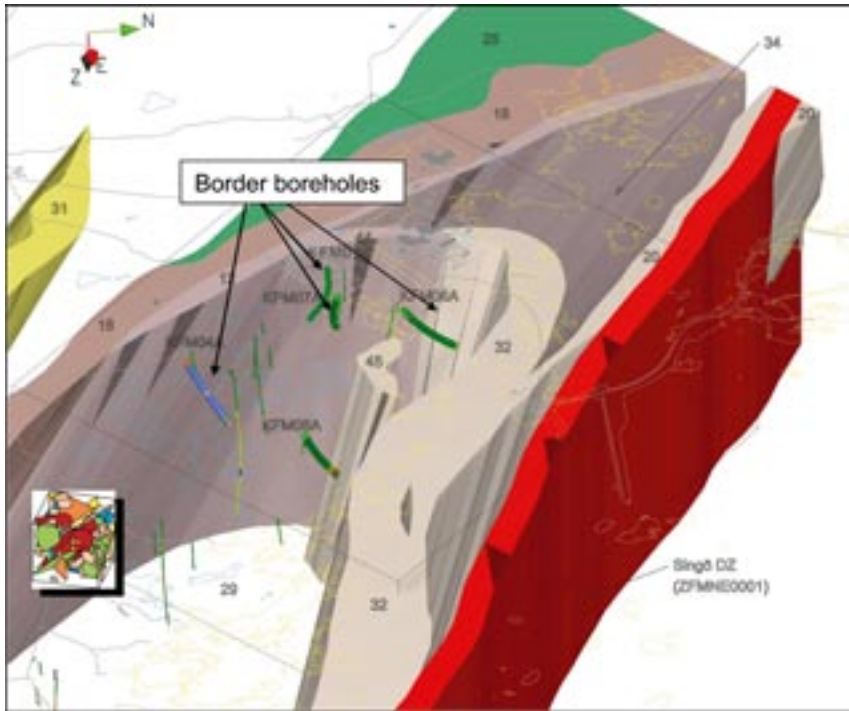


Figure A2-7. Three-dimensional model for rock domains (numbered) inside the target area, in the NW part of the candidate site. The model is viewed to the west from approximately the position of SFR. Boreholes KFM04A, 6A, 7A and 8A intersect the boundary rocks to the candidate repository area and constrain the boundaries between the different domains /SKB 2006a/.

These structural divisions, and corresponding differences in transmissivity, have been used to present and interpret the updated hydrochemistry data. This is illustrated in Figures A2-8 to A2-11.

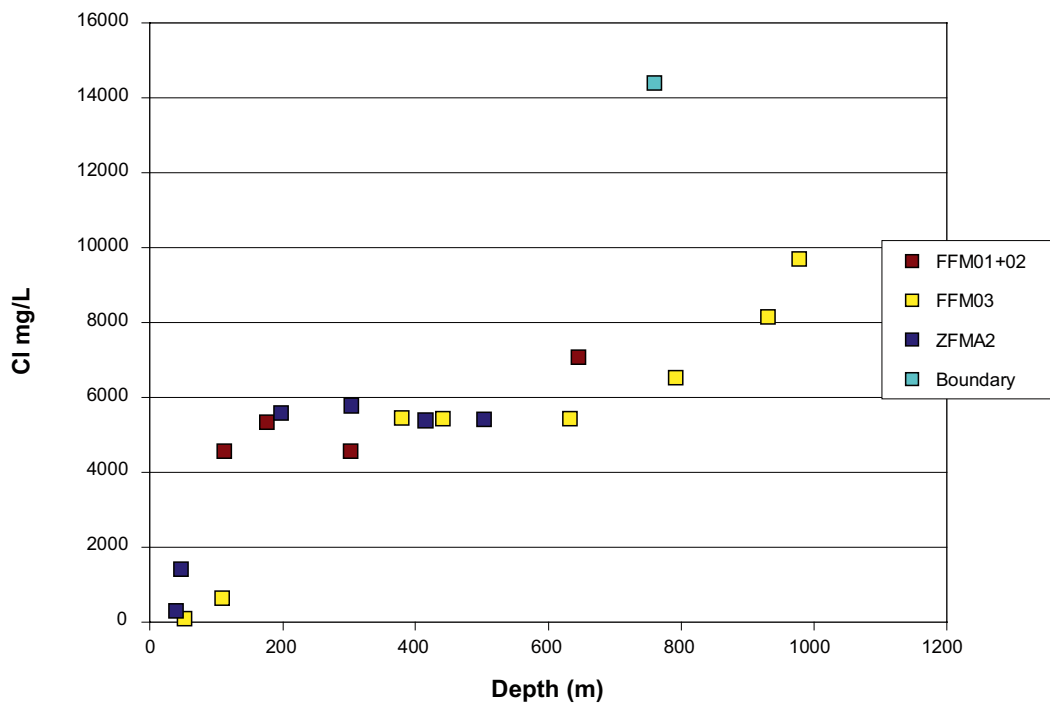


Figure A2-8. Chloride versus depth (see Figure A2-6 for structural boundaries).

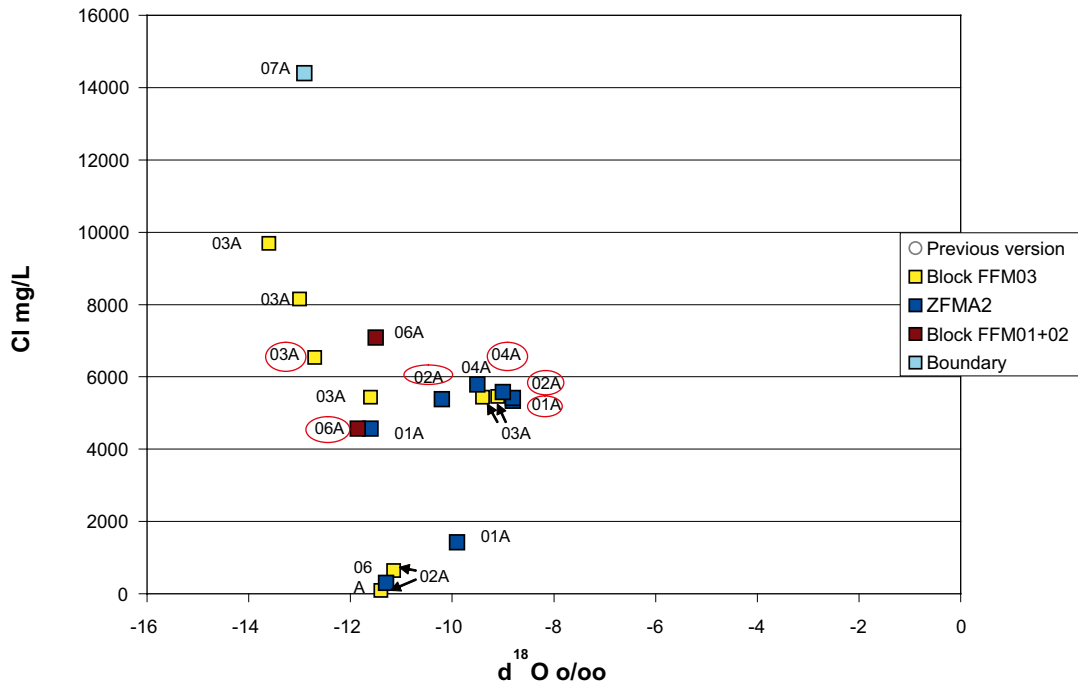


Figure A2-9. Chloride versus $\delta^{18}O$ (see Figure A2-6 for structural boundaries).

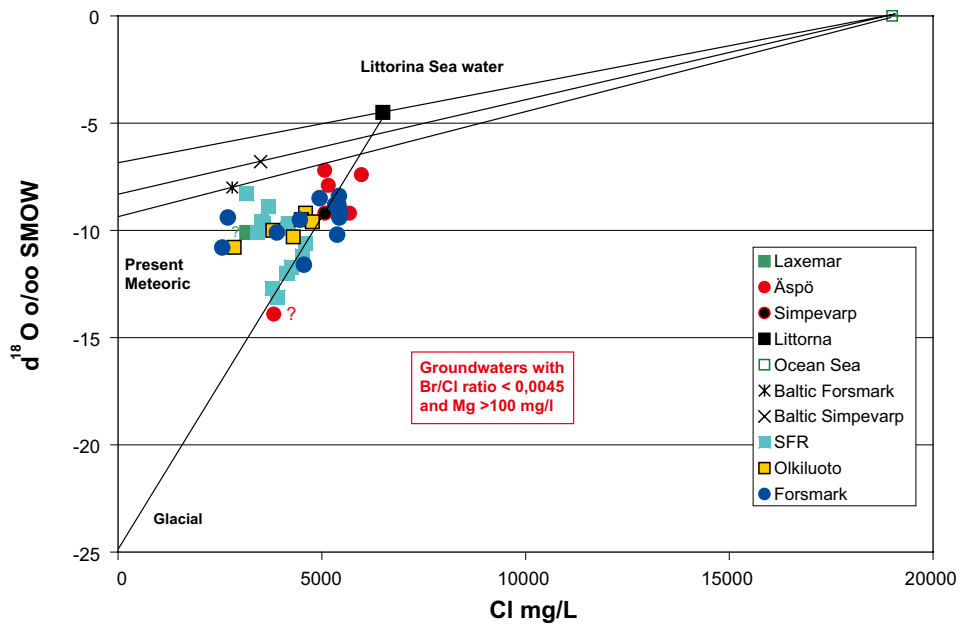


Figure A2-10. Chloride versus $\delta^{18}O$ for groundwater with marine components (identified as $Br/Cl < 0.0045$); all groundwaters show $Mg > 100$ mg/L with two exceptions, one sample from Laxemar and one from Äspö, both denoted with question marks.

In Figure A2-8 there are two similar and fairly well defined trends: a) related to the gently-dipping deformation zone ZFMA2, and b) related to the hanging wall of ZFMA2 in the Fracture Domain Block (FFM03). Taken together, from the surface to depth the salinity is seen to rapidly increase from fresh water values close to the surface (< 300 mg/L Cl), through low saline values (300 – $2,000$ mg/L Cl) to brackish values (around $4,300$ mg/L Cl) at around 100 m depth. The salinity then evens out forming a plateau at $5,000$ – $6,000$ mg/L Cl until around 600 m depth where there is a gradual but consistent increase to just under $10,000$ mg/L Cl at $1,000$ m depth.

At the foot wall of ZFMA2, i.e. Fracture Domain Blocks (FFM01+02), there are too few data. However there may be a suggestion of a separate salinity trend with a more restricted brackish groundwater plateau and a more rapid increase in salinity at 600 m to the highest value measured for Forsmark at around 14,800 mg/L Cl at just under 800 m depth.

Figure A2-9, plotting chloride against $\delta^{18}\text{O}$, shows three general groupings: a) shallow, fresh to low saline groundwaters, with values of $\delta^{18}\text{O}$ ranging from -12 to -10‰ SMOW, b) brackish groundwaters with a large range in $\delta^{18}\text{O}$ (-14 to -8‰ SMOW), and c) high saline groundwaters with values restricted to depleted $\delta^{18}\text{O}$ (-14 to 12.5‰ SMOW). The fresh to low saline groundwaters have typical recharge $\delta^{18}\text{O}$ values, and the deep, high saline groundwaters with depleted $\delta^{18}\text{O}$ values signify a cold climate component. The brackish groundwaters are more complex since they are a mixture of an ancient cold climate recharge component (depleted $\delta^{18}\text{O}$ signature), an old Littorina Sea component (enriched $\delta^{18}\text{O}$ signature) and, more recently, of meteoric waters (modern recharge-type $\delta^{18}\text{O}$ signature).

The complexity of the brackish groundwaters is exemplified further in Figure A2-10, where groundwaters with Br/Cl ratios < 0.0045 and Mg values higher than 100 mg/L are shown in a Cl versus $\delta^{18}\text{O}$ plot. It is obvious that the marine water samples in the bedrock at Forsmark and SFR follow two major trends: a) one indicating mixing between Littorina Sea water and glacial meltwater, and b) the other indicating mixing between Littorina Sea, glacial meltwater and modern meteoric groundwater. The latter is common for the groundwater sampled in the percussion boreholes whereas the deeper groundwater sampled in the cored boreholes follows the former trend. The mixing of modern Baltic Seawater is evident in a few samples such as percussion boreholes HFM08 and HFM 22.

Related to the structural subdivisions, deformation zone ZFMA2 is characterised by a more dominant Littorina Sea component and a less cold climate or glacial signature than FFM01+02 (in particular, although data are very limited) and to a lesser extent FFM03. A cold climate recharge component mixed with old saline groundwater dominates at depth in both the FFM01 and FFM01–02 structural domains.

Figure A2-11 plots bromide against depth; this reflects the chloride distribution and trends discussed above (Figure A2-8), i.e. one trend within the gently/dipping ZFMA2 deformation zone which is characterised by Littorina and therefore shows marine signature. The other trend is outside ZFMA2 and common to the other fracture domains. This represents an increasing non-marine salinity with depth to the highest concentration at the boundary. Increasing salinity represents increasing water/rock interaction and longer residence times, typical of Shield basement groundwaters.

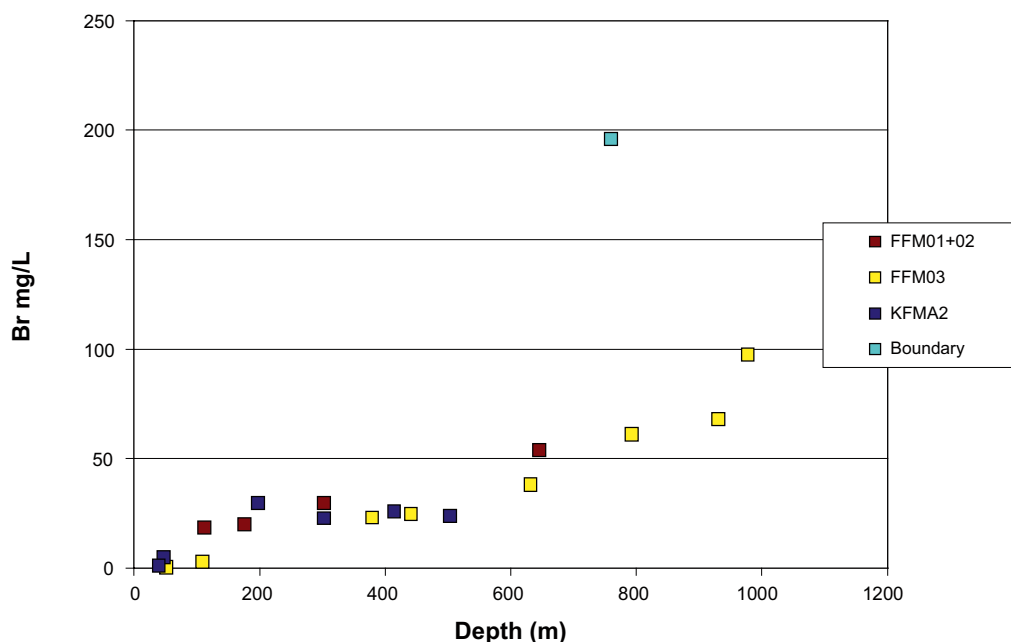


Figure A2-11. Bromide versus depth (see Figure A2-6 for structural boundaries).

Figure A2-12 of bromide against chloride shows a normal close correlation and illustrates clearly the difference between the ZFMA2 deformation zone dominated by a marine Br/Cl ratio (Littorina Sea) signature. Two near-surface samples (KFM01A at ~ 100–180 m borehole length) from structural blocks FFM01+02 also indicate a Littorina component. Otherwise the plot does not provide any further insight into structural controls at the Forsmark site.

A2.1.3 Deformation zone ZFMA2

Because of the importance of zone ZFMA2 in interpreting the hydrogeological and hydro-geochemical evolution of the Forsmark area, some of the hydrochemical issues brought up in section A2.1.2 are further addressed below.

In terms of vertical hydrochemical variation, Figure A2-13 traces the groundwater chemistry in zone ZFMA2 down to approx. 500 m depth in groundwater samples collected from several intersecting boreholes. As shown in Figure A2-8 there is a systematic change in salinity with depth from near-surface modern (1.9–5.6 TU), fresh to low-saline (178–857 mg/L Cl) groundwaters in the upper approx. 100 m of bedrock, to a rapid change to older (< 0.8 TU) and brackish (4,950 mg/L Cl) groundwaters at around 150 m depth. This brackish salinity continues to increase with depth to a maximum of 5,800 mg/L Cl at approximately 350 m, and this seems to continue to around 500 m depth.

Increased salinity is accompanied by an increase in magnesium ranging from 8.1 to 34.9 mg/L in the upper 100 m, followed by a sharp increase to 138 mg/L at 150 m and a further increase to 165–198 mg/L down to 500 m. The increase in salinity and magnesium is matched by a decrease in HCO₃ from high contents in the upper 100 m (314–640 mg/L) to a marked reduction to lower contents (138 mg/L) at around 150 m depth. From here there is a small decrease to 46–98 mg/L which seems to represent the range to around 500 m depth.

The δ¹⁸O signature shows typical recharge values of around –11.5 to –9.2‰ SMOW in the upper 100 m; these values increase to –8.5‰ SMOW at around 150 m depth and then decrease to –10.2 to –9.5‰ SMOW down to 500 m due to an increased component of glacial melt water at depth.

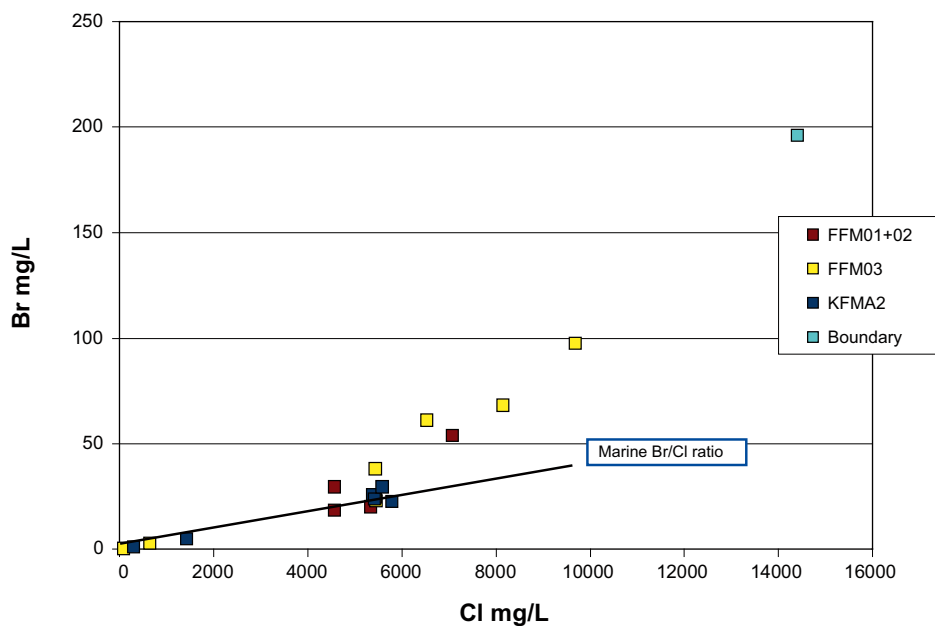


Figure A2-12. Bromide versus chloride (see Figure A2-6 for structural boundaries).

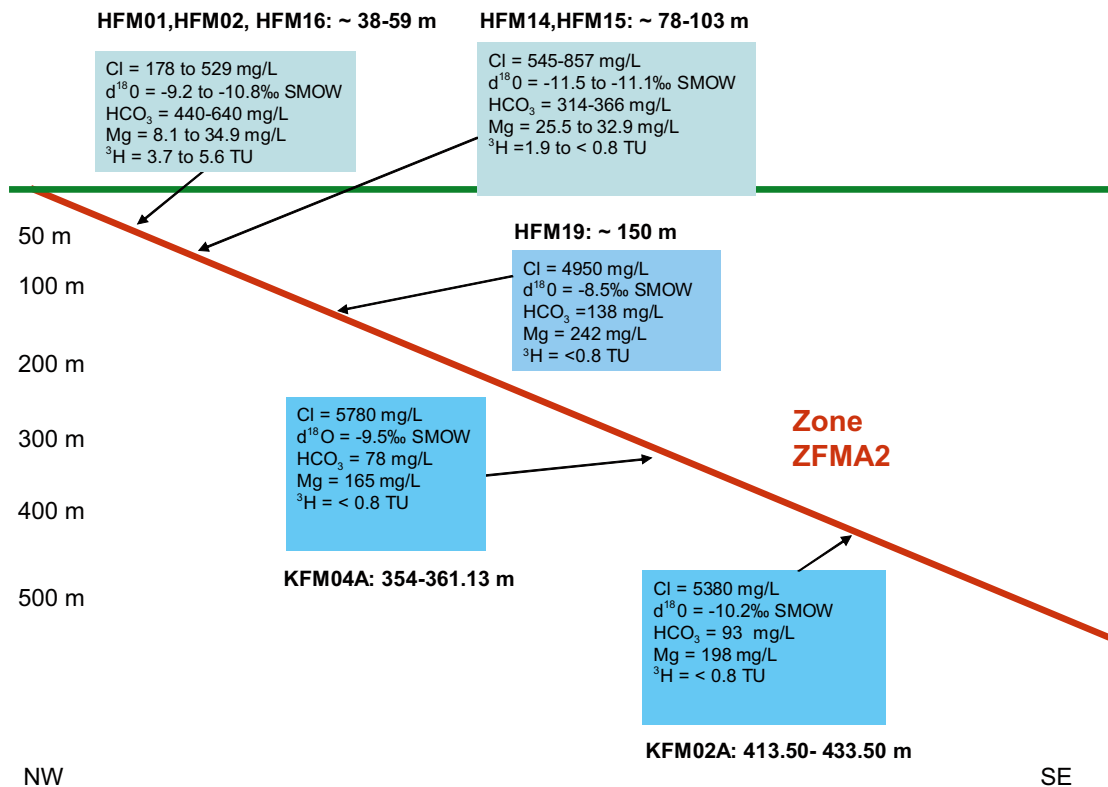


Figure A2-13. Schematic representation of variation in groundwater chemistry (0–500 m) along the gently-dipping deformation zone ZFMA2.

Based on previous understanding of groundwater evolution at Forsmark, the hydrochemical data in zone ZFMA2 represent from approx. 0–100 m a mixture of fresh to low saline groundwaters with strong indications of a modern recharge character. Some mixing may be expected from the longer packed-off sections sampled in the five HFM-percussion boreholes which represent the upper 100 m. However the slightly higher than normal salinity so close to the surface, combined with the rapid increase to brackish groundwater at around 150 m, suggest some discharge along ZFMA2 from deeper, more saline levels.

The brackish groundwaters from approx. 130–500 m, with a slightly more enriched $\delta^{18}O$ and a significant increase in magnesium, represent typical signatures for a Littorina Sea component in the Forsmark area. In addition to zone ZFMA2, Littorina-type groundwaters have also been sampled in other gently-dipping subhorizontal deformation zones such as ZFMA7 where it is intersected by KFM03A further to the SE (i.e. Fracture Domain FD03; Figure A2-6), and also in subvertical zones such as zone ZFMA4, also located to the SE of ZFMA2. These zones essentially have preserved groundwaters which reflect the palaeo-evolution of the Forsmark site prior to, and since, the last glaciation some 10,000 years ago. Where Littorina Seawaters have accumulated, mixing with the earlier glacial melt component has undoubtedly occurred, but since the Littorina Sea water originally has had a very enriched $\delta^{18}O$ signature, the glacial component is not that obvious in terms of depleted $\delta^{18}O$ values. Some exceptions, however, do exist where a glacial signature is more significant (e.g. KFM01A:180 m; $\delta^{18}O = -11.6\%$ SMOW; Figure A2-6).

A3 Conceptual modelling in 2D and 3D (Issue #2)

A3.1 Large-scale conceptualisation approach

The updated Forsmark 2.1 SICADA database has served to confirm the 2D conceptual presented for Forsmark 1.2, reproduced below in Figure A3-1 which is modified from /SKB 2005a/.

For the Forsmark 2.2 model version several improvements will be attempted to further quantify model version 1.2. This will include: a) a closer integration of hydrochemistry and hydrogeology based on 2D and 3D mathematical modelling, and b) use a modified version of the hydrogeological conceptual model (cf. Figure A2-5) as a framework to integrate the hydrochemistry.

For improved hydrogeological and hydrochemical integration a 3D model will be produced showing the locations of the general lithological units, the major fracture zones, and the cored boreholes sampled for hydrochemical characterisation. Based on this 3D model, strategic 2D cutting planes will be selected to best illustrate from the Forsmark site: a) the vertical and lateral spatial distribution of the groundwater chemistry, and b) where possible to illustrate the variation of groundwater chemistry along chosen fracture planes (e.g. zone ZFMA2) and, if possible, to integrate hydraulic flow properties from head measurements. To further embellish these cutting planes with additional hydrogeochemical information, manually-based 2.2 versions (based on Figure A2-5) will also be produced, for example illustrating the major groundwater types, isotopic data, main geochemical reactions etc, as shown in Figure A3-1.

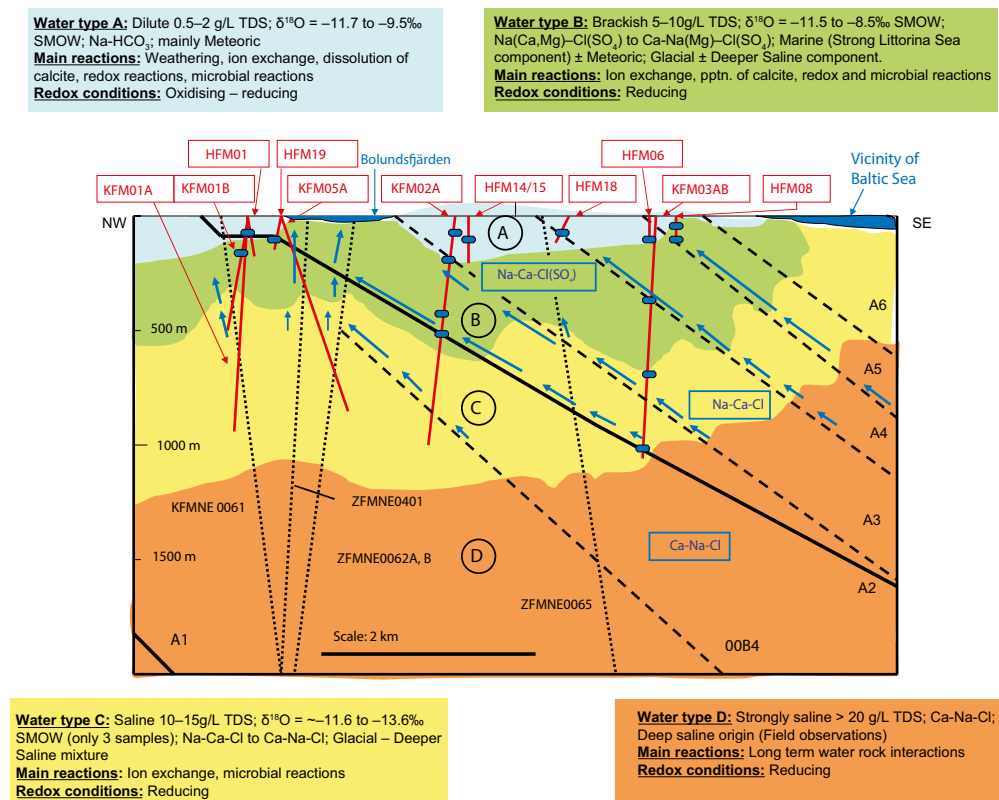


Figure A3-1. Forsmark 1.2 conceptual 2D model /modified from SKB 2005a/.

A3.2 Small-scale conceptualisation approach

To widen the scope of Figure A3-1 for Forsmark 2.2, effort will be put into small-scale conceptualisation of specific issues such as: a) pore water chemistry, b) fracture mineralogy, and c) redox front evolution. A preliminary conceptual example is given below in section A3.2.1 for the matrix pore water studies. Similar approaches are also planned for the fracture mineralogy and redox front evolution studies. The present status of these latter two studies is outlined in sections A3.2.2 and A3.2.3.

A3.2.1 Matrix pore water

Figures A3-2 and A3-3 illustrate how the matrix pore water studies may be conceptualised on a decimetre scale. This has been approached by enlarging selected portions of the bedrock at different depths (Figure A3-2) in a manner that conveys more realistically rock textures (i.e. fracture frequency, size and hydraulic properties) and the chemical variability of fracture groundwaters and matrix pore waters in relation to these rock textures. Observe however that this example is borehole specific for KFM06A and the variation with depth should not be extrapolated to represent the Forsmark site.

Figures A3-3a–d show each of the selected levels recording: a) fracture frequency, b) bedrock transmissivity, c) pore water salinity, and d) fracture groundwater salinity. Observe the representation is schematic and not to scale. The larger fractures illustrated are water-conducting with a hydraulic conductivity sufficiently high ($K > 10^{-8} \text{ ms}^{-1}$) to allow groundwater sampling using standard methods, and these sampled groundwaters are referred to as fracture groundwaters. The smaller, single fractures may also be water-conducting but at a level where standard sampling methods are not applicable ($K < 10^{-9} \text{ ms}^{-1}$). If possible, during initial sampling of the drillcore,

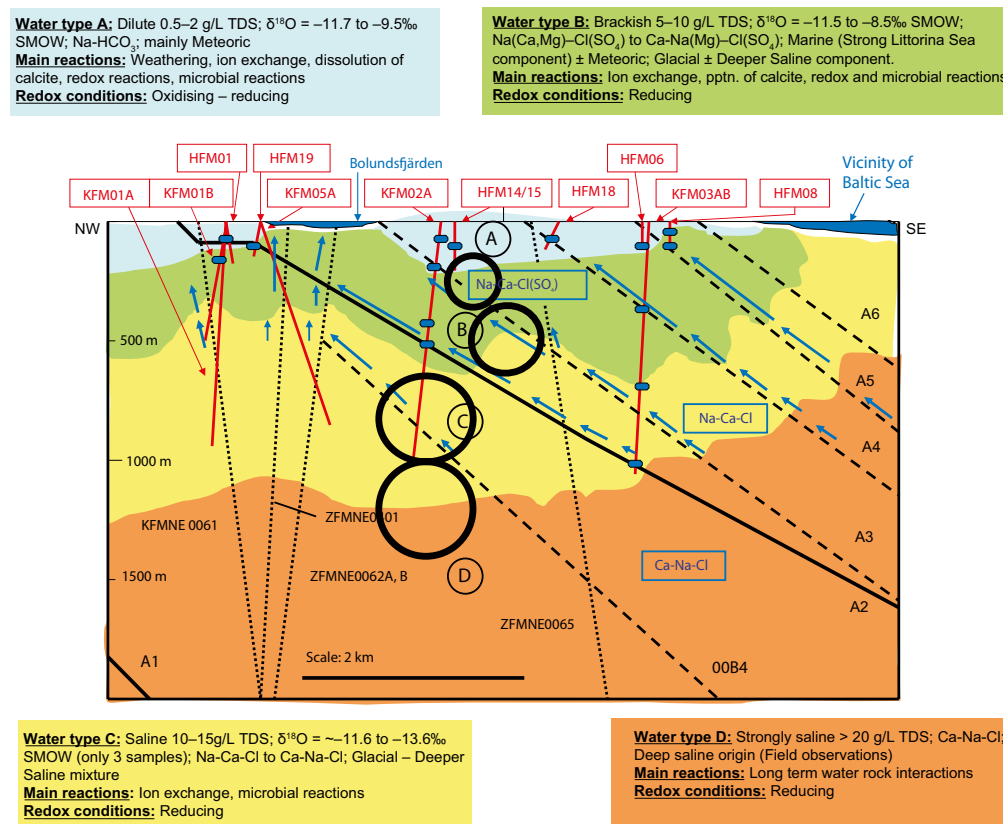


Figure A3-2. Based on the location and data of KFM06A, four bedrock levels have been selected from Figure A3-1 to best illustrate the depth dependency of fracture frequency, size and rock mass hydraulic properties, and how these parameters relate to the chemical variation in formation groundwater and matrix pore water.

the core length for study was selected at least approx. 5 m from the nearest hydraulically active large fracture. Since sampling had to be carried out during drilling, this was mostly, but not always successful. The location of the core sample selected for analysis is arbitrarily shown by the red spot in relation to the large sampled fractures, but correctly related to the matrix pore water salinity. In each figure an attempt is made to illustrate the diffusive transition in the rock matrix between the different salinities by a gradual phasing in or out in the blue colouration. This has only partly been successful and will be further improved upon. In addition, similar transitions are occurring between the formation groundwater in the hydraulically active fractures and the adjacent rock matrix when the fracture groundwater is more saline. Visually, these transitions also will be improved upon.

Depth location – 100–150 m

Figure A3-3a illustrates the upper approx. 100–150 m of bedrock characterised by medium to high fracture frequency; no samples were taken from < 100 m because this level represents the approximate depth of the percussion borehole which is cased prior to the core drilling. The fractures at this depth are considered mostly interconnected and dead-end fractures are thought to be uncommon. Bedrock transmissivity is high (full range $10^{-8.5}$ to $10^{-4.5}$ ms^2s^{-1} with much in the range of 10^{-7} to $10^{-4.5}$ ms^2s^{-1}) and the matrix salinity is less or equal to the fracture groundwater salinity. The residual, higher pore water salinity areas within the matrix ($> 1,500$ mg/L Cl), are assumed for illustrative purposes, to give a more realistic impression of older salinity concentrations which have not been removed by previous diffusion processes when the fracture groundwaters were more dilute than present. Transient conditions prevail and the diffusive gradients are presently active from the fracture groundwater to the surrounding matrix.

Depth location – 150–400 m

Figure A3-3b illustrates the approx. 150–400 m of bedrock characterised by medium to high fracture frequency (< 3 – 10 fractures/m). In common with the 100–150 m level, the fractures are interconnected and few dead-end fractures are envisaged. Furthermore the bedrock transmissivity is still high (range of 10^{-7} to 10^{-5} ms^2s^{-1} to 250 m and 10^{-9} to 10^{-7} ms^2s^{-1} from 250–400 m)

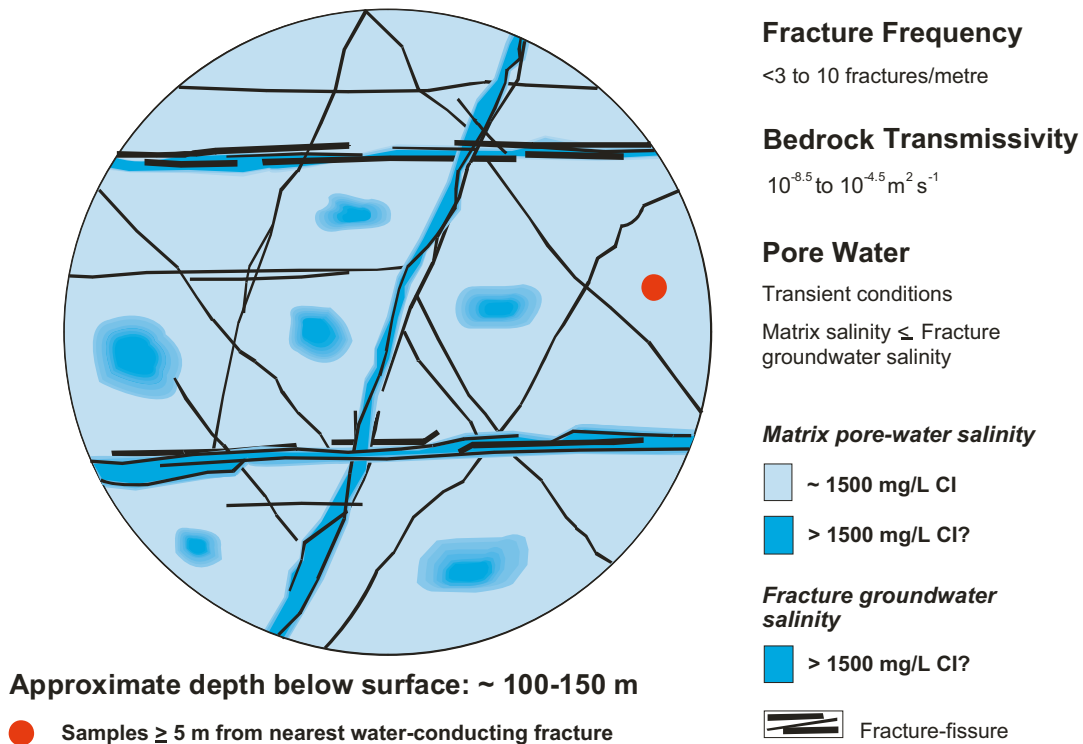


Figure A3-3a. Visualisation at level 100–150 m of borehole KFM06A.

and the matrix salinity is less or equal to the fracture groundwater salinity. Generally there is an increase in salinity both in the rock matrix and in the fracture groundwater with increasing depth. Transient conditions prevail and diffusive gradients are presently active from the fracture groundwater to the surrounding matrix.

Depth location – 400–700 m

Figure A3-3c illustrates the approx. 400–700 m of bedrock characterised by low fracture frequency (< 3 fractures/m). At this level because of the reduction in the fracture frequency there is less interconnection and therefore dead-end fractures are assumed to be more common. In addition, the overall bedrock transmissivity is very low (< 10^{-9} ms²s⁻¹). The matrix salinity is greater or equal to the fracture groundwater salinity and compared to the previous level there is a marked increase in salinity both in the rock matrix and in the fracture groundwater. Transient conditions prevail and the diffusive gradients are presently active from the fracture groundwater to the surrounding matrix.

Depth location – > 700 m

Figure A3-3d illustrates > 700 m of bedrock characterised by low fracture frequency (< 3 fractures/m), a low level of fracture interconnection and therefore dead-end fractures are likely to be more common.

The overall bedrock transmissivity continues to be very low (< 10^{-9} ms²s⁻¹) with only two fractured sections at around 750–770 m recording up to $10^{-6.5}$ ms²s⁻¹. The matrix salinity is approximately equal to the fracture groundwater salinity and compared to the previous level there is an increase in salinity both in the rock matrix and in the fracture groundwater. Close to steady state conditions prevail.

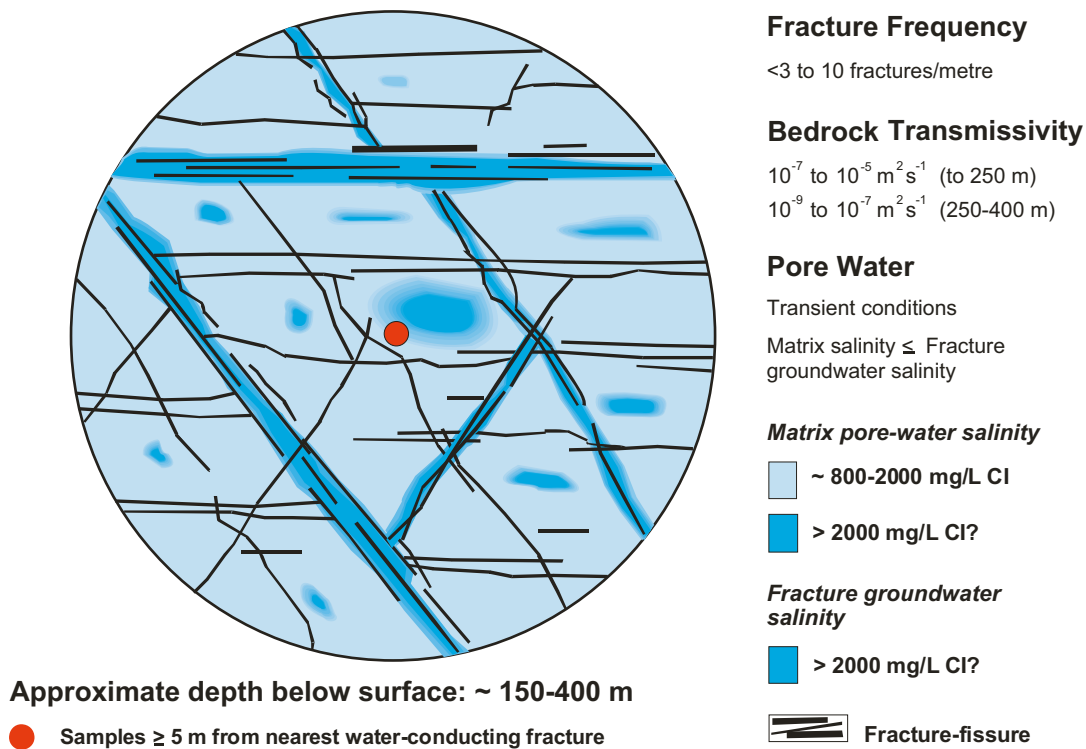


Figure A3-3b. Visualisation at level 150–400 m of borehole KFM06A.

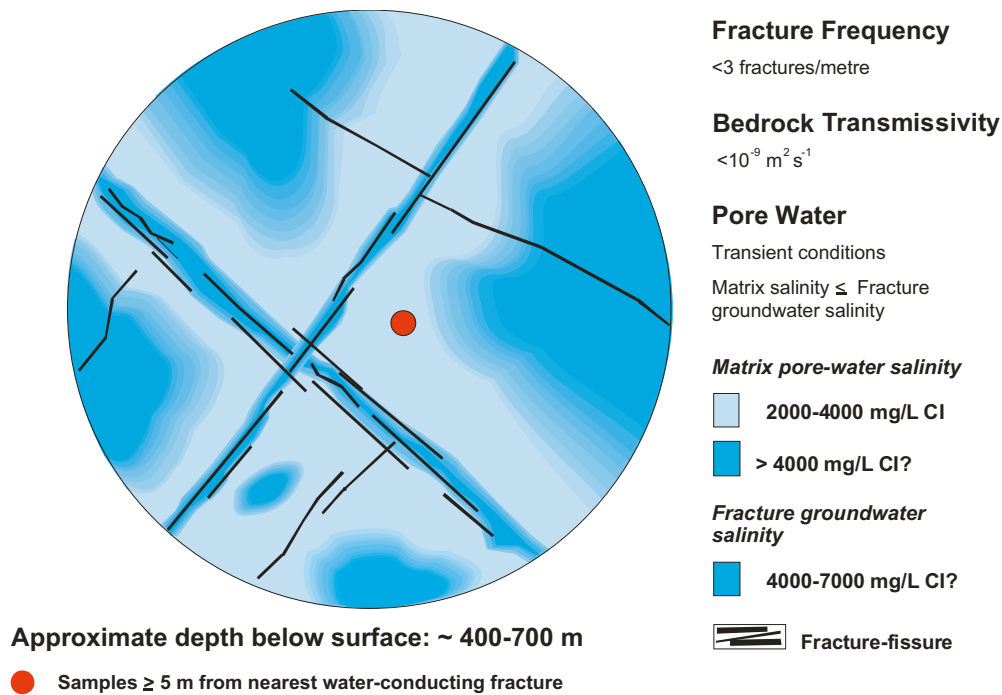


Figure A3-3c. Visualisation at level 350–700 m in borehole KFM06A.

In conclusion, pore water compositions differ from those of fracture groundwaters depending on the distance between the location of the pore water sample in the rock matrix and the nearest water-conducting fracture, and the time period of constant composition of the fracture groundwater. Combined with measured hydraulic properties of the bedrock, these compositional differences support diffusion-dominated solute transport in the low-permeable rock masses. From the present investigations it can be concluded that in such a rock mass as present in Forsmark (and Laxemar) the diffusion-accessible porosity extends over significant distances (at least metres to tens of metres) /Waber and Smellie 2006/.

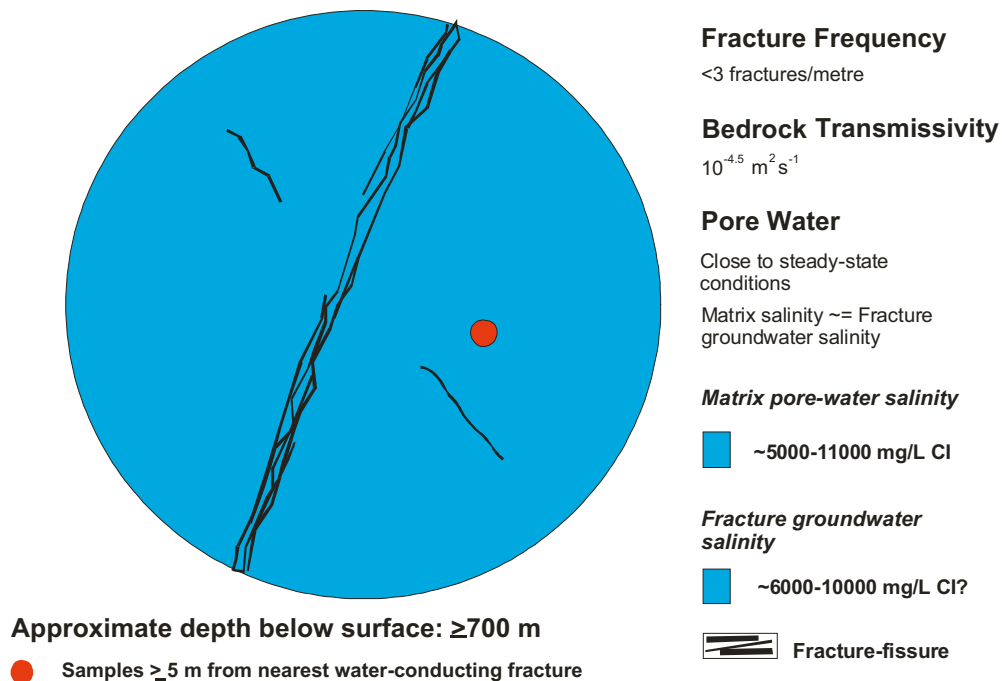


Figure A3-3d. Visualisation at level > 700 m in borehole KFM06A.

A4 Fracture mineralogy (Issues #1 and #17)

As with other aspects of the Forsmark site characterisation studies, each data freeze represents additional sampling and analytical data of mineral phases selected from open and closed fractures and the near-vicinity rock matrix. P-Reports are produced following each data freeze stage representing an updated interpretation based on all preceding P-Reports and the most recent information. On-going studies of the fracture mineralogy in Forsmark have revealed four different generations of fracture mineralisations /Sandström and Tullborg 2005/. Table A4-1 summarises the four main sequences of mineral paragenesis and their relationship to major structural features.

These mineral generations in Table A4-1 are separated in time, and age constraints are given by radiometric dating reported in the Forsmark 2.2 data freeze. Based on formation temperatures of the minerals and the known geological evolution of the area /SKB 2005b/, Generations 1 and 2 are Precambrian, Generation 3 probably Palaeozoic and Generation 4 was formed from Late Palaeozoic to recent. The geochemistry and mineralogy of the fracture minerals, altered wall rock and reference matrix rock are compiled in /Drake et al. 2006/. A comprehensive reporting on the fracture mineralogy integrating all data freeze stages is planned during the Forsmark 2.2/2.3 modelling stages.

Table A4-1. Relative sequence of fracture mineralisations in the Forsmark region.

1.	Epidote – quartz – chlorite (found mainly in NW-trending fractures and some gently-dipping structures) > 1,600 Ma, > 350°C.
2.	Adularia – prehnite – laumontite – calcite – haematite (found mainly associated in NE-trending, steeply-dipping structures) > 700 Ma, > 150°C.
<i>Dissolution by circulation of hydrothermal fluids (< 200°C). Sequence of precipitation with decreasing temperature (probably Palaeozoic at 570–245 Ma) found in mainly reactivated and gently-dipping structures.</i>	
3.	a. Euhedral quartz – albite b. Corrensite – calcite – pyrite – adularia – analcime (< 100°C). c. Asphaltite – galena – chalcocopyrite – sphalerite.
4.	Clay minerals – calcite (possibly Quaternary at ambient temperatures)

A5 Redox front evolution (Issue #5)

An integral part of the fracture mineralogy studies is to evaluate any evidence of oxidation/reduction processes which may demarcate the penetrative level of redox front propagation in the bedrock. In the Forsmark area redox changes in recharging waters from oxidising to reducing occur to the largest extent in the overburden. Consequently the majority of all groundwater samples from the percussion boreholes and all groundwater samples from the cored boreholes are reducing. Increasing reducing conditions with depth are reflected generally in the fracture mineralogy by a decrease in Fe-oxyhydroxide phases and an increase in pyrite. In addition, the presence of Fe-oxyhydroxides tend to correlate with a general absence of calcite (due to active dissolution from oxidising bedrock recharge), and precipitation of calcite (due to supersaturation with increasing depth) generally correlates with more reducing conditions and therefore with the presence of pyrite.

Of importance for understanding the present-day evolution of the groundwater chemistry and, potentially, modelling of future redox conditions, is to identify any evidence of possible former redox fronts in the bedrock. During periods when the overburden has been much less developed or possibly even absent, the fracture minerals have acted as reducing media in direct contact with the oxygenated water. Furthermore, during glacial activity, in particular the incursion of dilute, aggressive oxygenated ice melt water to great depths, may also have left its signature with the fracture filling minerals. Therefore interpretations based on changes in fracture mineralogy versus depth (e.g. Fe-oxyhydroxides, pyrite and calcite) can help to detect traces of oxidation and, together with the frequency of other Fe(II) containing minerals, confirm the available reducing capacity along the downward penetrating groundwater flow paths.

Present interpretation of the Forsmark area is reported in /Drake et al. 2006/. Only four drill cores covering the upper 100 metres of the bedrock are available so far (KFM01B, KFM03B, KFM06B and KFM08B). Compilation of the fracture mineralogy from the 'boremap' log showed that goethite is present in the fractures down to 60 m with some scattered observations deeper down. Pyrite, however, is present in open fractures from 5 metres depth downwards and in the crush zones goethite has been mapped down to 500 metres. The distribution of the goethite and pyrite reflects the flow situation at Forsmark characterised by large variations in transmissivities in large transmissive zones compared to the very tight host rocks between. The interpretation of the fracture mineralogy from the subsequently drilled boreholes will be included in the planned background report for the fracture mineralogy

A6 Interaction of surface and deep groundwater systems (Issue #3)

A6.1 General

The area of interaction of surface/deep groundwater or overburden/geosphere studies has not been well defined in model versions 1.2 and 2.1. The demarcation between ChemNet, SurfaceNet (Surface Chemistry Group) and RetNet (Radionuclide Retention Group) has not been clear due to the overlap of interests. For example, ChemNet needs to know the recharge groundwater chemistry entering the bedrock from the overburden via the surface environment (i.e. the surface end member used in modelling), and also if there is any evidence of a discharge chemical or isotopic signature from the bedrock to the overburden and eventually to the surface environment. This latter information is required also by SurfaceNet and RetNet in order to characterise the surface environment and locate potential areas of radionuclide uptake and retardation, respectively.

At Forsmark the overburden/bedrock studies are complicated by the hydrogeological conditions. The upper 100 m of bedrock is dominated by one or more shallow, horizontal, highly transmissive zones which effectively channel any recharge water towards the NE of the site close to the Baltic Sea /Follin et al. 2005/. In addition, any discharging groundwater from depth is also flushed away along the same zone, or at least mixed with fresh recharge groundwaters. This hydrological 'cage-effect' means that the chances of detecting surface discharge groundwater locations related to specific underlying bedrock fractures is small, and likewise locating active surface recharge locations directly feeding underlying fractures in bedrock is also small.

A6.2 Future strategy

Before Forsmark model version 2.2 gets under way a series of meetings to better integrate the interests of the three groups are planned. The aim is to demarcate clearly the areas of approach for each group. Detailed descriptions of the surface water chemistry are available /SKB 2005b/ based on a statistical Principal Component Analysis approach, but no attempt has been made to explain the distributions or the main chemical processes which have given rise to such anomalies. Furthermore, little use has been made in modelling the surface water chemistry and less so in model integration with the deeper bedrock system.

For further understanding and integration between the surface and geosphere hydrochemical systems, the main questions to be answered are:

1. What are the chemical and isotopic signatures of deep bedrock groundwaters?
2. What are the characteristic signatures of recharge and discharge groundwaters?
3. What are the redox conditions and the chemical processes that can influence such conditions in the surface water environment?

To help address these questions the following important points have been identified:

- Identification and seasonal variability of chemical and isotopic parameters to describe the surface environment.
- Parameters to include: Temperature, groundwater level, Eh, O₂, DOC, Cl, HCO₃, SO₄, Fe, Mn, U, La, δ¹⁸O, δ²H, ¹³C, ¹⁴C, ³⁴S, and ^{87/86}Str.
- Model integration (hydrochemical; hydrogeological) between the surface and geosphere environments.

A7 Uranium, thorium, radium and radon (Issue #11)

Uranium, radium and radon contents have been analysed in surface waters (lakes and streams), in near-surface groundwaters from soil pipes and in groundwaters from the percussion and cored boreholes.

A7.1 Uranium and thorium

The surface and near-surface waters are characterised by values between 0.05 and 37 µg/L U. Large variations in uranium content in surface waters are common and are usually ascribed to various redox states (i.e. oxidation will facilitate mobilisation of uranium) and various contents of complexing agents, normally bicarbonate which will help maintain the mobility of the uranium. Plotting uranium versus bicarbonate (Figure A7-1) for deep groundwaters (from cored boreholes) and near-surface groundwaters (from soil pipes) shows no clear trends, although taking only the near-surface groundwaters into account there is a tendency of higher uranium contents associated with increasing bicarbonate up to 400 mg/L. At higher bicarbonate contents, however, the uranium tends to decrease, which may be due to very low redox potential in these waters caused by the microbial reactions producing the bicarbonate. For the deep, cored borehole groundwaters it can be concluded that the samples showing uranium contents greater than 5 µg/L also show greater than 50 mg/L HCO₃. The samples from one section in KFM03A:639–646 m show, however, lower HCO₃ (22–25 mg/L) but still very high uranium contents (46 to 58 µg/L). Groundwaters from this borehole section indicate a mixed marine and deep saline groundwater origin. The deep saline groundwaters with extremely low HCO₃ contents (< 10 mg/L) are, however, low in uranium.

In Figure A7-2 it is shown that groundwater samples between approx. 200 and 650 m depth are all enhanced in uranium (values > 5 µg/L) with the exception of two samples close to 400 m depth showing values of 2.2 and 3.5 µg/L respectively.

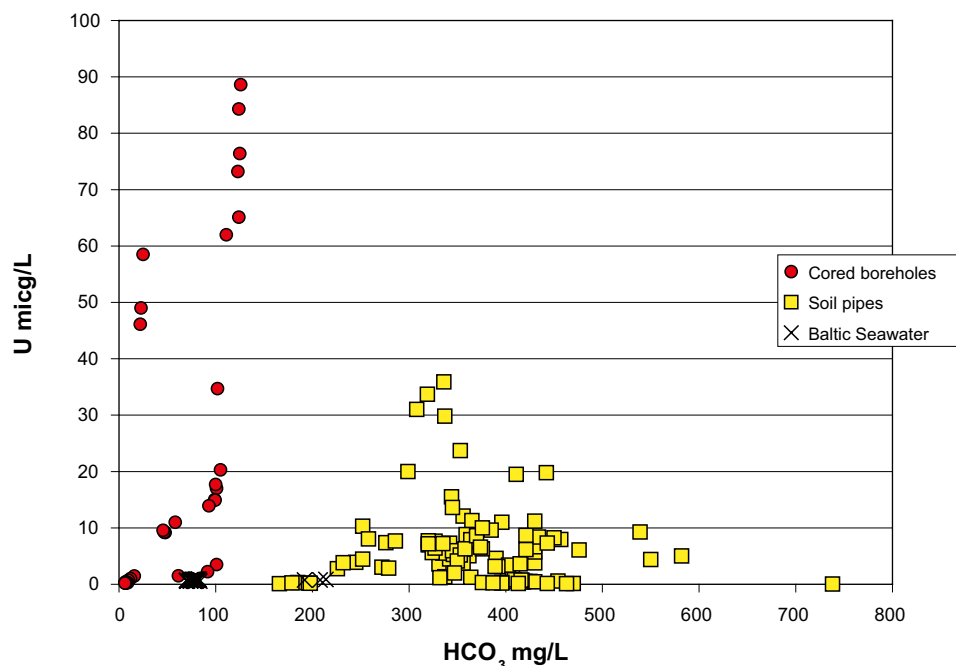


Figure A7-1. Uranium versus HCO₃ in surface and groundwaters from the Forsmark area.

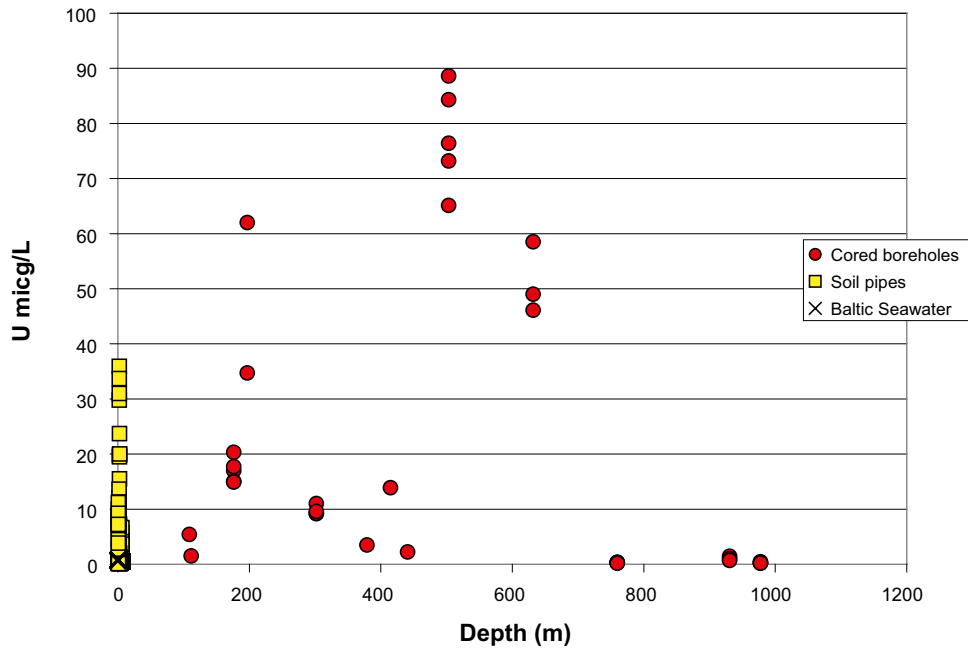


Figure A7-2. Uranium versus depth in surface waters and near-surface and deep groundwaters from the Forsmark area.

Uranium versus chloride (Figure A7-3) shows that in the deeper cored borehole groundwaters the highest uranium contents are associated with chloride values around 5,000–5,500 mg/L, i.e. the brackish groundwaters dominated by a Littorina Seawater component. However, additional data that will be included in the next model version (2.2) indicate a more complicated pattern and it is obviously too early to draw leading conclusions concerning high uranium contents being restricted solely to Littorina Sea-type groundwaters.

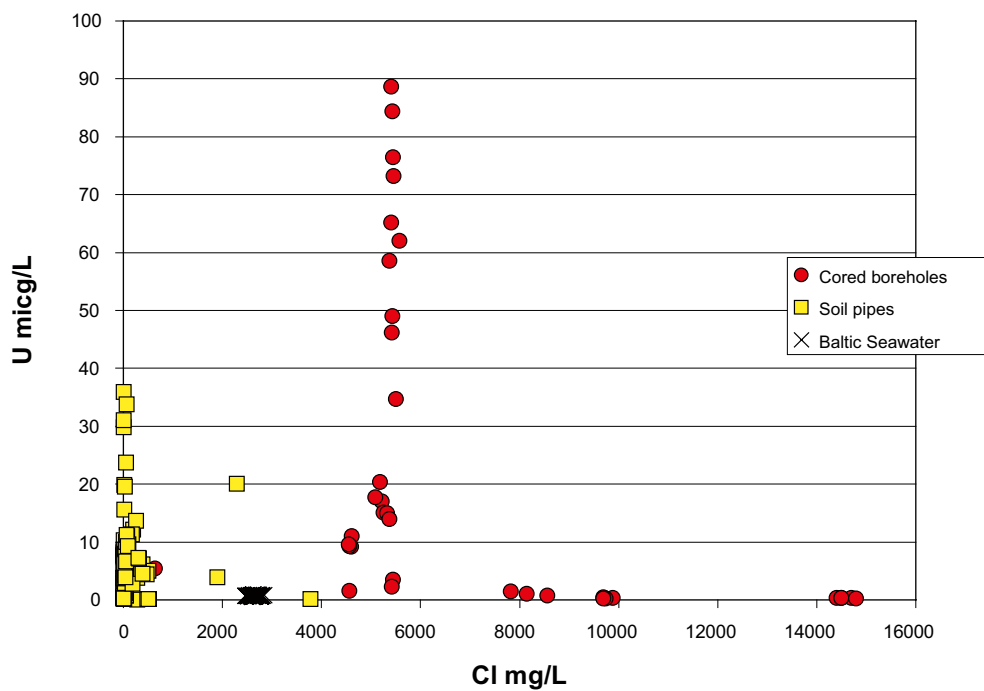


Figure A7-3. Uranium versus Cl in surface waters and near-surface and deep groundwaters from the Forsmark area.

As reported in earlier model versions, results of natural uranium decay series measurements carried out on groundwaters during the initial phase of the site investigations showed questionable results. To resolve this issue an inter-laboratory study of reference samples has been performed and presently available data show $^{234}\text{U}/^{238}\text{U}$ activity ratios between 2–4 in deep groundwaters (i.e. common values for groundwaters) whereas the near-surface groundwaters show values between 1–2, considered typical for oxidising conditions and fast groundwater circulation (cf. Gascoyne, Appendix F; this report).

One of the key questions regarding the high uranium contents in the groundwater samples has been whether or not these are produced by ongoing oxidation. Oxidation state determinations of the dissolved uranium show that it is mainly in the form of U(VI) (J. Suksi, written comm., 2007; data to be fully reported in Forsmark Model version 2.2.).

Figure A7-4 shows Mn^{2+} and Fe^{2+} contents versus uranium in groundwaters from cored boreholes at Forsmark. This plot indicates that higher uranium contents appear to relate to higher Mn and Fe contents; the three anomalous samples (with low Mn and Fe) are due to the mixing of different water types in the borehole section. Furthermore, measured redox potentials suggest reducing groundwater conditions. Despite these negative Eh values, however, Gimeno et al. (Appendix C; this report) points out that the high uranium values in the groundwaters are restricted to samples showing mildly reducing conditions (Eh between –140 to –200 mV) whereas the more reducing groundwaters are low in uranium. They also conclude that these mildly reducing conditions allow for uranium-carbonate complexation.

Figure A7-5 shows a clear relationship between enhanced Fe and Mn (> 0.5 mg/L) and typical brackish groundwaters, most of Littorina-type..

In summary, high and variable uranium contents are found in mildly reducing groundwaters with chloride contents up to 6,000 mg/L. Most of the groundwaters with high uranium are Littorina Seawater in type with a glacial meltwater component, but the uranium contents are not restricted to this water type solely. The high uranium is found down to depths of 650 m. It is however indicated by Gimeno et al. (Appendix C; this report) that the limiting factors are Eh and suitable conditions for carbonate complexation, whereas the association with chloride content and depth may be a secondary effect.

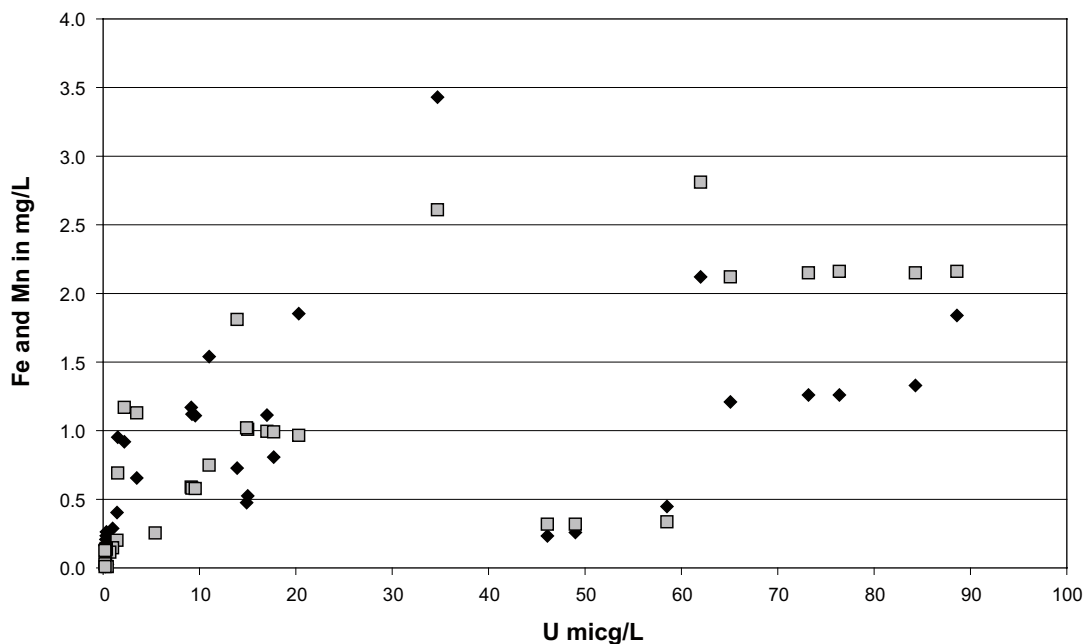


Figure A7-4. Uranium versus Mn (squares) and Fe (diamonds) in groundwaters from cored boreholes.

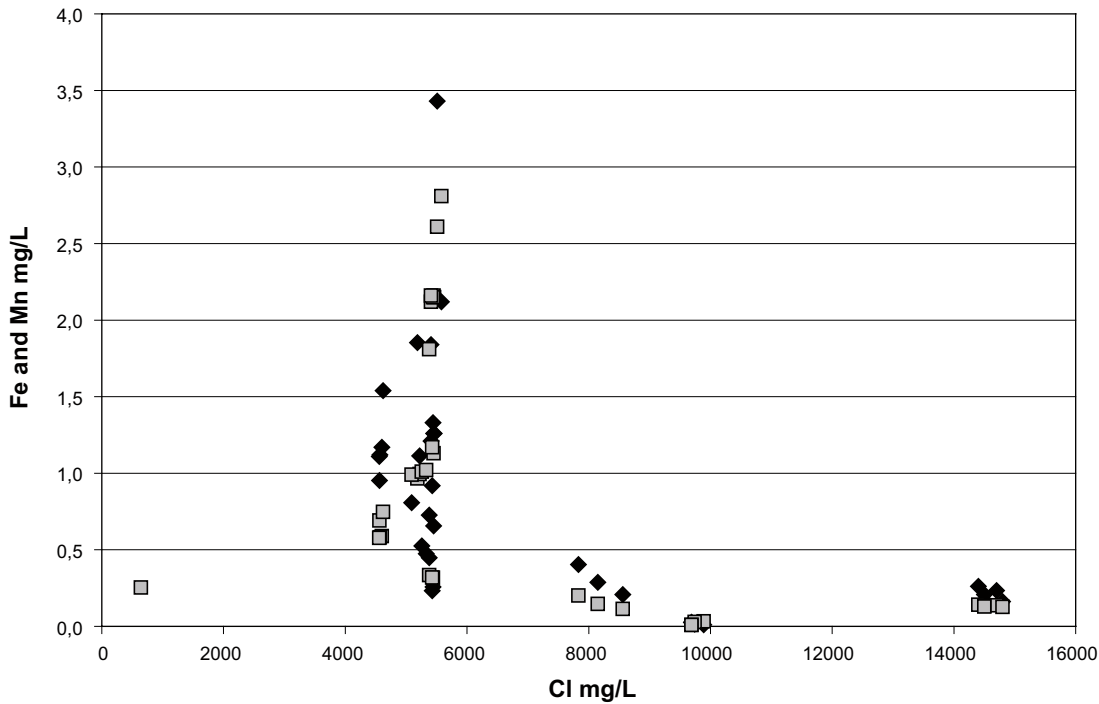


Figure A7-5. Chlorine versus Mn (squares) and Fe (diamonds) in groundwaters from cored boreholes.

A number of processes may contribute to providing suitable conditions for maintaining uranium mobility in solution. Different possibilities have been forwarded by the ChemNet members, for example the relation of high uranium contents to drilling fluid contamination (Buckau, Appendix G; this report), and microbial activity (Hallbeck, Appendix B; this report).

Figure A7-6 shows the percentage of drilling fluid versus uranium content. It is evident that for some boreholes there is a positive correlation between drilling fluid and uranium content. There is, however, no support for the possibility that the uranium content is introduced by the drilling fluid itself. One possibility is that the drilling fluid is slightly oxidising (although this not supported by in situ monitoring measurements) or contains larger amounts of complexing agents.

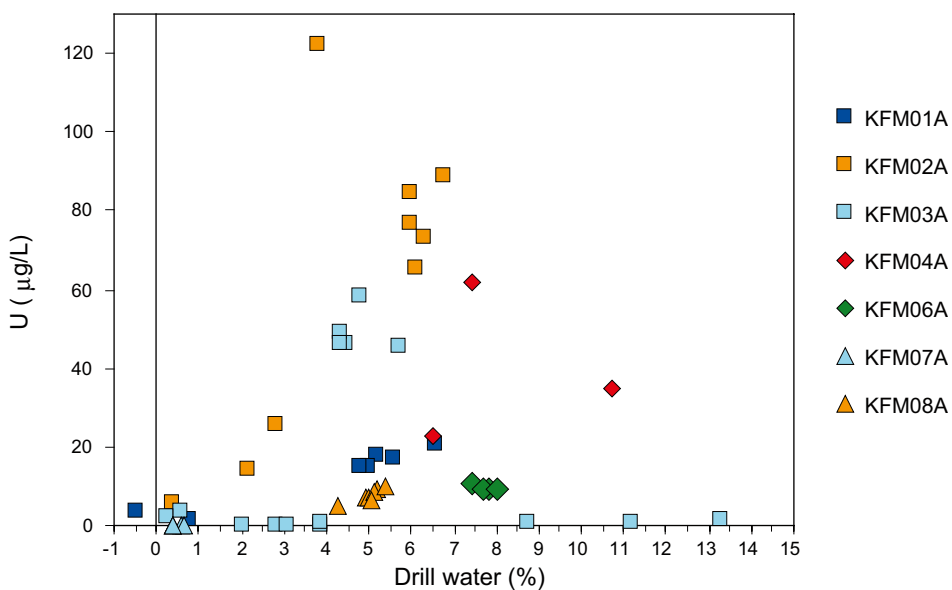


Figure A7-6. Percentage of drilling fluid versus U content in groundwaters from cored boreholes at Forsmark.

A second possibility is that the drilling fluid activates microbial activity which in turn will affect the minerals, such that uranium is mobilised together with Fe and probably Mn (cf. Hallbeck, Appendix B; this report). This is supported by the higher Mn and Fe contents present in these groundwaters (cf. Figure A7-4).

From all indications mentioned above, it is reasonable to assume that the source of uranium in the groundwater originates from one or several different solid phases present in the hydraulically-active fracture system being sampled.

From fracture mineral analyses of drillcore material from Forsmark it is obvious that uranium is usually enriched in the fracture coatings compared with the host rock. Figure A7-7 shows uranium versus thorium for fracture coating samples /Sandström and Tullborg in press/. The U /Th ratio in the rock is around 0.3 to 0.4 whereas in the fracture coating material the ratio exceeds 1 in the majority of samples. It is also evident that the uranium contents in the fracture coatings are highly variable, ranging from less than 1 to 2,300 ppm.

Uranium mineralisations are found in relation to many of the iron ores known in the northern Uppland area /Figure A7-8; Welin 1964/. Three types of mineralisation are known: 1) The oldest (ca. 1,785 Ma) is related to the Late Svecofennian epoch consisting of disseminated uraninite precipitated from oxidation-reduction reactions in the iron-bearing skarn ores. 2) The second type of mineralisation (ca. 1,585 Ma) occurs in the fissured bedrock resulting in the formation of pitchblende, haematite and some sulphides related to mineralised fractures or veins of chlorite, calcite and quartz. 3) A younger, less well-constrained period of uranium mineralisation was distinguished consisting of pitchblende precipitation in a chemically reactive 'ferriferous rock' /Welin 1964/. Based on this information it is not unexpected that fracture coatings with a large variation in uranium content occurs in the fractures at Forsmark, and therefore it is not surprising that pitchblende has been identified in one fracture coating sample from KFM03A /Sandström and Tullborg 2005/.

Finally, there seems to be an association between the uranium content in fracture coatings and uranium dissolved in groundwater collected from the same borehole/drillcore section (Figure A7-9). In addition, natural uranium decay series measurements on fracture coating samples also support a redistribution of uranium in hydraulically-active fractures during the latest 1 Ma (results to be compiled and reported in Forsmark Model Version 2.2)

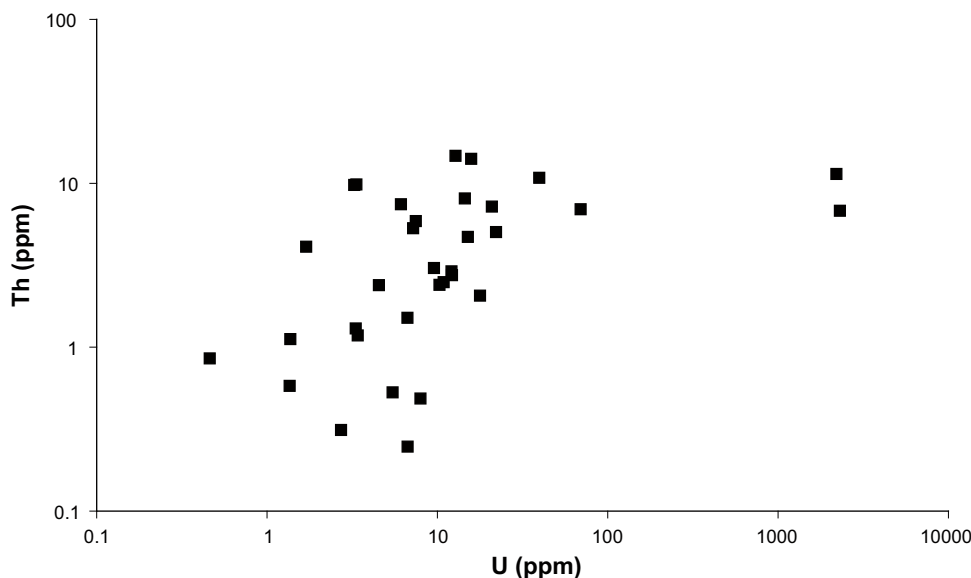


Figure A7-7. U versus Th determined in fracture coatings from Forsmark drillcore samples /Sandström and Tullborg in press/.

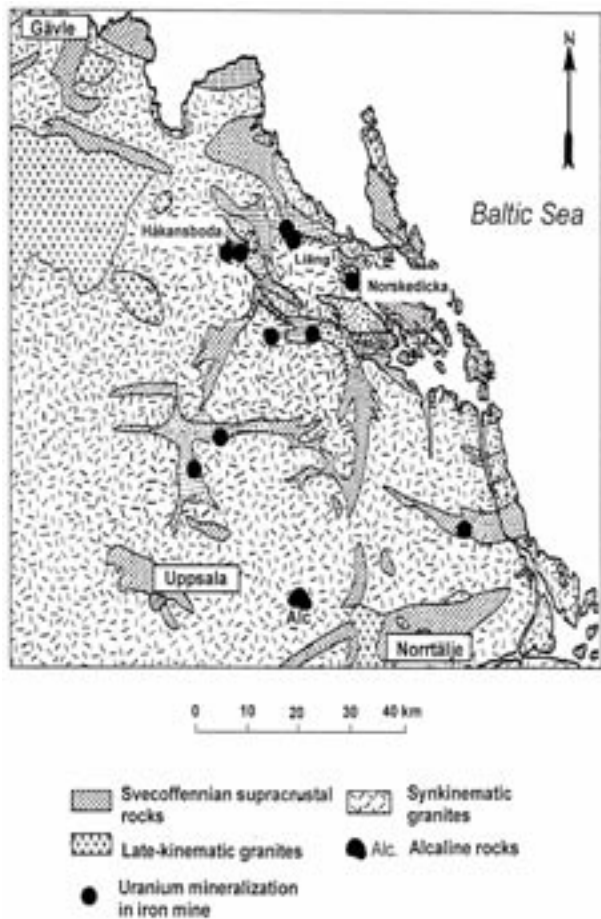


Figure A7-8. Localised uranium mineralisations in northern Uppland, near Forsmark /Welin 1964/.

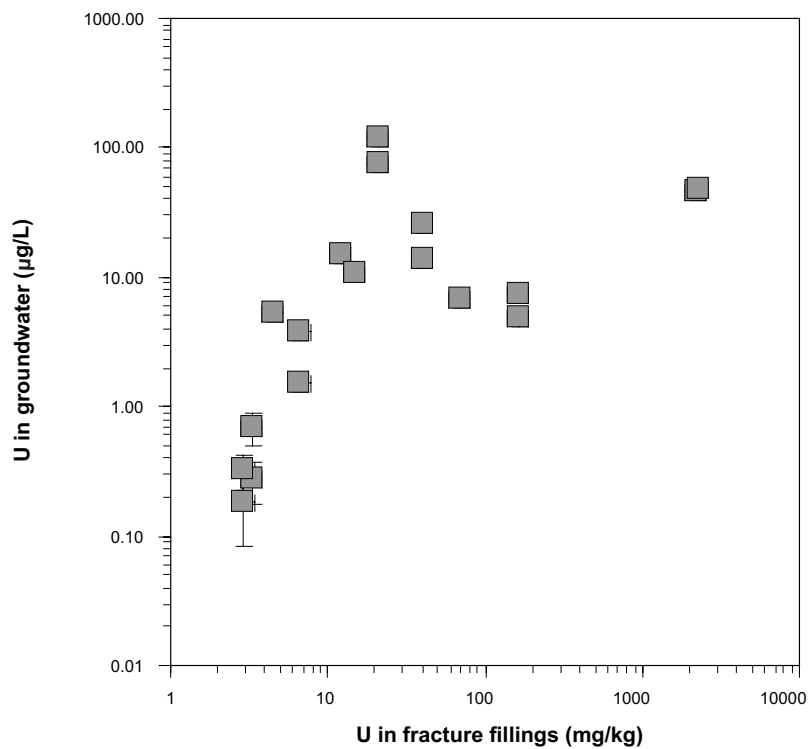


Figure A7-9. Uranium in fracture fillings versus uranium in groundwater samples collected from the same borehole/drillcore section.

A7.2 Radium

Radium (^{226}Ra) has been measured in groundwaters from 13 soil pipes and 11 sections in cored boreholes; Figure A7-10 shows the relationship of radium with chloride. Radium is most mobile in chloride-rich, reducing groundwaters with high TDS contents. Consequently higher radium values are to be expected in the deeper, more saline groundwaters (Figure A5-10) where it largely behaves like, for example, strontium and barium. One sample, KFM03A:638–644 m, deviates significantly from this trend. Although the reason for this is presently not known, it is noticeable that the sampled interval corresponds to the location where the U-rich fracture coating has been observed.

A7.3 Radon

Radon (^{222}Rn) has been measured in the same groundwaters as analysed for ^{226}Ra (Figure A7-11). The groundwater showing the highest ^{226}Ra and ^{222}Rn values is KFM03A: 639–646 m which also contains a high uranium content, both in groundwater (46 $\mu\text{g/L}$) and the fracture coating (2,200–2,300 ppm). Also, groundwaters from the zone ZFMA2 intersection in borehole KFM02A at 509–516 m show very high uranium values (65 and 88 $\mu\text{g/L}$). The increase in ^{226}Ra and ^{222}Rn (Figure A7-11) is however less pronounced (compared with KFM03A:639–646 m) and fracture samples from this section show also relatively low uranium values (below 50 ppm).

A7.4 Summary

The origin of the primary uranium in the Forsmark area is probably the result of oxidation and remobilisation of uranium from mineralisations found at several localities in Uppland, for example pitchblende vein fillings in skarn rocks that have been documented some kilometres from the site /Welin 1964/. Furthermore, pitchblende has been detected in fracture zones from the Forsmark site. The mobilisation/redistribution of the uranium has probably taken place on several different occasions during the geological history of the region, at least the last 300,000 years as indicated from natural uranium decay series analyses /Sandström and Tullborg 2006 P-Report in press/.

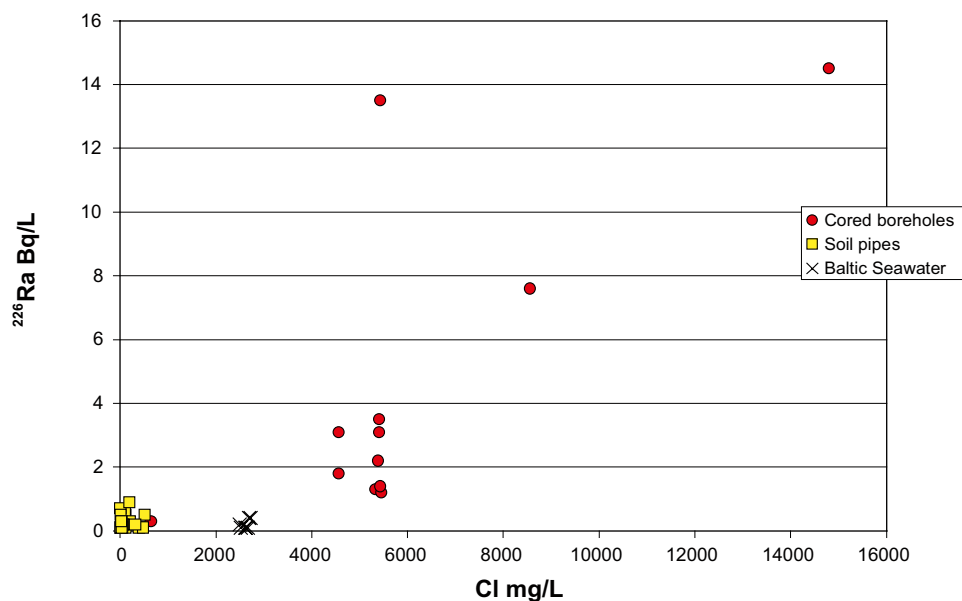


Figure A7-10. ^{226}Ra (Bq/L) versus Cl in shallow and deep groundwaters, and Baltic seawater, from the Forsmark area.

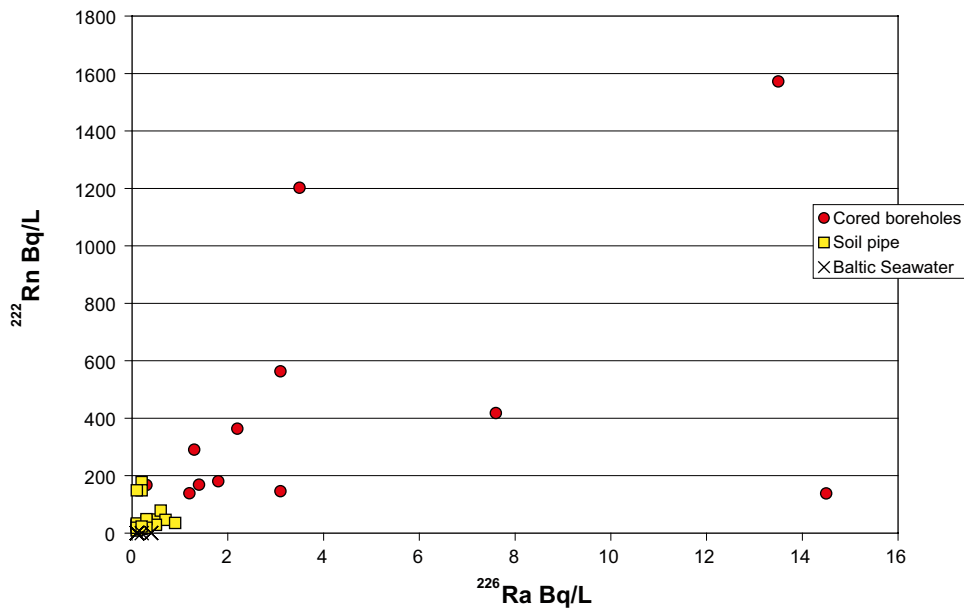


Figure A7-11. ^{222}Rn versus ^{226}Ra in near-surface and deep groundwaters from the Forsmark area.

The reason for the high uranium contents in the groundwaters at Forsmark seems to be a combination of available uranium, probably at least partly, from an amorphous U-phase present in parts of the fracture system as mentioned above, and also groundwater conditions that both mobilise uranium from this amorphous phase and keep it mobile in solution. Speciation calculations (Gimeno et al. Appendix C; this report) show how uranium can remain mobile due to the relatively mildly reducing conditions and presence of sufficient HCO_3^- to allow uranium-carbonate complexation. Microbial activity may have an important influence on uranium mobilisation (Hallbeck Appendix B; this report); Fe-reducing bacteria may produce strong ligands for complexation and it has even been suggested that uranium may be microbially oxidised during anaerobic conditions /Andersson and Lovely 2002/. It is also possible that microbial activity has increased due to mixing of groundwaters of different origins (e.g. related to the drilling fluid content).

A8 Summary and conclusions

Based on the Forsmark Site Descriptive Model (SDM) version 1.2, specific F. 2.1 issues have been identified and discussed with the objective to provide a more focussed approach to the final Forsmark SDM versions 2.2/2.3. Major issues have been addressed under the following headings: a) Groundwater origin and evolution, b) Conceptual modelling in 2D and 3D, c) Interaction of surface/deep groundwater systems, d) Uranium, thorium, radium and radon, and e) Redox front considerations. These are summarised below underlining their importance and where additional data are needed to fulfill SDM version 2.2/2.3 requirements.

Groundwater origin and evolution

- The potential relationship of hydrochemical evolution to major structural domains.
- Future interpretation of hydrochemical data should take the structural domains into consideration, and this should be clearly referred to in all chemical plots and modelling exercises.
- Interpretation will be further quantified by additional data, in particular strategic groundwater samples will be selected for ³⁶Cl dating analysis.
- Pore water data and their interpretation should further add to the overall palaeo-understanding of the site.

Conceptual modelling in 2D and 3D

- Continued up-dating of the 2D integrated conceptual models of the site.
- More effort to combine numerical hydrochemical and hydraulic models to construct an overall 3D conceptual model of the site.
- Ultimate objective is to provide cutting planes based on the 3D models to best illustrate specific aspects of the present hydrogeochemical system (e.g. repository conditions).

Interaction of surface/deep groundwater systems

- Understanding of the biosphere/geosphere interface hydrogeochemical systems.
- Requires close interaction between ChemNet and SurfaceNet.
- Objective to identify surface/near-surface recharge/discharge systems.
- Objective to identify the main input water end member to the bedrock environment.
- Objective to assess the importance of microbial reactions.

Uranium, thorium, radium and radon

- This is an underdeveloped area of understanding.
- Requirements include more analytical data for uranium, thorium, radium and radon.
- Interpretation of data (in particular radium and radon) require a good understanding of available transport pathways, i.e. structural networks.

Redox front considerations

- Understanding the evolution and depth penetration of redox fronts are important to evaluate the buffer capacity of the bedrock to the penetration of oxidising groundwaters.
- This requires detailed mineralogical and geochemical data from fracture zones and the adjacent rock matrix, coupled with in situ hydrochemical data.
- Requirements essentially underline the need for a large number of strategically related samples along groundwater pathways and good samples from fracture samples from the upper 100 metres in order to trace a potential redox front.

Appendix B

Chemnet's issue report – Forsmark area version 2.1

Lotta Hallbeck, Vita vegrandis

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B1 Introduction

This report is written as an issue report in which several items of special interests have been the main aim of the work. The work includes the issues concerning microbiology, colloids and gases. The report is divided into three main parts:

1. Issues where microbes are involved
 - #5 Redox front considerations
 - #8 Microbes
 - #9 High magnesium and uranium values
 - #10 Redox conditions
2. Gases
 - #8 Gases
3. Colloids
 - #8 Colloids

The data used in the report are from data freeze Forsmark 2.1 and the table created by Maria Gimeno, University of Zaragoza. Data for colloids are prepared in separate tables and deposited at the Project Place.

B2 Issues concerning #8 Microbes including #10 redox conditions, #5 redox front considerations, and #9 and #11 high manganese and uranium values

The metabolisms of microorganisms are oxidation-reduction reactions. In heterotrophic respiration oxidation of an energy and electron rich carbon compound with reduction of an oxidized electron accepting compound will supply the organisms with carbon and energy for growth and/or maintenance. In autotrophic metabolisms energy rich compounds are oxidized with reduction of carbon dioxide to organic material. The different metabolisms have their special redox couples. The redox of any system is a measure of its tendency to donate or accept electrons. A series of redox couples control the redox in aquatic systems, following a “ladder” from those very prone to accept electrons to those very prone to donate electrons. Although the list of couples can be made very long /cf. Stumm and Morgan 1996/, some redox couples are more predominant in crystalline bedrock groundwater than others. Redox couples commonly observed in groundwater from the water table and downwards to depths reaching 1,000 m or more are $\text{H}_2\text{O}/\text{O}_2$, $\text{Mn}^{2+}/\text{Mn}^{4+}$, $\text{Fe}^{2+}/\text{Fe}^{3+}$, $\text{S}^{2-}/\text{SO}_4^{2-}$, CH_4/CO_2 , $\text{CH}_3\text{COOH}/\text{CO}_2$ and H_2/H^+ . Those fit perfectly on the redox ladder typically depicted for microbiological metabolisms (Figure B2-1.).

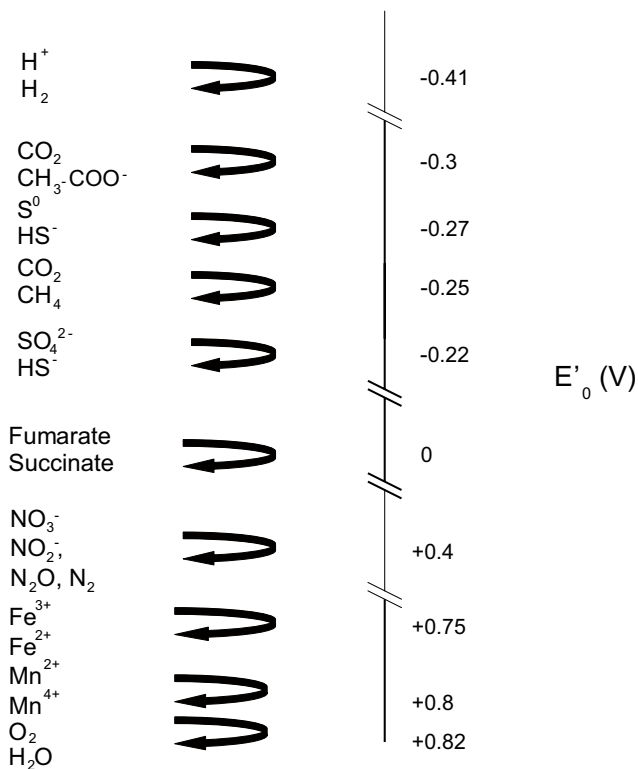


Figure B2-1. Redox couples that are found in deep groundwater and which various groups of microorganisms involve in their metabolism.

B2.1 Carbon and energy sources – the electron donors

Figure B2-2 shows a conceptual model of the microbiology in the subsurface system, E_h values with depth. It can be seen that the sources of energy and electron donors to microorganisms in deep groundwater are basically of two different kinds, organic and inorganic. From the ground surface, organic material will follow with recharging groundwater. This organic material is in many different stages of degradation, from particles to dissolved short organic acids. From deep sources underground, hydrogen and methane seep up /Sherwood Lollar et al. 1993a/. Some of this methane is produced by microorganisms /Sherwood Lollar et al. 1993b/. Microorganisms will consume and oxidise both of these sources of energy, but anaerobic methane oxidation remains to be demonstrated in deep groundwater. The utilisation of hydrogen from underground by autotrophic acetogens will generate acetate. Acetate is an excellent carbon and energy source for many microorganisms. The availability of electron acceptors in large will determine which microbial group that will dominate the system.

B2.2 Electron acceptors in the subsurface system

The major available electron acceptors in deep groundwater are solid phases of ferric iron and manganese (IV), and dissolved sulphate and carbon dioxide (Figure B2-2). Groundwater with a marine signature has plenty of dissolved sulphate. Close to the surface, when oxygen has been depleted, nitrate- iron- and manganese-reducing microorganisms will be dominant. With increasing depths, more and more reduced electron acceptors, such as ferrous iron, manganese(II) and sulphide will accumulate and force the redox toward more negative values.

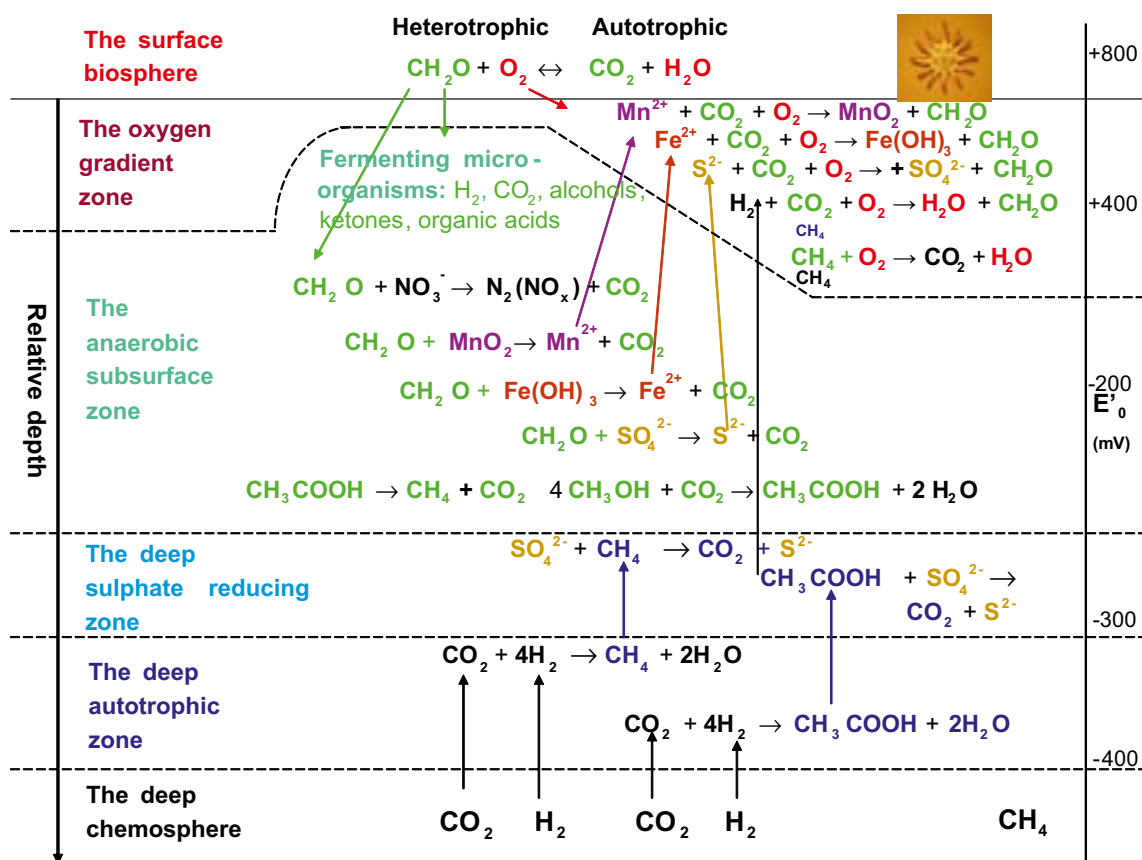


Figure B2-2. Conceptual model for microbial processes in Fennoscandian Shield groundwater. The reactions should be considered as descriptive and are not balanced.

B2.3 #10 Microbes and redox in Forsmark

The microbiological investigation in Forsmark includes determination of the most probable number (MPN) of iron- (IRB), manganese- (MRB) and sulphate-reducing bacteria (SRB) together with auto- and heterotrophic acetogens (AA and HA) and auto- and heterotrophic methanogens (AM and HM). MPN is a statistical cultivation method for numbering the most probable number of different cultivable metabolic groups of microorganisms (Am. Publ. Health Ass.,1992).

Figure B2-3a shows the measured oxidation-reduction potential (redox) and the numbers of the different cultivable microbial groups versus depth in Forsmark. At 112 m depth, the microbial community was dominated by iron-and manganese reducing bacteria and the measured redox value was -175 mV. At 930 m depth, sulphate-reducing bacteria together with acetogens dominated and the measured redox value was -250 mV. The redox electrodes used in the site investigation only measure redox couples that are sensitive to redox pairs that show electro-active behaviour. Of the microbially catalyzed redox reactions in granitic groundwater the electrodes are sensitive to IRB, MRB and SRB reactions.

The redox in the groundwater in Forsmark was in general relatively high for such deep groundwater compared to for example the Simpevarp site (Figure B2-3). The high redox in Forsmark might be due to the special salinity situation at the site. Figure B2-3b shows the variation of chloride against depth in Forsmark. There is a lens of groundwater with a chloride content of about $5,000 \text{ mg L}^{-1}$ from 150 m depth down to almost 700 m. The microbial abundance in this lens was low and these depths correspond to groundwater with the highest redox values (Figure B2-3a). The explanation can be that there is no or very low transport of photosynthetically produced organic carbon from the surface or chemotrophically produced acetate from the deeper regions because there was no density driven flow. The microbial activity was, therefore, low and the redox would not decrease. Simpevarp, on the other hand, had a completely different situation with a steep chloride gradient at the inland site, Laxemar subarea, and another gradient in the Simpevarp subarea which is more coastal. These gradients would allow transport of organic carbon both from surface and from depth and by that a high microbial activity which would give low redox.

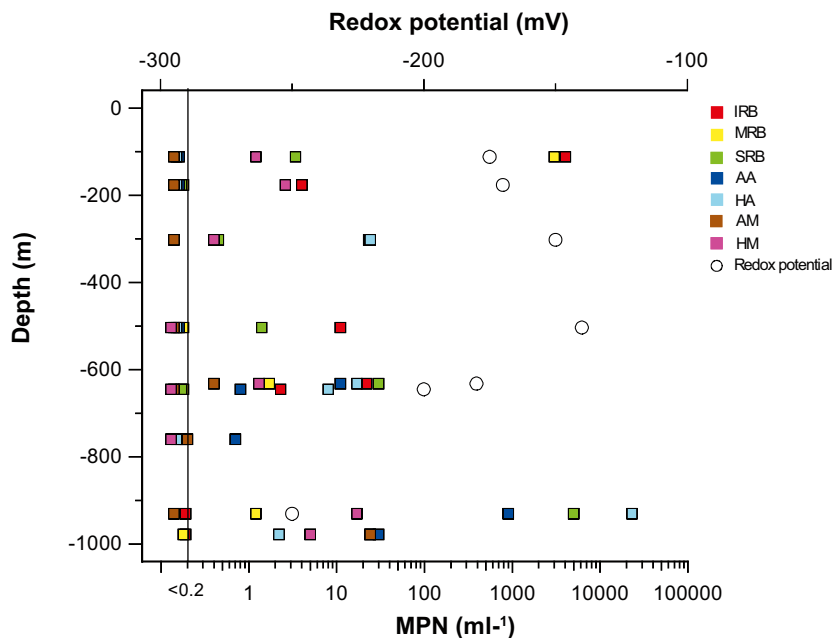


Figure B2-3a. Most probable numbers of different physiological groups of microorganisms and redox potential against depth in the Forsmark area. NRB; nitrate-reducing bacteria, IRB; iron-reducing bacteria, MRB; Manganese-reducing bacteria, SRB; sulphate-reducing bacteria, AA; autotrophic acetogens, HA; heterotrophic acetogens, AM; autotrophic methanogens, HM; heterotrophic methanogens

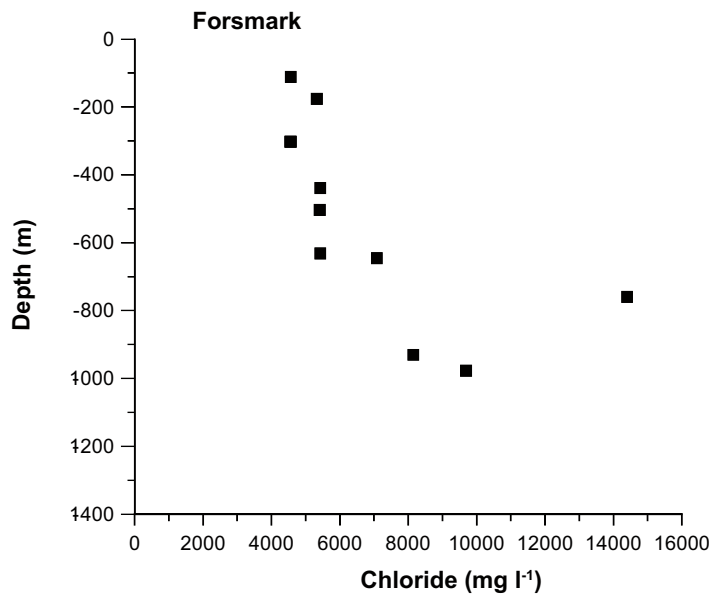


Figure B2-3b. Chloride content in groundwater against depth.

The lowest redox value was found at a depth of 930 m with -250 mV. This coincides with an increase in the number of SRB and, presumably in SRB activity. The sulphide produced lowering the measured redox. IRB, MRB and SRB usually utilize the same carbon compounds originating from surface. Due to the thermodynamics of the oxidation the IRB and MRB will dominate as long as oxidised iron- and manganese compounds are available. When these compounds are consumed or if they are absent, the SRB start to oxidise the organic compounds. The same succession of degradation is due for acetate, autotrophically produced from hydrogen and carbon dioxide.

B2.4 Conclusion

- Microbes are the poisoning agents for redox in groundwater. Their enzymes catalyze reactions that are energetically most favourable for the geochemical system they inhabit.
- The microbial oxidation of organic carbon and/or hydrogen will lower the redox in the groundwater system.

B2.5 #5 redox front considerations – biological oxygen reduction

The definition of the redox front is how deep into the subsurface oxic groundwater will reach. The input of organic material is the most important factor in the reduction of oxygen in recharging groundwater. In the temperate vegetation zone this input varies with seasonal cycles. Carbon dioxide is fixed into organic matter mainly in summer. This material is continuously degraded under consumption of oxygen over the year with peak activity during autumn and winter. When oxygen is depleted, anaerobic microorganisms continue the process of degradation. Examples of anaerobic microorganisms in ground water are nitrate-, iron-,

manganese- and sulphate-reducers. To get correct information on oxygen reduction and reducing capacity in shallow ground water it is necessary to sample ground water from different depths from surface and down. The biogeochemical modelling in the site investigation in Forsmark has so far been done on samples from 100 m and deeper.

Sampling and analyses of some chemical parameters in shallower groundwater have been done in soil pipes and hammer-drilled boreholes but no microbiology sampling has been done. Some of the soil pipes have been included in a chemical sampling program. The program lasted 24 months from May 2003 to April 2005. The data are reported in /Nilsson and Borgiel 2005/ and in /Tröjbom and Söderbäck 2006/.

To get a complete picture of the processes a sampling campaign of microorganisms in combination with chemistry in shallow ground water is planned. Before a decision of which soil pipes and hammered drilled boreholes should be sampled, data available have been compiled and analysed from a seasonal point of view and reported in a PM for SKB. Data mainly from pipes and boreholes in the vicinity of the core drilled boreholes sampled for microbes were explored. Microbial data have been gathered from six boreholes in the Forsmark area: KFM01A, KFM02A, KFM03A, KFM06A, KFM07A and KFM08A. To illustrate how the concentration of oxygen vary during the year, oxygen and ORP data for three soil pipes in drill site 1, in Forsmark are shown in Figure B2-4. ORP is the oxidation-reduction potential measured with an Ag/AgCl electrode and the measured potential is not corrected against the hydrogen gas electrode. The figure shows that there is a variation in the oxygen values over the year also in the deepest soil pipe SFM0003, although the concentrations were low.

Temperature values from soil pipes included in the compilation discussed above are plotted versus depth in Figure B2-5. The seasonal variation of the temperature in groundwater from soil pipes in Forsmark is found at depth down to at least 6 m. In the soil pipe with a depth of approximately 11 m, only a very small variation in temperature was observed.

Some sections in hammer-drilled boreholes are available for sampling. From these sections data from depth between 11 and 100 m could be gathered.

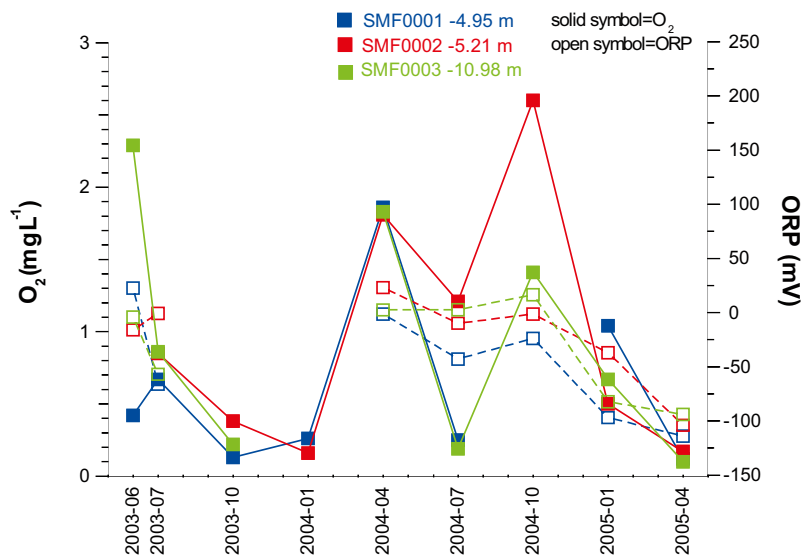


Figure B2-4. Oxygen and ORP during 24 months in the soil pipes SFM0001, SFM0002 and SFM0003 in Forsmark.

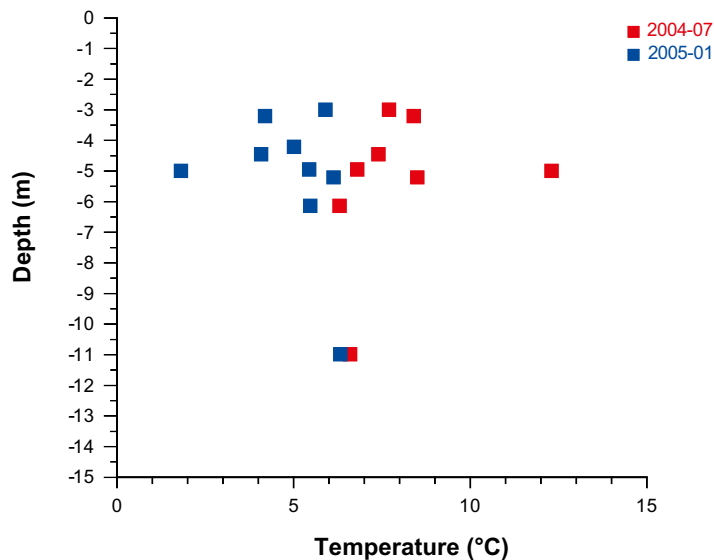


Figure B2-5. Temperatures in soil pipes in Forsmark measured in July 2004 and January 2005.

B2.6 Conclusion

The planned sampling campaign will hopefully fill the gap of knowledge of the oxygen reduction capability of the microbial system in shallow groundwater in Forsmark.

B2.7 #9 and #11 High manganese and uranium values in Forsmark

Some of the sampled sections in core-drilled boreholes in Forsmark showed very high values of uranium. The aim with this interpretation is to find microbial explanations of the high uranium and manganese values.

B2.7.1 Uranium versus manganese, iron and chloride

In Figure B2-6 uranium versus manganese are shown. There was a correlation between uranium and manganese for the three highest values of uranium. In borehole KFM02A at a depth of 503 m the value of uranium was $88 \mu\text{g l}^{-1}$ in KFM02A at a depth of 512 m. In Figure B2-7, ferrous iron versus uranium is plotted. There was no correlation between high ferrous iron values and high uranium values. On the other hand, ferrous iron and uranium values at a depth of 503 m in borehole KFM02A increased during the period of pumping, as shown in Figure B2-8. Ferrous iron and uranium in other sections showed the opposite trend, decreasing values with time of pumping.

There was a correlation between high uranium values and the groundwater lens of similar salinity found at depths between 300 and 700 m in Forsmark (Figure B2-9 and Figure B2-3b).

B2.7.2 Uranium and microorganisms

There were iron- and manganese-reducing bacteria in the groundwater in Forsmark, especially at depths of about 115 m in borehole KFM01A but also in other boreholes but in lower numbers (Figure B2-10).

The high uranium values observed here, correspond with observations of high uranium concentrations in bottom water in the lake Tranebärssjön and leach water from covered mine waste dumps in the same area. Even though this system was anaerobic, high amounts of uranium were released to the water /Sternbeck et al. 2005/. The following possible microbiological explanations for the high uranium values was suggested for the Ranstad site and are here suggested also for Forsmark.

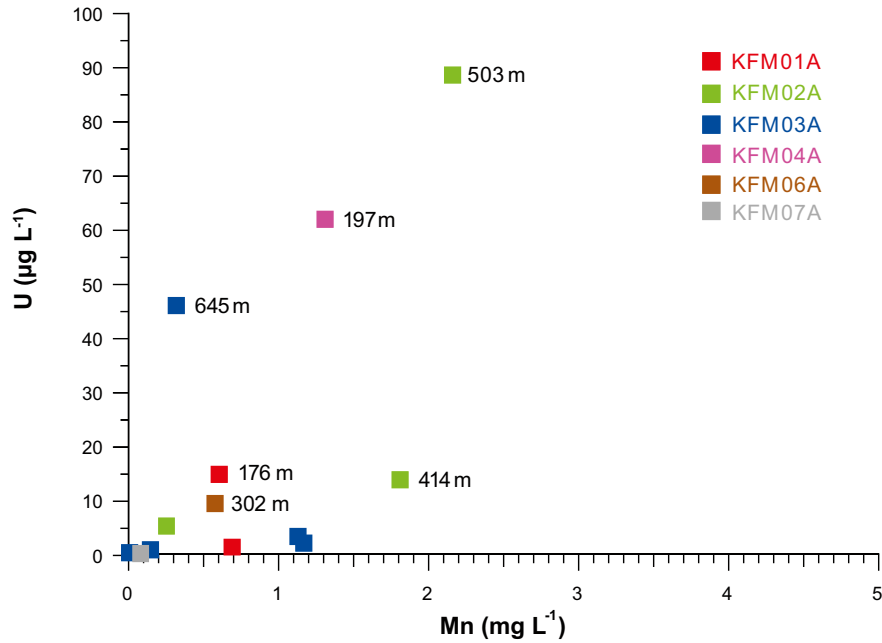


Figure B2-6. Manganese versus uranium in core-drilled boreholes in Forsmark.

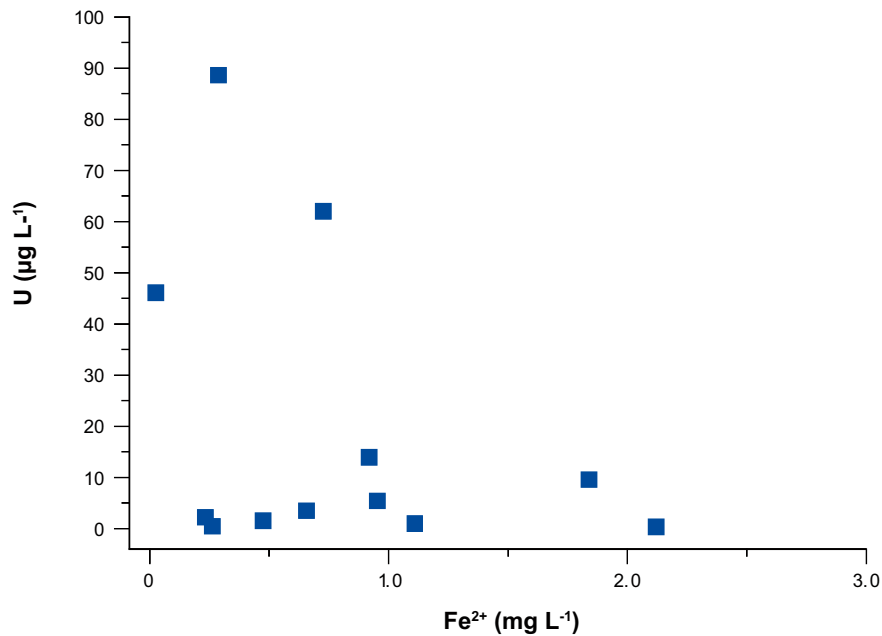


Figure B2-7. Ferrous iron versus uranium in core-drilled boreholes in Forsmark.

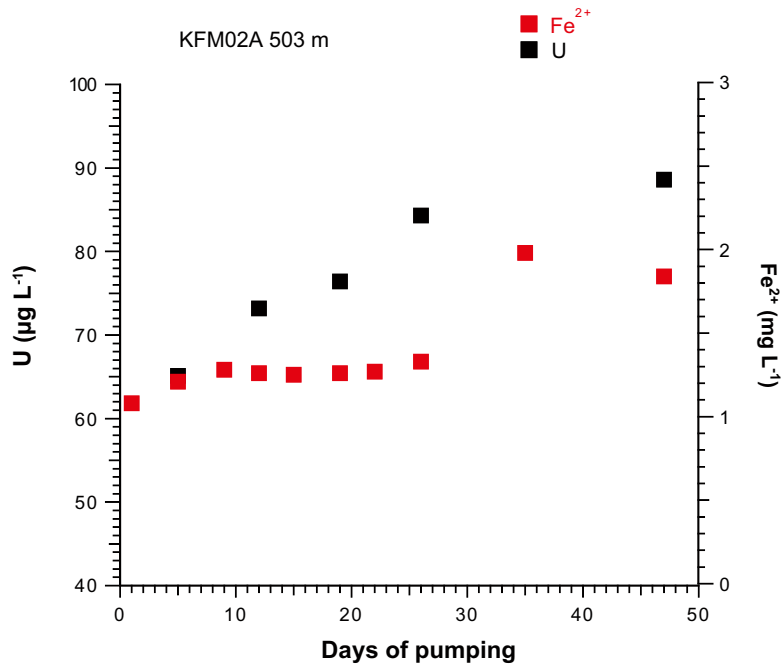


Figure B2-8. Uranium and ferrous iron versus time of pumping at a depth of 503 m in borehole KFM02A in Forsmark.

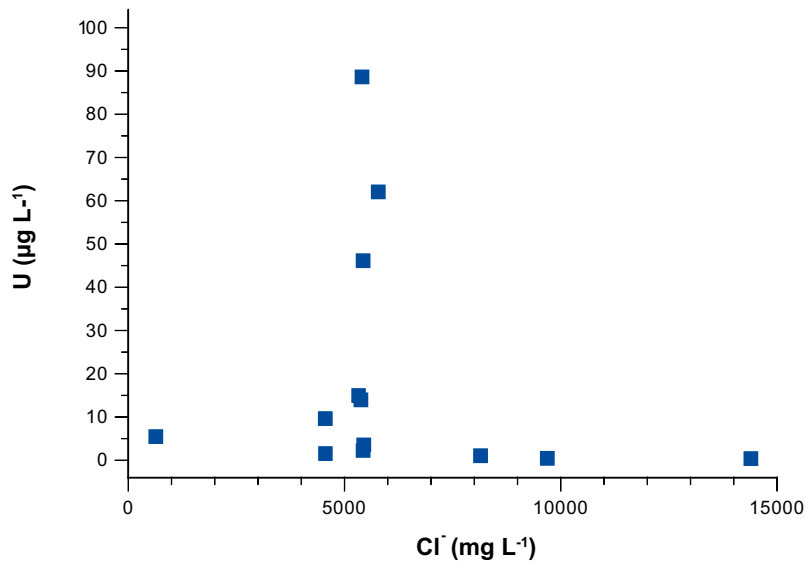


Figure B2-9. Chloride versus uranium in core-drilled boreholes in Forsmark.

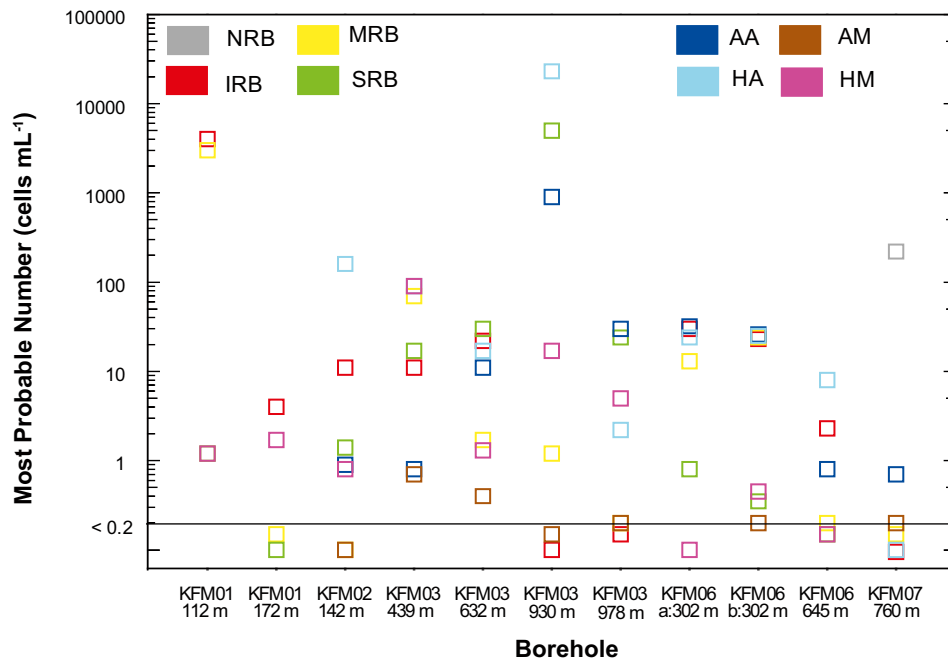


Figure B2-10. The most probable numbers of different physiological groups of microorganisms in the Forsmark area. NRB; nitrate-reducing bacteria, IRB; iron-reducing bacteria, MRB; Manganese-reducing bacteria, SRB; sulphate-reducing bacteria, AA; autotrophic acetogens, HA; heterotrophic acetogens, AM; autotrophic methanogens, HM; heterotrophic methanogens. The horizontal line is the detection limit of $< 0.2 \text{ mL}^{-1}$.

Possible microbial explanations for the high uranium values

1. Microbially produced complex-forming compounds

Some microorganisms produce complex-forming compounds. The most well-known of these are iron-binding molecules so called siderophores. The hypothesis why such molecules are produced is that iron is limiting for growth in the many aerobic environments. By a production of molecules with high affinity for iron, the microbes will get an advantage and by that can out-compete other species.

It has been shown that *Pseudomonas fluorescens*, isolated from groundwater at Äspö HRL, produced complex-binding molecules identified as a pyoverdine chelator. When the bacterium was grown on both weathered and non-weathered uranium shale from Ranstad, a closed uranium-mine in Sweden, measurable amounts, one to five % of the uranium content in the shale, was mobilised. *P. fluorescens*, also mobilised iron from the shale concomitant with the uranium mobilisation /Kalinowski et al. 2004/. Recently, anaerobic production of a uranium complexing substance by *P. fluorescens* has been demonstrated (Johnsson et al. accepted for publication).

One explanation for the high uranium values in Forsmark might be that microorganisms in fractures produce complex-binding molecules that bind to uranium and thereby mobilise high amounts.

2. Microbial iron- and/or manganese-reduction

A prerequisite for the approach is that the uranium at start is incorporated in manganese- and/or iron bearing minerals on fracture surfaces. It has been suggested by several authors that indirect redox reactions whereby iron/manganese oxyhydroxide dissolution by iron- or manganese reducing bacteria may cause dissolution of associated actinide elements /Lienert et al. 1994, Morris and Raiswell 2002/. Anaerobic iron- and manganese reducing microorganisms have been demonstrated in ground water in Forsmark (Figure B2-10) /SKB 2006b/. During the metabolism of these microorganisms they reduce oxidised iron- and/or manganese in fracture

minerals and thereby dissolve the minerals. If uranium is associated with the minerals there could be a simultaneous release of uranium to the groundwater. Increased uranium values have been found in sections where iron- and manganese-reducers were present.

3. Anaerobic uranium-oxidation

Aerobic uranium oxidation has been known for several years /Anderson and Lovely 2002/. Anaerobic uranium oxidation by nitrate reduction by the bacterium *Thiobacillus denitrificans* was recently reported /Beller 2005/. This bacterium is autotrophic and needs no organic carbon- and energy-source.

There is no information available of the oxidation state of the uranium in the minerals or in the groundwater, although pitchblende has been identified in fracture minerals by electron microscopy (Smellie and Tullborg, Appendix A, this volume). Especially fracture filling from the borehole KFM03A section at a depth of 645 m showed a very high value of 2,200 ppm uranium. If anaerobic uranium oxidation occurs in groundwater in Forsmark, uranium will be oxidized and thus more mobile than in its reduced form.

Where do we find high uranium values?

Figure B2-11 shows that the highest values of uranium in core-drilled boreholes were found borehole KFM02A at a depth of 503 m, borehole KFM04A at a depth of 197 m and in borehole KFM03A at a depth of 645 m. High values were also found in KFM01A at a depth of 176 m, KFM03A at a depth of 414 m and in KFM06A at depth of 302 m. In Figure B2-11, the boreholes are shown together with the main fracture zone at the site A2 and minor fracture zones A3–A6. The boreholes KFM02A, KFM03A and KFM06A are all connected with A2 and the sections with high uranium values are close to the fracture zone. KFM01A is not directly connected to A2 but horizontal fractures in the upper 100 m might be connected.

There are also high uranium values in groundwater from soil pipes. Table B2-1 shows the soil pipes with values above $2 \mu\text{g L}^{-1}$. All of these soil pipes are located along the stretch of A2.

In conclusion all sampled groundwater with high uranium values are located in or very close to fracture zone A2.

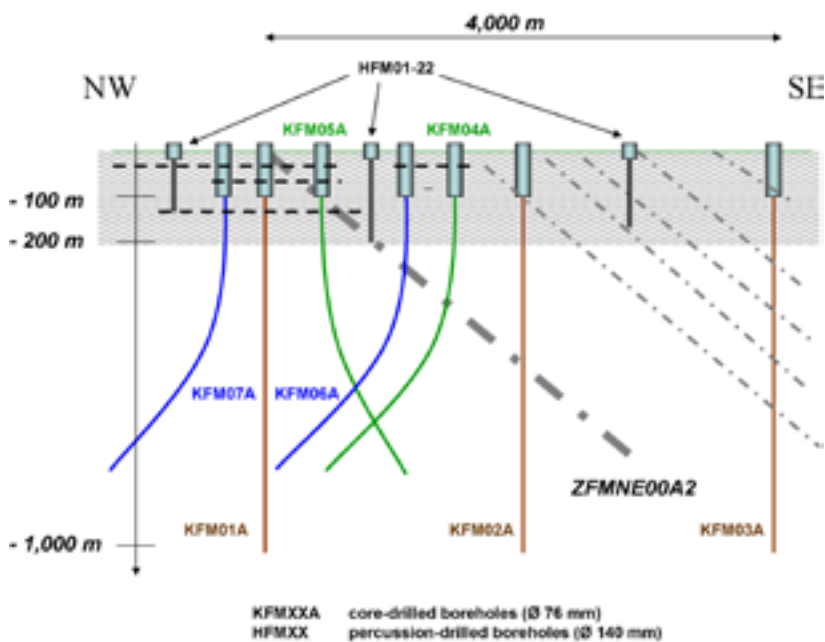


Figure B2-11. Schematic cross section through the central part of the tectonic lens. High values of uranium are added to the borehole sections where they are found. Adapted from /SKB 2006/.

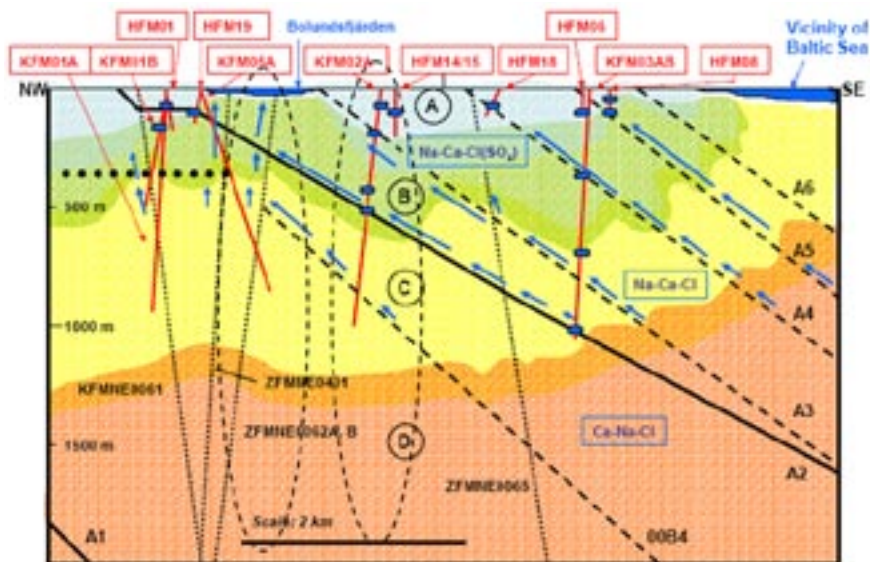


Figure B2-12. Schematic 2D map of major fracture zones and core drill boreholes in Formark. Conceptual flow directions in the fracture zones are shown. /From SKB 2005/.

Table B2-1. The average uranium content in groundwater sampled from soil pipes in Forsmark.

Soil pipe	Depth	U ($\mu\text{g L}^{-1}$) average value
SFM0001	4.45	4.1914
SFM0002	4.71	5.6714
SFM0005	2.71	4.4775
SFM0009	2.50	8.1167
SFM0006	3.71	19.6250
SFM0008	5.64	11.0650
SFM0009	2.50	8.1167
SFM0012	5.85	20.000
SFM0029	7.50	4.2700
SFM0031	4.50	7.7800
SFM0032	4.00	5.9900
SFM0037	2.50	9.1280
SFM0057	3.95	5.7840
SFM0060	7.10	32.6000

B2.7.3 High uranium and drill water content

The high uranium values are connected with the fracture zone A2 and other fracture zones in connection to A2. This is valid for both values from deep core-drilled boreholes and values from shallow groundwater from soil pipes.

It has been suggested that the increased uranium values is a consequence of high residue of oxidized drill-water (Buckau, Appendix G, this volume). The water flow in fracture zones enhances microbiological activity by increased transport of energy sources and nutrients. Presence of fractures gives increased inflow of drill water during drilling. This increases the need for pumping to reduce the drill water content and by that the flow of groundwater and transport also increase. There is no contradiction between high drill-water content and increased uranium values related microbial activity.

The drill-water comes from a deep drilled well and is kept under nitrogen if it has to be stored in a tank. If oxygen had entered the fractures during pumping it would be consumed immediately by microorganisms and any oxidation of uranium would have occurred for a very short period of time. The high uranium values have been measured over a period of years.

B2.8 Conclusion

There are three possible microbiological explanations for the high uranium values in Forsmark:

1. Production of complex-forming compounds by microorganisms.
2. Release of uranium from fracture minerals by iron- and/or manganese-reducing bacteria during reduction of iron and/or manganese fracture minerals.
3. Anaerobic uranium oxidation, giving oxidised uranium in solution.

B3 #6 Gases

Earlier studies of groundwater in the Fennoscandian Shield have found high amounts of dissolved gases. If the total amount of gas exceeds saturation, gas bubbles may form /Pedersen 2002/. The surface tension of the bubbles can capture different compounds, such as radionuclides attached on colloids or microbes, from the groundwater. The bubbles will move rapidly in groundwater and can cause the dispersion of radionuclides over large areas, in particular, to the ground surface. In a site investigation it is therefore crucial to evaluate gas data, and to include it in hydrogeochemical models.

Some gases are involved in microbiological reactions. The most important of these gases are oxygen, methane, carbon dioxide, and hydrogen. Methane is produced by methanogens in reduced anaerobic environments and can be used as a substrate by methanotrophic bacteria. Carbon dioxide is used as a carbon source by autotrophic organisms and is the end product of microbial degradation. Hydrogen is the energy and electron source for methanogens, acetogens, and some other autotrophic micro-organisms, i.e. various sulphate reducers. It is also one of the end products of microbiological fermentation.

Table B3-1 shows the boreholes and depths from which data have been available for the time of the 2.1 data freeze.

B3.1 Total volume of gas

Figure B3-1 shows the total volume of gas for all groundwater samples. The volume of gas in samples from Forsmark follows the common trend for groundwater in the Fennoscandian Shield, it increases with depth. This pattern can be seen in Olkiluoto in Finland /Pitkänen et al. 2004/ and in the Laxemar area in Sweden /SKB 2006b/. The only exception from this trend is the gas volume in one sample from KFM07A that shows a greater volume of gas than the deeper samples from KFM03A (Figure B3-1).

Table B3-1. Boreholes, depths, sampling dates, and gas volumes available in SICADA for analysis in the Forsmark, version 2.1.

Borehole	Depth centre (m)	Gas volume (ml l ⁻¹ of groundwater)
KFM01A	176	57.3
KFM02A	503b	73.0
	503a	83.0
KFM03A	442	79.5
	631.9	97.2
	977.7	127
KFM06A	645	106
KFM07A	759.7	160

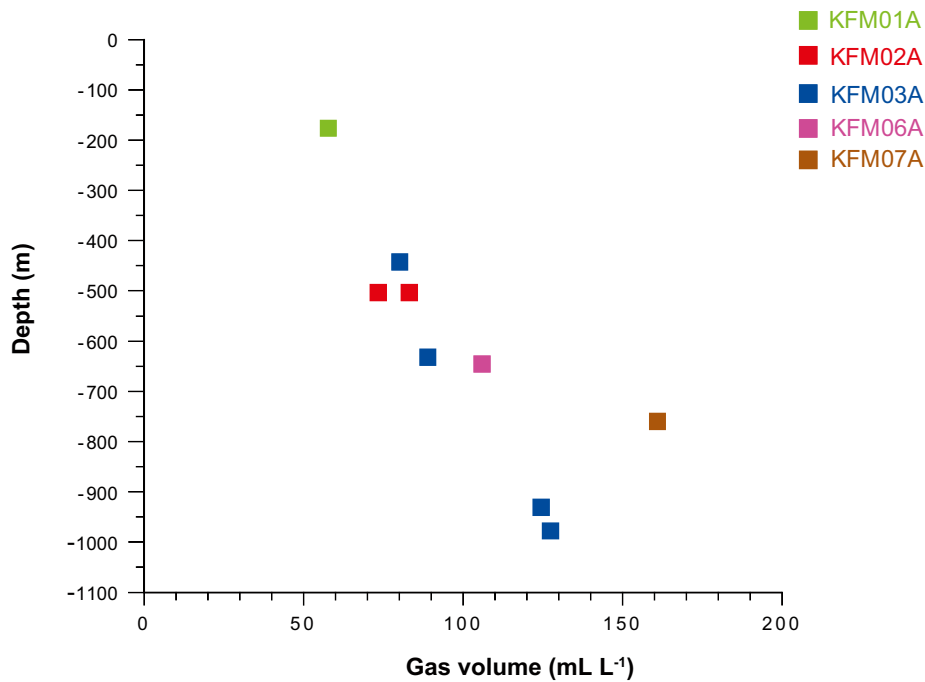


Figure B3-1. The total volume of gas in samples from the Forsmark area.

B3.2 Nitrogen, helium and argon

The dominant gas in groundwater from Forsmark is nitrogen. The compositions of the gas in the Forsmark are shown in Figure B3-7a–h. This corresponds with the gas content in some groundwater in Olkiluoto, Finland, for example, although some samples from there contain more methane than nitrogen /Pitkänen et al. 2004/. The content of nitrogen in the volume of gas calculated in ppt decreases slightly with depth, mainly because the content of helium increases with depth (Figure B3-2 and B3-3). The source of nitrogen and helium in deep groundwater is considered to be crustal and mantle degassing. Another source of helium may be radioactive decay, occurring in the bedrock. Argon is a gas that is present in quite high concentrations. It has a tendency to decrease with depth when helium increases (Figures B3-7a–h).

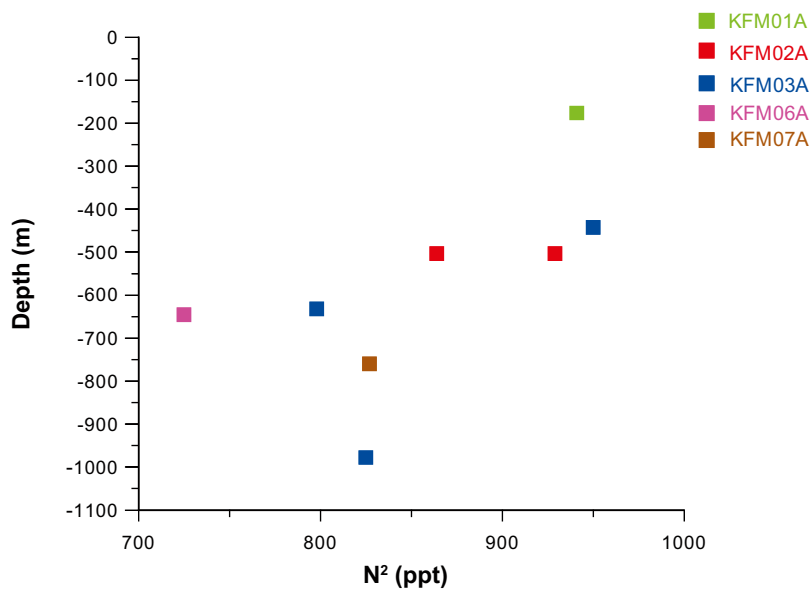


Figure B3-2. The partial content of nitrogen in gas samples from the Forsmark area.

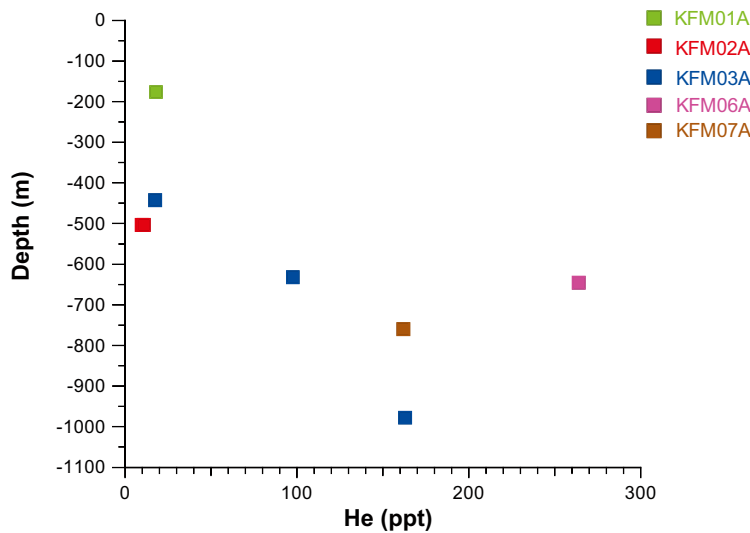


Figure B3-3. The partial content of helium in gas samples from the Forsmark area.

B3.3 Carbon dioxide and methane

Carbon dioxide in groundwater is a dissociation product of dissolved carbonates from fractures in the bedrock, but can also be a degradation product of organic carbon or volcanic/mantle gas. The carbon dioxide concentrations in samples from Forsmark display a decreasing trend with depth (Figure B3-4). This is probably because the degradation of organic material is greater at shallower depths and because autotrophic metabolism with the fixation of carbon dioxide in organic carbon compounds is more common at greater depths. This pattern has been observed for carbon dioxide concentrations in groundwater from the Olkiluoto site in Finland /Pitkänen et al. 2004/.

Figure B3-5 shows the decreasing trend of methane in groundwater of Forsmark. The origin of methane in groundwater can be either biotic or abiotic. Biotic methane is produced by methanogenic archaea, a group of prokaryotic organisms that can utilise either organic C₁ compounds or acetate; the case of acetate is presented in Equation B1. Methanogens can also assimilate carbon dioxide, using hydrogen gas as the energy and electron source (see Equation B2). The origin of their substrate can be biodegraded organic matter, as in sea and lake sediments or composts, or carbon dioxide and hydrogen originating in the mantle /Apps and van de Kamp 1993/.

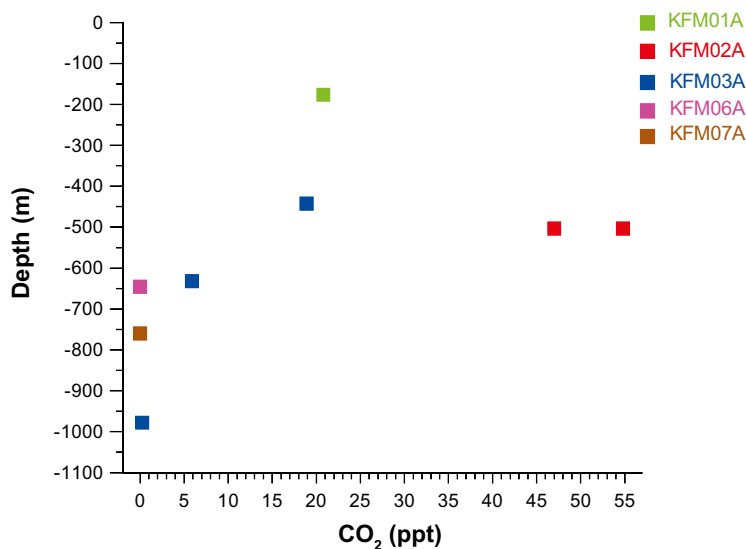


Figure B3-4. The partial content of carbon dioxide in gas samples from the Forsmark area.

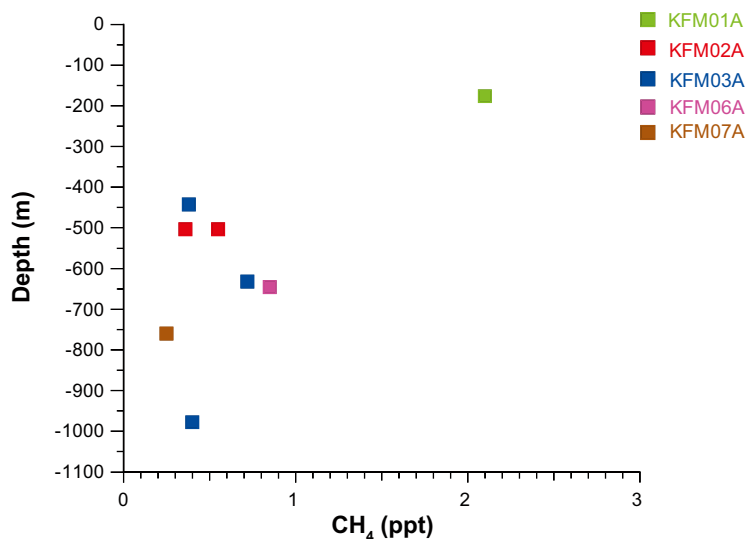


Figure B3-5. The partial content of methane in gas samples from the Forsmark area.



Abiogenic methane is produced in, for example, hydrothermal systems during water–rock interactions involving the Fischer–Tropsch synthesis reaction, which is the same as Equation B2 above. This methane can act as precursor for polymerisation to higher hydrocarbons, such as short-chain alkanes (see section on hydrocarbons).

The amount of methane in Forsmark is the highest at the shallower depths and very low at a depth of 922 m. This is likely because there is some biological methanogenesis at these depths. The ratio of methane to C₂ and C₃ hydrocarbons at these depths is not greater than 10³ but higher than 10 indicating a mixture of biotic and abiogenic methane at all depths (Table B3-2) (see section on hydrocarbons).

B3.4 Hydrocarbons

In Figure B3-7a–h, the hydrocarbon content is indicated by the small segment in the circle graphs labelled “övriga”. There is no obvious trend with depth for the hydrocarbons in Forsmark.

The hydrocarbons come from deep abiogenic processes in the mantle and move slowly by diffusion towards the surface. Calculating the C₁/(C₂+C₃) ratio can elucidate the source of the methane found. If this ratio is high, greater than 1,000, it is considered to indicate biogenic methane. In contrast, thermogenic and abiogenic methane will give a ratio of approximately 10 (Sherwood-Lollar et al. 1993, 2002, 2005, Clark and Fritz 1997, Whiticar 1990). The ratios for the gas samples are presented in Table B3-2. From this ratio it can be concluded that the methane present is mostly of abiogenic origin. To be able to state this conclusively, more hydrocarbon data need to be generated together with stable isotope values for methane.

Table B3-2. The ratio of methane to C₂ and C₃ hydrocarbons in the Forsmark area.

Borehole	Depth centre (m)	C ₁ /(C ₂ + C ₃)
KFM01A	176.3	40
KFM02A	503.3a	–
	503.3b	81
KFM03A	442.3	88
	631.9	106
	977.7	62
KFM06A	645	40
KFM07A	759.7	61

B3.5 Hydrogen

Hydrogen is an important gas in several anaerobic microbial metabolisms, such as methanogenesis and acetogenesis. Autotrophic iron- and sulphate-reducing bacteria can also use hydrogen as an energy and electron source concomitant with iron or sulphate reduction.

There are at least six possible processes in which crustal hydrogen is generated: (1) reaction between dissolved gases in the C-H-O-S system in magmas, especially in those with basaltic affinities; (2) decomposition of methane to carbon (graphite) and hydrogen at temperatures above 600°C; (3) reaction between CO₂, H₂O, and CH₄ at elevated temperatures in vapours; (4) radiolysis of water by radioactive isotopes of uranium, thorium, and their decay daughters, and potassium; (5) cataclasis of silicates under stress in the presence of water; and (6) hydrolysis by ferrous minerals in mafic and ultramafic rocks /Apps and van de Kamp 1993/. It is important to explore the scale of these processes and the rates at which the produced hydrogen becomes available to deep microbial ecosystems.

Hydrogen could be measured only in samples from shallower depths than 400 m. This could be due to problems with a too high detection limit for hydrogen in the gas analysis. Measurable amounts of hydrogen at concentrations between one and ten ppm has been reported from the MICROBE site at Äspö HRL by the use of a gas chromatograph with high sensitivity /Pedersen 2005ab/. The lowest reported value here was 94 ppm. The highest amounts of hydrogen in Forsmark were found at a depth of approximately 500 m, with approximately 2,700 ppm.

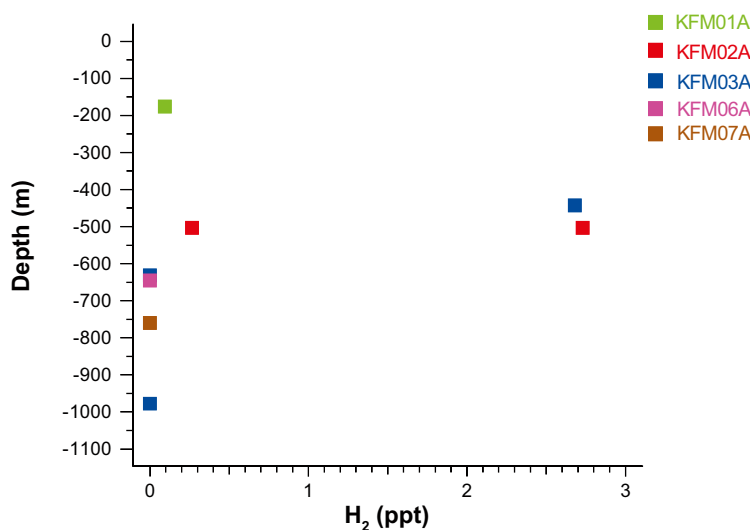
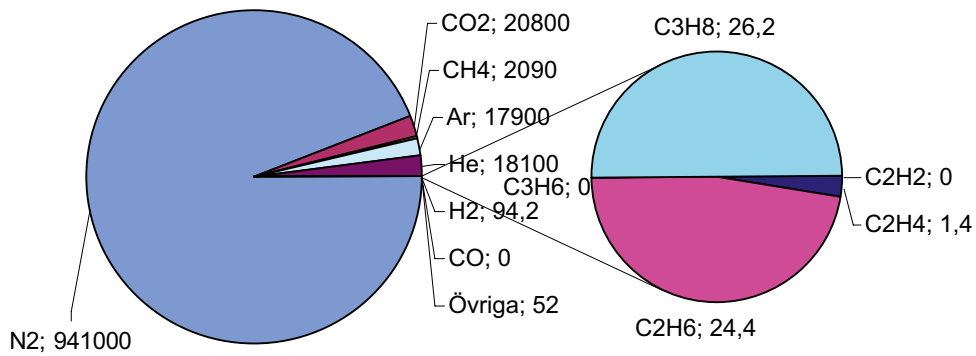


Figure B3-6. The partial content of hydrogen in gas samples from the Forsmark area.

B3.6 Conclusions

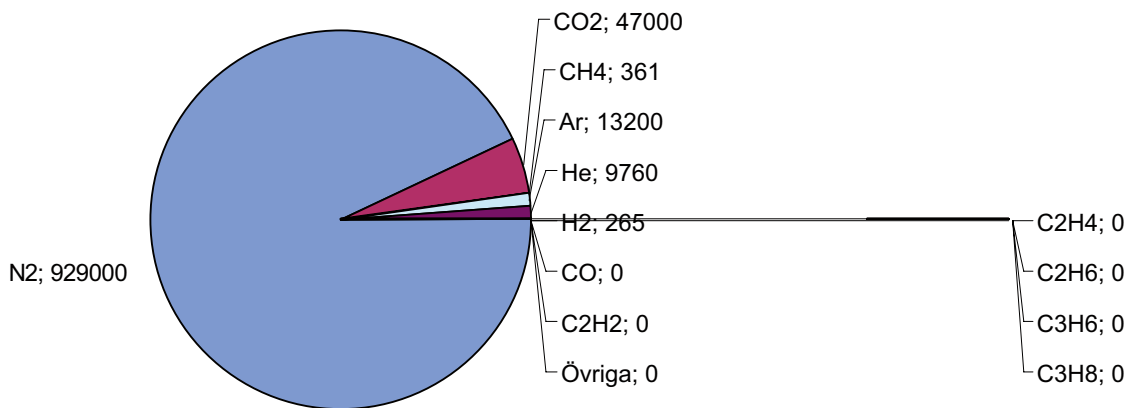
- Nitrogen gas is the dominant gas at all depths.
- Helium increases with depth – presence indicate groundwater of deep origin or long residence time.
- Methane, carbon dioxide and hydrogen decrease with depth.
- Difficulties with the detection limit of hydrogen could possibly give to low values for this gas.

KFM01A, -176.3 m 57.3 ml/l



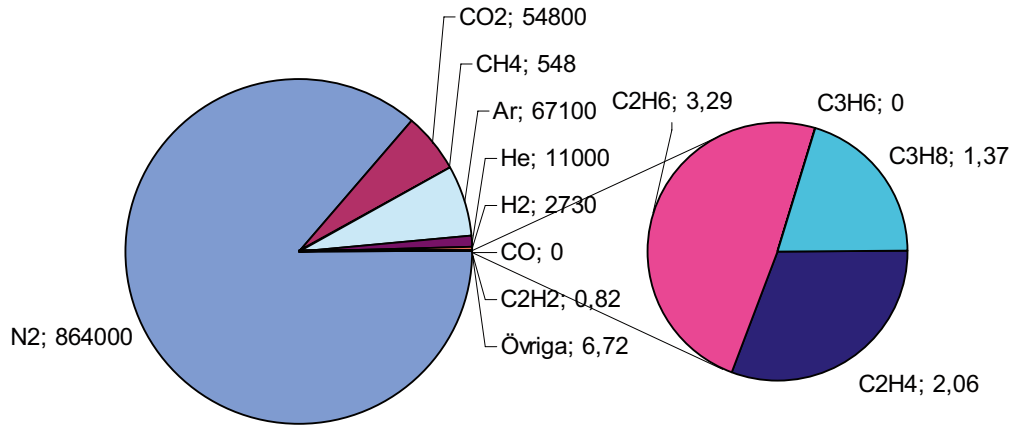
- a)
- | | | | | | | | |
|--------|--------|--------|--------|------|------|------|--------|
| ■ N2 | ■ CO2 | ■ CH4 | ■ Ar | ■ He | ■ H2 | ■ CO | ■ C2H2 |
| ■ C2H4 | ■ C2H6 | ■ C3H6 | ■ C3H8 | | | | |

KFM02A 503.3 83 ml/l



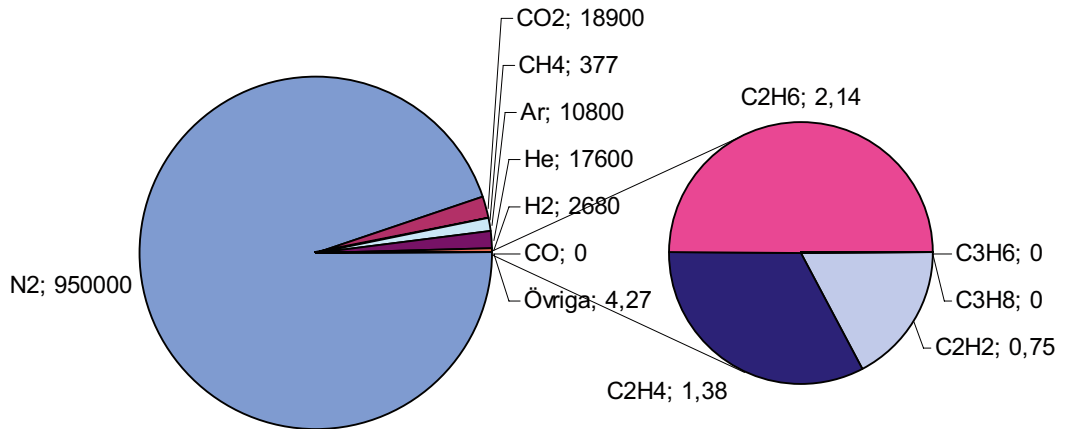
- b)
- | | | | | | | | |
|--------|--------|--------|--------|------|------|------|--------|
| ■ N2 | ■ CO2 | ■ CH4 | ■ Ar | ■ He | ■ H2 | ■ CO | ■ C2H2 |
| ■ C2H4 | ■ C2H6 | ■ C3H6 | ■ C3H8 | | | | |

KFM02A, -503.3 m b 73 ml/l



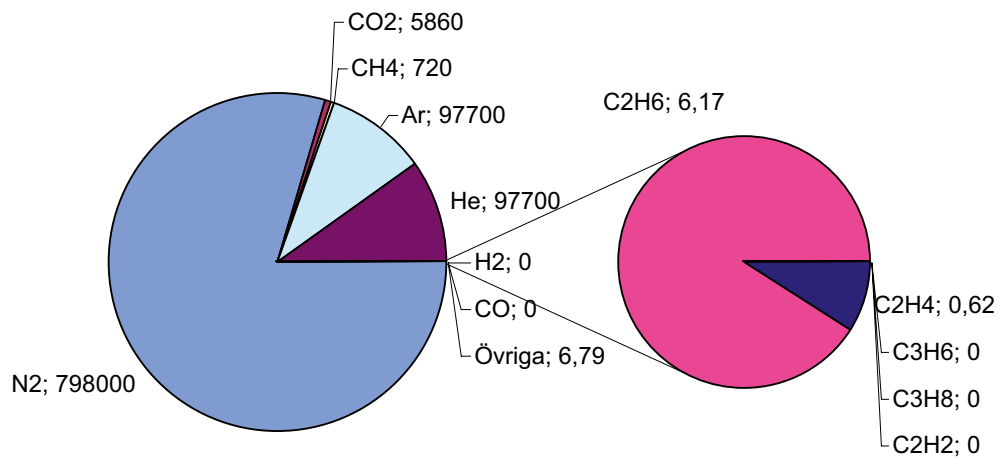
- c)
- | | | | | | | | |
|--|---|--|---|--|--|--------------------------------------|---|
| ■ N2 | ■ CO2 | ■ CH4 | ■ Ar | ■ He | ■ H2 | ■ CO | ■ C2H2 |
| ■ C2H4 | ■ C2H6 | ■ C3H6 | ■ C3H8 | | | | |

KFM03A, -442.3 m 79.5 ml/l



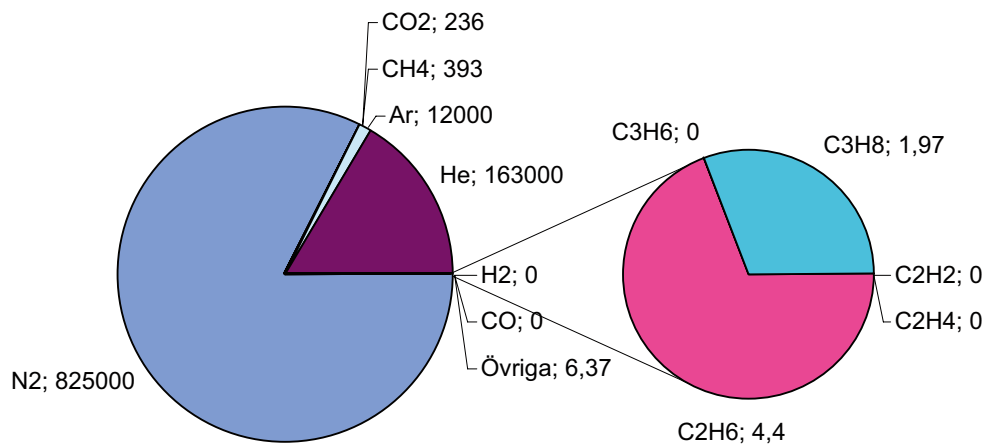
- d)
- | | | | | | | | |
|--|---|--|---|--|--|--------------------------------------|---|
| ■ N2 | ■ CO2 | ■ CH4 | ■ Ar | ■ He | ■ H2 | ■ CO | ■ C2H2 |
| ■ C2H4 | ■ C2H6 | ■ C3H6 | ■ C3H8 | | | | |

KFM03A, -631.9 m 97.2 ml/l



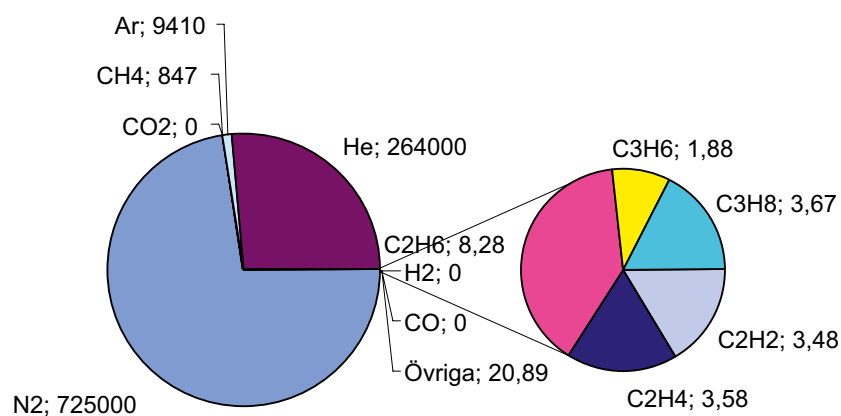
- e)
- | | | | | | | | |
|---|---|---|---|--|--|--|--|
| ■ N ₂ | ■ CO ₂ | ■ CH ₄ | ■ Ar | ■ He | ■ H ₂ | ■ CO | ■ C ₂ H ₂ |
| ■ C ₂ H ₄ | ■ C ₂ H ₆ | ■ C ₃ H ₆ | ■ C ₃ H ₈ | | | | |

KFM03A, -977.7 m 127 ml/l



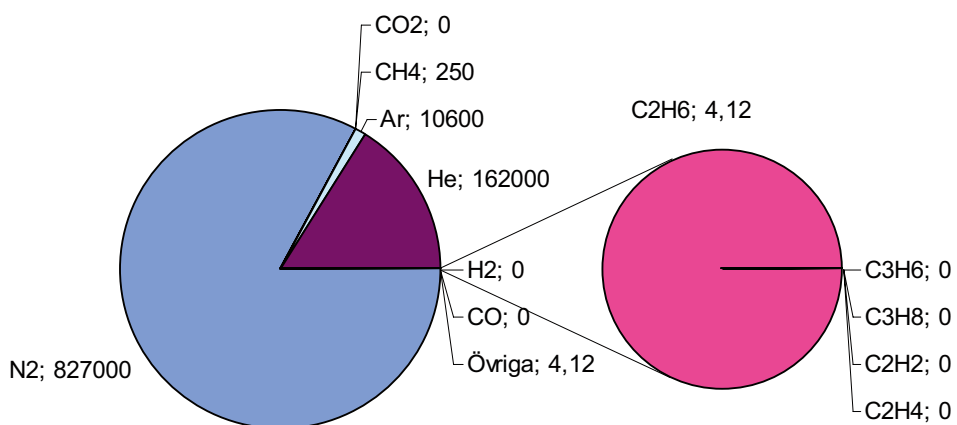
- f)
- | | | | | | | | |
|---|---|---|---|--|--|--|--|
| ■ N ₂ | ■ CO ₂ | ■ CH ₄ | ■ Ar | ■ He | ■ H ₂ | ■ CO | ■ C ₂ H ₂ |
| ■ C ₂ H ₄ | ■ C ₂ H ₆ | ■ C ₃ H ₆ | ■ C ₃ H ₈ | | | | |

KFM06, -645 m 106 ml/l



g) ■ N₂ ■ CO₂ ■ CH₄ ■ Ar ■ He ■ H₂ ■ CO ■ C₂H₂ ■ C₂H₄ ■ C₂H₆ ■ C₃H₆ ■ C₃H₈

KFM07A, -759.7 m 160 ml/l



h) ■ N₂ ■ CO₂ ■ CH₄ ■ Ar ■ He ■ H₂ ■ CO ■ C₂H₂
■ C₂H₄ ■ C₂H₆ ■ C₃H₆ ■ C₃H₈

Figure B3-7a-h. Volumes and distribution of the measured gases in samples from the Forsmark area.

B4 Colloids

Particles in the 10^{-3} to 10^{-6} mm size range are regarded as colloids. Their small size prevents them from settling and gives them the potential to transport radionuclides in groundwater. The aim of the colloid study in the Laxemar site investigation is to quantify and determine the composition of colloids in groundwater from boreholes. The results will be included when modelling the hydrochemistry at the site.

The amount of colloids in the Forsmark area was very low. Table 4 shows the amounts of colloids in the different size fractions from groundwater in Forsmark. The amount was approximately $20 \mu\text{g l}^{-1}$ or below. The colloid values obtained from the Forsmark area agreed well with data from colloid studies in Switzerland, i.e. 30 ± 10 and $10 \pm 5 \mu\text{g l}^{-1}$ /Degueldre 1994/, but are approximately ten times lower than those reported from Canada, i.e. $300 \pm 300 \mu\text{g l}^{-1}$ /Vilks et al. 1991, Laaksoharju et al. 1995/.

B4.1 Conclusion

The amount of colloids in Forsmark is in general low. The data so far showed similar trends as in groundwater at other places in Sweden. It was for example shown that colloid content was higher in low salinity water than in high salinity) /SKB 2005a/ With the data available so far it is difficult to elucidate the source of the colloids or their ability to bind different molecules.

Table B4-1. Element analyses of the 0.05 and 0.2 µm colloid fractions and the 0.4 µm precipitation fraction from the Forsmark area.

Borehole	KFM01A 111.8 m			KFM01A 176.3 m			KFM02A 503.3 m			KFM03A 440.8 m			KFM03A 632 m			
Pore Size (µm)	0.05	0.2	0.4	0.05	0.2	0.4	0.05	0.2	0.4	0.05	0.2	0.4	0.05	0.2	0.4	
Chloride (mg l ⁻¹)	4,562.8	4,562.8	4,562.8	5,329.5	5,329.5	5,329.5	5,410	5,410	5,410	5,430	5,430	5,430	5,430	5,430	5,430	
Colloid phase (µg l ⁻¹)																
Ca as Calcite CaCO ₃	0.89	b.d.	1.36	0.21	0.10	0.14	d.m.	d.m.	0.20	0.49	1.30	0.50	1,412	d.m.	628	
Fe as Fe(OH) ₃	5.74	12.44	443.47	0.38	0.51	9.06	d.m.	d.m.	3.64	3.06	4.59	27.5	1.1	d.m.	5.0	
S as sulphur	61.25	b.d.	40.95	22.10	15.5	18.48	d.m.	d.m.	b.d.	30	72	16	28	d.m.	b.d.	
Mn as Mn(OH) ₂	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	d.m.	d.m.	0.405	0.65	1.78	1.46	0.2	d.m.	0.2	
Al as K-Mg-illite clay: K _{0.6} Mg _{0.25} Al _{2.3} Si _{3.5} O ₁₀ (OH) ₂	71.36	14.9	29.45	10.39	8.30	20.21	d.m.	d.m.	2.90	2.5	2.5	172.2	4.1	d.m.	18.7	
Si as SiO ₂	365.91	601.33	729.93	b.d.	b.d.	b.d.	d.m.	d.m.	b.d.	b.d.	b.d.	b.d.	b.d.	d.m.	b.d.	
Sum (ppb, (µg l ⁻¹))	505.15	628.67	1,245.16	33.08	24.41	47.8				7.145	36.7	82.17	217.66	1,445	–	651.9
Sum omitting calcite	504.26	628.67	1,243.8	32.87	24.31	47.66				6.945	36.21	80.87	217.16	33.4	–	23.9
Sum omitting calcite and sulphur	< 443.01	< 628.67	< 1,202.85	< 10.77	< 8.81	< 29.18	–	–	< 6.945	< 6.21	< 8.87	< 201.16	< 5.4	–	< 23.9	

b.d. below detection limit.
d.m. data missing.

Borehole	KFM03A 930.5 m			KFM03A 977.7 m			KFM06A 302.0 m			KFM06A 645.3 m		
Pore Size (µm)	0.05	0.2	0.4	0.05	0.2	0.4	0.05	0.2	0.4	0.05	0.2	0.4
Chloride (mg l ⁻¹)	8,500	8,500	8,500	9,690	9,690	9,690	4,560	4,560	4,560	7,080	7,080	7,080
Colloid phase (µg l ⁻¹)												
Ca as Calcite CaCO ₃	1,689	d.m.	1,214	d.m.	d.m.	657.5	232.5	b.d.	191	977	981	484
Fe as Fe(OH) ₃	1.0	d.m.	3.05	d.m.	d.m.	3.05	2.1	0.6	3.9	1.2	1.3	3.15
S as sulphur	b.d.	d.m.	b.d.	d.m.	d.m.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Mn as Mn(OH) ₂	0	d.m.	0	d.m.	d.m.	0	0.1	0	0.1	0	0	0.55
Al as K-Mg-illite clay: K _{0.6} Mg _{0.25} Al _{2.3} Si _{3.5} O ₁₀ (OH) ₂	18.7	d.m.	0.5	d.m.	d.m.	4.2	3.3	1.7	7.9	2.1	1.7	7.05
Si as SiO ₂	b.d.	d.m.	b.d.	d.m.	d.m.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Sum (ppb, (µg l ⁻¹))	1,708.7	–	1,217.55	–	–	664.75	238.0	2.3	202.9	980.3	984	494.75
Sum omitting Calcite	19.7	–	3.55	–	–	7.25	5.5	2.3	11.9	3.3	3.0	10.75
Sum omitting calcite and sulphur	< 19.7	–	< 3.55	–	–	< 7.25	< 5.5	< 2.3	< 11.9	< 3.3	< 3.0	< 10.75

b.d. below detection limit.
d.m. data missing.

Table B4-2. Colloid sampling by filtration in Forsmark area 2.1.

Bore hole	Depth center (m)	Filter pore size (µm)	Number of samples	Al P as K-Mg-Illite (ug/l)	Ca P as CaCO ₃ (ug/l)	Fe P as Fe(OH) ₃ (ug/l)	Mn P as MnO ₂ (ug/l)	Si P as SiO ₂ (ug/l)	S P (ug/l)
KFM03A	632	0.05	2 (1)	4.1	1,412	1.1	0.2	**	28
	632	0.2	1	*	*	*	*	*	*
	632	0.4	2	18.7±4.1	628±221.73	5.0±0	0.2±0	**	**
KFM03A	930.5	0.05	2 (1)	1.7	1,689.2	1.0	0	**	**
	930.5	0.2	1	*	*	*	*	*	*
	930.5	0.4	2	0.5±0.14	1,214±1,416	3.05±0.78	0	**	**
KFM03A	977.7	0.05	2	*	*	*	*	*	*
	977.7	0.2	1	*	*	*	*	*	*
	977.7	0.4	2	4.2±1.2	657.5±161.8	3.05±0.78	0	**	**
KFM06A	302	0.05	2	3.3±	232.5±328	2.1±1.1	0.1±0.14	**	**
	302	0.2	1	1.7	**	0.6	0	**	**
	302	0.4	2	7.9±0.56	191.4±23.0	3.9±0.14	0.1±0.14	**	**
KFM06A	645.3	0.05	2	2.1±0.56	977.2±5.3	1.2±0.14	0	**	**
	645.3	0.2	1	1.7	981	1.3	0	**	**
	645.3	0.4	2	7.05±4.17	484.2±12.4	3.15±0.35	0.55±0.78	**	**

* broken filter.

** below detection limit.

Appendix C

Chemnet's issue report, Forsmark area version 2.1, UZ/SKB/06/02 – Internal report

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Contribution of the University of Zaragoza
Earth Science Department

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C1 Introduction

This report is written as an issue report in which several items of special interests have been the main aim of the work and are comprehensively described.

The items presented here have been organised in four main parts:

1. Redox conditions including the following items:
 - Redox conditions.
 - Integration of hydrochemical data with mineralogical and microbial data.
 - Revision of conceptual model (role of monosulfides).
 - Elevated Uranium contents.
 - Manganese contents.
2. New hypothesis for the constant Cl value zone in the Forsmark groundwaters.
3. Revision of conceptual models.
4. Feedback to the Site.

For this new Site Descriptive Modelling phase (Forsmark 2.1), the dataset supplied by SICADA as Data Freeze 2.1, includes old (Data Freeze 1.2) and new (post-Data Freeze 1.2) samples. Forsmark 1.2 data freeze included samples and data taken before June 2004, however, some of these samples were incomplete and updated with new data later on (between June 2004 and July 2005). This new information was included in the delivery of Forsmark 2.1 data freeze (July 2005). The samples and chemical data included in this data freeze were shown in the previous report /SKB 2006b/.

Groundwaters in Forsmark area were already divided into three groups in the SDM F1.2, based on their salinity: (1) **Saline groundwaters** with a brine signature, (2) **Brackish-saline groundwaters** with an important and relatively constant Littorina component and (3) **Non saline groundwaters**. The new samples have confirmed this grouping and increased the number of samples in the more saline group (new samples with higher salinity). The mixing and reaction processes reported in SDM F1.2 have been also confirmed, except in the case of the redox control of the system. Data used in SDM F1.2 for redox modelling indicated that the redox state was mainly controlled by the sulphur system. New data of Eh loggings, redox pairs, solubility calculations and microbiological analysis have shown that an active sulphate-reduction process must have been effective in the past but it is very limited at present, at least in the 0–600 m depth range. In this situation, the iron system could be one of the main controllers of the redox state, but it is affected by oxygen intrusion problems.

In general terms the geochemical understanding of the site has improved with the new F2.1 data because: (1) they have supported previous findings from F1.2, and (2) they have also confirmed some of the predictions made in F1.2 based on the limited knowledge gathered up to then. The confidence concerning the three-dimensional variability of processes and properties has also improved due to the addition of both new data in previously drilled boreholes and new boreholes in specific key areas. Thus, the new data have allow to produce a more detailed geochemical process modelling and redox description, which are presented here.

C2 Redox system modelling

Understanding the redox state is fundamental for safety requirements, since reducing conditions will help to guarantee that radionuclides are not transported to the biosphere in case of canister failure. Therefore, redox modelling is a key step during site investigation. The two possibilities suggested in previous studies about which are the main compositional variables influencing the redox state of the groundwaters, namely the iron system /Grenthe et al. 1992; section C2.3/ or the sulphur system /e.g. Nordstrom and Puigdomenech 1986; section C2.4/, have been revisited. However, due to the elevated dissolved uranium contents found in Forsmark, a specific analysis of this redox element and its relation to the rest of the redox elements is also presented in a separate section (section C2.5). Finally, the behaviour of manganese is described in the framework of the redox system in section C2.6.

Therefore, here we present a detailed description and discussion of the redox system including the geochemical characterisation of iron, sulphur, uranium and manganese. The section starts with an evaluation of the data and continues with a comprehensive modelling exercise including redox pairs analysis, some redox minerals solubility calculations, and the integration of these results with the available microbiological and mineralogical data.

C2.1 Presentation and selection of redox data

C2.1.1 Selection of representative Eh values

Physicochemical data from the Forsmark area, as compiled and supplied by SKB's geodatabase SICADA, have a different number of working Eh electrodes (from one to five) in the examined sections and the logging time is also rather variable. This facts clearly demonstrate the technical difficulties associated with the determination of Eh in groundwaters even with the sophisticated SKB methodology.

We decided to re-analyse all the available continuous logs from the Forsmark area in order to select a high-quality Eh and pH subset based on a common and well defined set of criteria. The aim of this exercise is to create an Eh database as complete as possible which can be used for geochemical modelling. For a more detailed description of the SKB methodology and the problems associated with the potentiometrically measured Eh, /see Auqué et al. 2007 submitted/.

The selection of an Eh value for an specific borehole section must be based on a very careful analysis of the results obtained with the three different electrodes (Au, Pt and C) both at depth and at the surface, the logging time, the pH, the conductivity, and the dissolved oxygen values. The basic requirement is that the measured potential correspond to the equilibrium potential and this fact can only be demonstrated if the different electrodes give coincident results. Ideally, the values selected as representative should only be those obtained simultaneously by the six electrodes within a small Eh range (± 50 mV) over a long period of time. However this criterion is excessively restrictive as there can be undesirable effects selectively affecting one electrode or the other, or technical problems affecting one of the two measurement cells (downhole or at the surface) that can reduce the number of active electrodes /Auqué et al. 2007 submitted/.

Taking into account all these issues, we decided to apply the following selection criteria:

- logs longer than a week (logging times of selected representative values are between 13 and 68 days),
- logs with stable and coincident readings (in a range smaller than 50 mV) by several electrodes in the long term; and
- logs with simultaneous and stabilised pH values (in order to minimize the uncertainty associated with the pH).

The sets of Eh logs that fulfilled these criteria were then checked for the quality of the redox values. We defined two groups of representative Eh values depending on the number of electrodes giving coincident readings:

- Group 1 Eh values: stable and coincident readings in, at least, three electrodes, two of them at depth.
- Group 2 Eh values: stable and coincident readings in two electrodes, at depth or at the surface.

This grouping reflects the difference in the quantity and quality of the information used to define the representative Eh value. Group 1 includes Eh values with more complete information and based on readings at depth, which are, in principle, more reliable. Group 2 includes good quality values but limited in reliability by frequently interrupted logs, different recording times for each electrode, or other technical difficulties.

There are 14 sets of logs in the Forsmark area corresponding to 14 different packered sections in 6 boreholes (KFM01A, 02A, 03A, 04A, 05A, 06A), ranging in depth from 110 to 950 m. Seven of them passed the initial selection criteria and six of them were included in Group 1 (only one log was included in Group 2, see Table C2-1). The retained and eliminated Eh values agree very well with the recommendations suggested in the specific P-reports where the hydrochemical characterisation of each borehole is summarised /Wacker et al. 2003, 2004abc, 2005abc/.

This set of high-quality Eh values has been used to analyse the redox state of the groundwater system, plotting their distribution against depth and pH and using them in the geochemical modelling. For this last task, complementary information from redox pairs, solubility calculations and microbiological data has also been used.

C2.1.2 Selection of samples for redox modelling

As it was already advanced in /SKB 2006a/, one of the main problems affecting the available samples is the high percentage of drilling water in most of them, lower than 10% but usually higher than 1% (the maximum recommended value; e.g. /Wacker et al. 2004ab/. In spite of the important efforts made by the Site Characterisation team, this problem has persisted in the sampled sections during Forsmark 2.1 datafreeze. As a consequence, the number of samples useful for redox modelling is very small (only three samples with less than 1% drilling water, see Table C2-2).

Table C2-1. Eh values selected in this work and in previous works in Forsmark area where SKB methodology has been used. Except the value corresponding to KFM03A between 639 and 642 m depth, (which has been considered a Group 2 value), the rest of the values are Group 1 values. The pH values correspond to the values selected from Chemmac logs, down-hole or surface, considering logs longer than a week and with stable and coincident readings.

Area	Borehole	Borehole length (m)	Depth (m) (elevation secmid coordinate)	Eh value (mV)	pH value this work
Forsmark	KFM01A	110–120	–112	–195	7.65
		176–183	–176	–188	7.41
	KFM02A	509–516	–503	–143	6.93
	KFM03A	448–455	–442	–176	7.27
		639–646	–632	–196	7.48
		939–946	–931	–245	7.53
KFM06A	353–360	–302	–155	7.33	

Table C2-2. Important chemical and physicochemical parameters for the selected samples in the Forsmark area. The last four rows show the four samples taken from the next data freeze and used in this work.

Bore-hole KFM	Sample	Depth (m) (elevation secmid)	pH	Eh	Cl	Alk	SO42-	Fe ²⁺	Mn	S ²⁻	U (·10 ⁻³)	CH ₄ (ml/l)	DOC	% Drilling water
01A	4538	-112	7.65	-195	4,563	61.0	315.6	0.953	0.691	0.014	1.51	-	1.5	0.76
	4724	-173	7.41	-188	5,329	99.0	547.0	0.475	1.02	bdl	14.9	0.12	2.3	4.80
02A	8016	-503	7.0	-143	5,410	126.0	498.0	1.84	2.16	bdl	88.6	0.04	2.1	6.77
03A	8017	-442	7.29	-176	5,430	91.8	472.0	0.919	1.17	bdl	2.21	-	1.2	0.25
	8273	-632	7.48	-196	5,430	22.0	197	0.223	0.319	bdl	46.1	0.07	1.6	4.35
	8281	-931	7.4	-245	8,560	9.0	73.9	0.208	0.144	0.06	0.7	0.06	1.5	8.75
	8152	-978	8.0		9,690	6.0	46.7	0.026	0.01	0.033	0.45	0.05	1.4	3.85
04A	8267	-197	7.36		5,580	111.0	514.0	2.12	2.81	bdl	62.0	-	1.4	7.45
06A	8808	-302	7.35	-155	4,850	47.7	157.0	1.1	0.621	bdl	9.6	-	bdl	7.0
	8785	-645	8.31	-	7,080	5.72	35.5	0.051	0.08	0.022	-	0.09	1.6	1.55
07A	8879	-760	8.04		14,800	6.19	99.3	0.162	0.127	0.171	0.184	0.04	bdl	0.35
02A	12002	-418	7.36		5,440	96.5	435	1.36	1.84	0.058	25.9	-	1.2	2.85
	12004	-495	7.19		5,540	126.0	507.0	2.26	2.07	0.066	122.0	-	1.5	3.80
03A	12001	-631	7.49		5,640	33.7	230.0	1.06	0.51	0.71	45.2	-	1.4	5.27
	12005	-969	-	-	10,500	10.7	47.0	1.36	0.089	0.84	0.27	-	13.0	2.80

The estimation of the undisturbed concentration of the redox elements (such as Fe²⁺, S²⁻, etc) from the composition of the drilling water and the percentage of mixing is very difficult because, apart from the effects due to mixing, different reequilibria can be over-imposed.

Drilling water could contain some oxygen despite efforts to remove it before injection down-hole. In some sections (e.g. KFM04A at 230–237 m, or KFM03A at 448.5–455.6 m borehole length), apart from a high percentage of drilling water, low although measurable oxygen levels have been measured by Chemmac continuous logging. Even corrosion of the drilling material has locally been reported /Wacker et al. 2004a/. However, in most studied sections Chemmac measurements fail to detect any trace of oxygen over the measurement period.

Small amounts of oxygen, incorporated with the drilling water or by direct contamination through air, can produce important changes in the redox system of the groundwaters, although they are not detectable during Chemmac logging. These modifications could produce the precipitation of ferric oxyhydroxides /Grenthe et al. 1992/, the depletion of S²⁻ concentrations, the removal of uranium (if uranium mineral phases are present), etc.

As a trade-off between quality and quantity, we decided (as in previous phases, /SKB 2006b/) to work with *samples with less than 10% of drilling water*. This means accepting a level of uncertainty on the original redox characters of the system but, at least, we are able to study whether the mentioned alterations have occurred and their possible effects on the undisturbed conditions. So, for this modelling exercise samples with less than 10% of drilling water and enough redox data were selected (Table C2-2). This includes Eh and pH data from continuous loggings (selected with the criteria described above), analytical data for Fe²⁺, U, S²⁻ and CH₄, and microbiological information.

The selected samples cover a wide range of depths (from 110 to 950 m; Table C2-2) and represent two different water types in the Forsmark groundwater system: most selected samples belong to the group of brackish-saline groundwaters (Cl = 4,500–5,500 mg/L) with an important Littorina signature, distributed from 110 to 630 m; the remaining samples correspond to the

deepest and more saline groundwaters (from 760 to near 1,000 m) representative of the group with a more important brine component.

Due to the smallness of the dataset (after applying all the above quality criteria), we have included *four samples from the next Datafreeze* (samples 12001, 12002, 12004 and 12005, part of the September, 2006, 2.2 Phase). Explicit indication of the use of these additional samples is acknowledged in the corresponding sections and graphs (with a different symbol or colour).

C2.2 General trends of redox data

Eh values in Forsmark range from -140 and -250 mV (Figure C2-1, panel a). The lack of very reducing values has nothing to do with the Eh selection criteria. It may be a sampling bias that could disappear as more samples are analysed.

As is obvious from the figure, the number of Eh values is not enough to obtain definitive conclusions, but some preliminary comments are worth including. The distribution of Eh with depth (Figure C2-1, panel b) do not seem to clearly show the trend observed in other crystalline systems (such as Palmottu -Finland, or Lac du Boneth batholith -Canada; /Blomqvist et al. 2000, Gascoyne, 1997, 2004/) and in most aquifers elsewhere, where a marked decrease of redox potential is observed as the residence time and depth of the waters increase /Drever 1997/. In this system the highest Eh values are found between 300 and 500 m depth, being more reducing both in shallower and deeper waters.

This fact could be the result of a modification in the original redox state in some groundwaters (see below) but it can also be the consequence of the complex hydrological setting and paleohydrogeological evolution of the Forsmark area, with both sub-vertical and sub-horizontal hydraulic structures and the presence of pockets and lenses of old sea water isolated in the bedrock. More data are needed in order to delimit better these two possibilities.

Samples in an Eh-pH diagram (Figure C2-1, panel a) are located in a clearly reducing zone but, as a whole, noticeably less reducing than the values found in Laxemar up to now (Figure C2-4, section C2.3.1). In any case, the position of most of the selected Forsmark samples in the Eh-pH diagram coincide with the range defined by /Drever 1997/ for groundwaters buffered by sulphate-reduction (Figure C2-1, panel a and Figure C2-4), as it also happens in Laxemar. These mildly reducing conditions dominant in Forsmark groundwaters are the cause of the poor results that are obtained when using the /Grenthe et al. 1992/ calibration for the electroactive redox pair $\text{Fe}(\text{OH})_{3(s)}/\text{Fe}^{2+}$. This was already reported in the Forsmark 1.2 phase report /SKB 2005/ and is described in depth below.

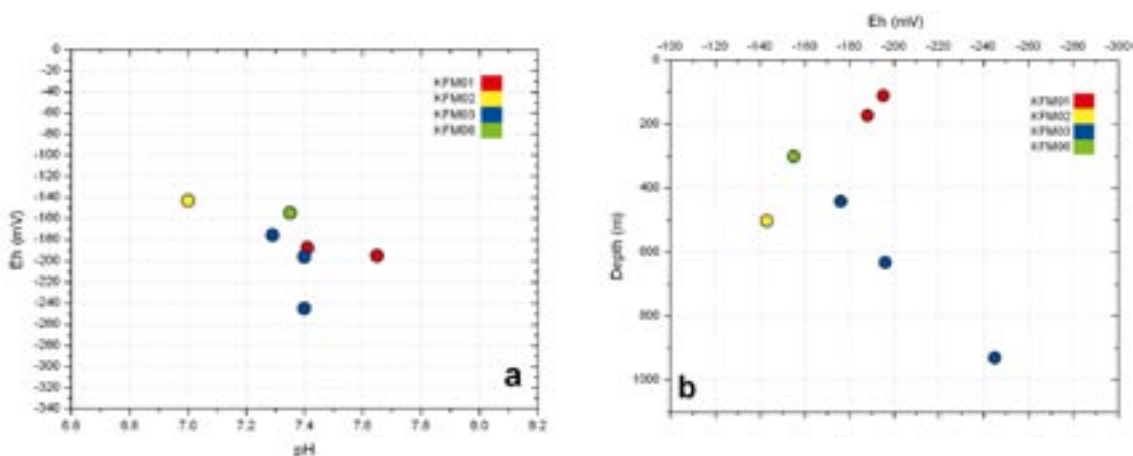


Figure C2-1. (a) pH-Eh plot for the Forsmark area groundwaters. (b) Eh distribution with depth in the Forsmark area groundwaters.

Iron, manganese, sulphide and uranium concentrations do not show a clear trend with chloride (Figure C2-2, panels a, b, c, d). This is mainly due to the wide range of concentrations of these elements in Littorina-rich groundwaters with 5,500 mg/L of chloride, where also the maximum concentrations are found. The samples taken from the next data freeze confirm this behaviour for S^{2-} (Figure C2-2, panel c). Some non-redox major ions also show this peculiar distribution /SKB 2005/. The identification of the cause for such a distribution is the fundamental goal of this report (see also Chapter C3).

Apart from the lack of a clear depth dependence, the concentration of iron, manganese, sulphide and uranium do show some regularities worth mentioning (Figure C2-3). Fe^{2+} and Mn^{2+} follow roughly parallel trends, with variable but high concentrations between 100 and 600 m (in waters with a high Littorina proportion), and low concentrations in deeper and more saline waters (Figure C2-3, panels a and b). Also remarkable is the high Mn^{2+} content of some brackish groundwaters.

S^{2-} contents from the surface to 600 m depth are very low (or below detection limit) and increase from there downwards (Figure C2-3, panel c). It is interesting to notice the change in behaviour that implies the introduction of the new samples of the next datafreeze, with the highest S^{2-} contents at 630 m depth (sample 12001, 0.7 mg/l) and at 969 m (sample 12005, 0.84 mg/l; Table C2-2).

As for uranium (Figure C2-3, panel d), it shows variable concentrations but usually high (up to 0.122 mg/l) at depth between 100 and 650 m, again in those waters with a high Littorina percentage. In deeper waters U concentrations decrease drastically.

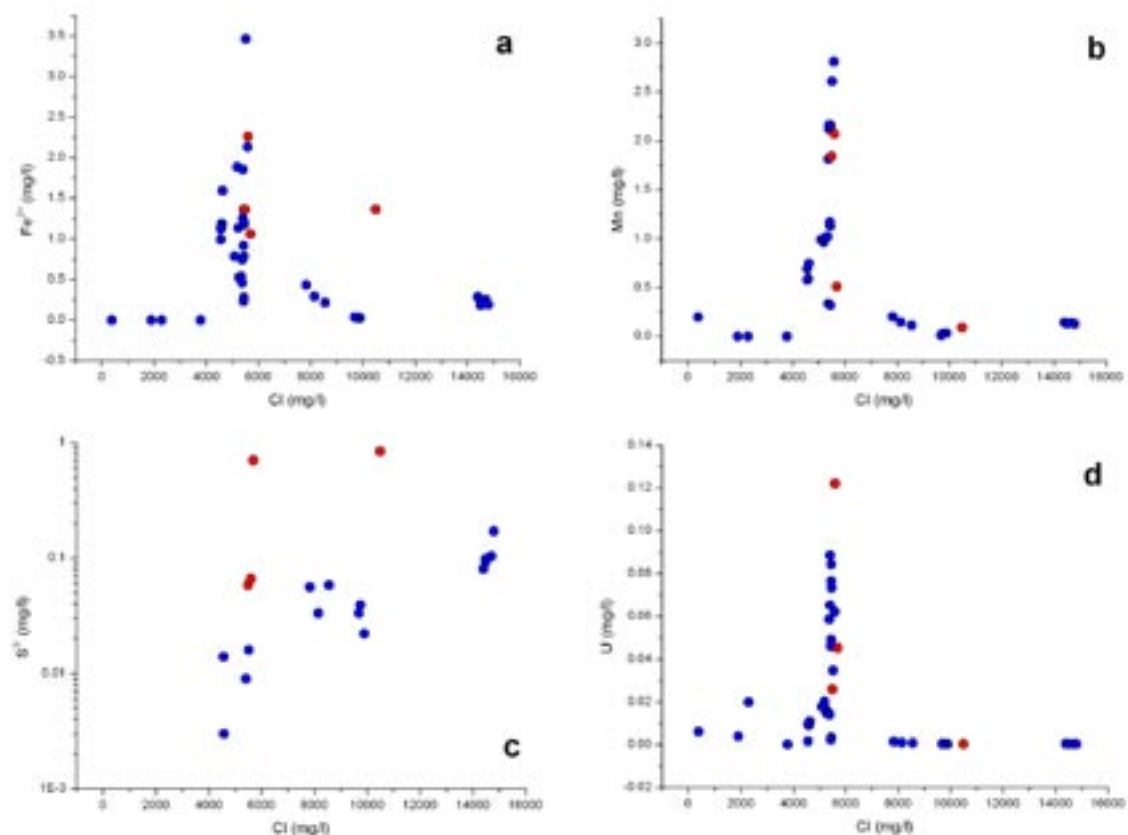


Figure C2-2. Redox elements distribution with chloride in the Forsmark area groundwaters. (a) Ferrous iron; (b) Manganese; (c) Sulphide; and (d) Uranium. Samples taken from the next data freeze are represented as red circles in these plots and in the following figures.

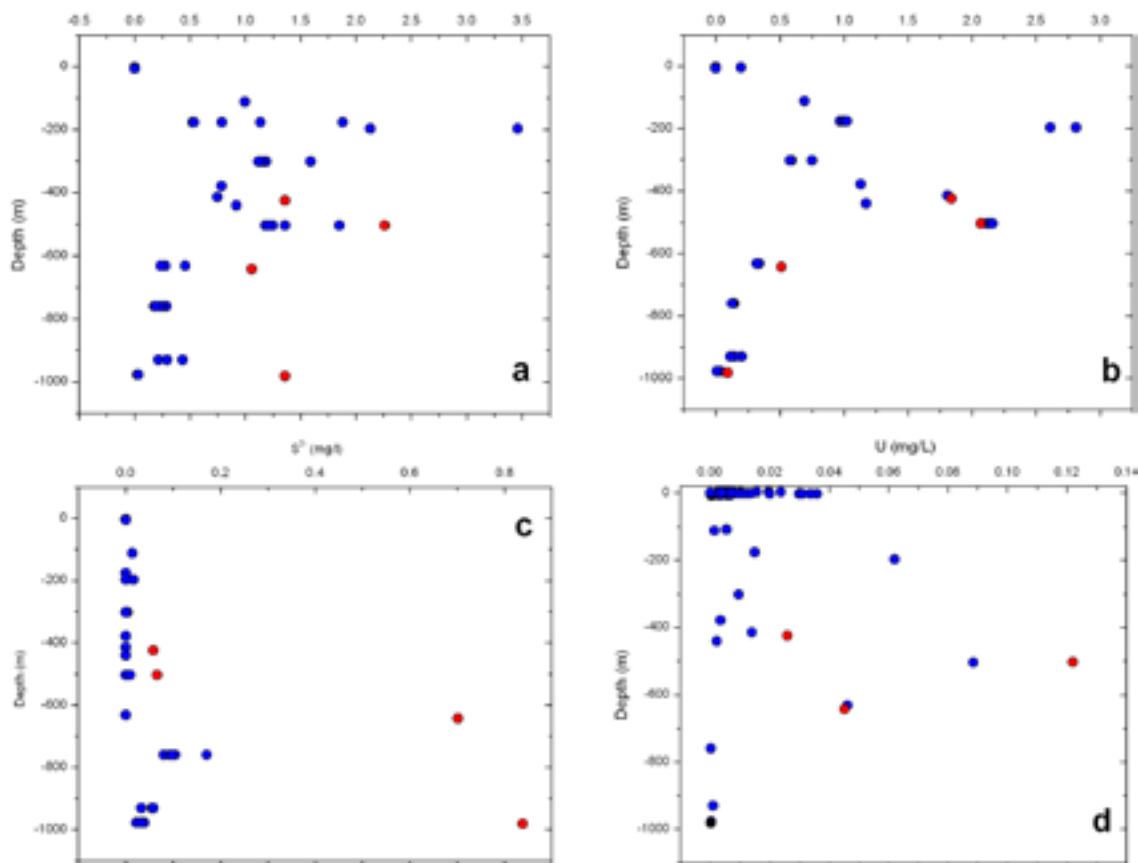


Figure C2-3. (a) Redox elements distribution with depth in the Forsmark area groundwaters. (a) Ferrous iron; (b) Manganese; (c) Sulphide; and (d) Uranium.

All these observations suggest that there is a depth range, around 600–700 m, where an important change in the dominant species or the components that buffer the redox system occurs. This change coincides with the transition from brackish, high *Littorina* waters (Cl^- between 4,500 and 5,500 mg/l) to more saline groundwaters ($\text{Cl}^- > 7,000$ mg/l), which is an indication of the existence of groundwater layers with different hydrochemical characters and different geochemical evolution.

In the following sections we analyse separately each one of the redox elements iron, sulphur, uranium, and manganese, as each of them have interesting particularities important for a comprehensive understanding of the natural system and the perturbations that could have affected it.

C2.3 Redox pair modelling and the iron system

The redox pairs that have been analysed here are: the dissolved $\text{SO}_4^{2-}/\text{HS}^-$ and CH_4/CO_2 redox pairs, and the heterogeneous couples¹ $\text{Fe}(\text{OH})_3/\text{Fe}^{2+}$, $\text{S}_{(\text{c})}/\text{HS}^-$, $\text{FeS}_{\text{am}}/\text{SO}_4^{2-}$ and pyrite/ SO_4^{2-} . These are the redox pairs that apparently have given better results in similar systems elsewhere in the Scandinavian Shield /Nordstrom and Puigdomenech 1986, Grenthe et al. 1992, Glynn and Voss 1999, Blomqvist et al. 2000, Pitkanen et al. 2004/. Most of them have already been used in previous works in Forsmark and Laxemar /e.g. SKB, 2004, 2005, 2006a/.

¹ The electroactive $\text{S}_{(\text{c})}/\text{HS}^-$ pair, although successfully used in other Swedish groundwaters /Nordstrom and Puigdomenech 1986/, systematically gives less reducing Eh values than those found in Forsmark. Therefore, their values have not been included in this study.

Calculations are performed with PHREEQC and the WATEQ4F database, except in the case of the heterogeneous pair $\text{Fe}(\text{OH})_3/\text{Fe}^{2+}$. Previous studies in Forsmark have shown that this pair, one of the few clearly electroactive, is extremely sensitive to the crystallinity of the solid oxyhydroxide used. A consequence of this is that /Grenthe et al. 1992/ calibration does not give good results in most Forsmark groundwaters /SKB 2005/. This problem is undertaken in detail here.

The Eh value given by the redox pair represented by the reaction



depends on the solubility of the oxyhydroxide phase used. This is equivalent to saying that it depends on the value of the equilibrium constant for the reaction



We have used three different sets of log K values for this reaction: (1) the set of values proposed by /Nordström et al. 1990/ included in WATEQ4F database (log K = 3 to 5, corresponding to amorphous- microcrystalline hydrous ferric oxides, HFOs, or ferrihydrites; Figure C2-5); (2) the value derived from the calibration proposed by /Grenthe et al. 1992/ for a wide spectrum of Swedish groundwaters (log K = -1.1 for a crystalline phase such as hematite or goethite); and (3) the value of log K = 1.2 defined by /Banwart 1999/ using the same methodology as /Grenthe et al. 1992/ but working with groundwaters from the Äspö large-scale redox experiment².

C2.3.1 Results

Results are summarised in Table C2-3 and Figure C2-4. As it was already reported in /SKB 2005/ the results obtained with the $\text{Fe}(\text{OH})_3/\text{Fe}^{2+}$ redox pair considering a microcrystalline $\text{Fe}(\text{OH})_3$ are much more oxidising than the measured ones, and they are not included in the table. The Eh calculated with the $\text{Fe}(\text{OH})_3/\text{Fe}^{2+}$ redox pair and Grenthe's calibration agree well with the single Eh value measured in the deepest sample (sample 8281, Table C2-3). For the rest of the samples considered, all brackish groundwaters ($\text{Cl}^- = 4,500\text{--}5,500$ mg/l), this calibration gives values more reducing than the measured ones.

On the contrary, the Eh calculated with the same redox pair and Banwart's calibration coincides reasonably well with all measured values in brackish groundwaters but not with the deepest one (sample 8281; Table C2-3). This fact suggests that the redox state of these two kinds of groundwaters can be controlled by different iron oxyhydroxides (or by iron oxyhydroxides with a different degree of crystallinity).

Sulphur redox pairs show, in general, a good agreement with the potentiometrically measured Eh values (Table C2-2; Figure C2-4). There are only three values for the $\text{SO}_4^{2-}/\text{HS}^-$ redox pair (comparable with Chemmac; Table C2-3) and some of the dissolved sulphide content is between the detection and the reporting limit /e.g. Wacker et al. 2004b/. However there is a surprisingly good agreement between the potentiometrically measured Eh and the values calculated using the *non-electroactive* $\text{SO}_4^{2-}/\text{HS}^-$ pair.

This unexpected agreement was already pointed out by /Glynn and Voss 1999/ for some Laxemar groundwaters and has repeatedly been mentioned in later studies /SKB 2004, 2005, 2006 in press/. The frequent and proved occurrence of sulphate reducing bacteria in Laxemar groundwaters suggests that the electrodes could be responding to sulphur species generated during sulphate-reduction /SKB 2006b/. Nevertheless, the activity of this kind of bacteria in Forsmark groundwaters is much lower than in Laxemar (see below).

² The equilibrium constant for reaction (1) was obtained by /Banwart 1999/ using the same methodology as /Grenthe et al. 1992/ with groundwaters from the Äspö large-scale redox experiment sampled during three years. In this project, a vertical fracture zone exposed during the works at the tunnel entrance was used to study the performance of the geological system to buffer groundwater redox conditions against an intrusion of dissolved O_2 /Banwart et al. 1994, Banwart 1999/.

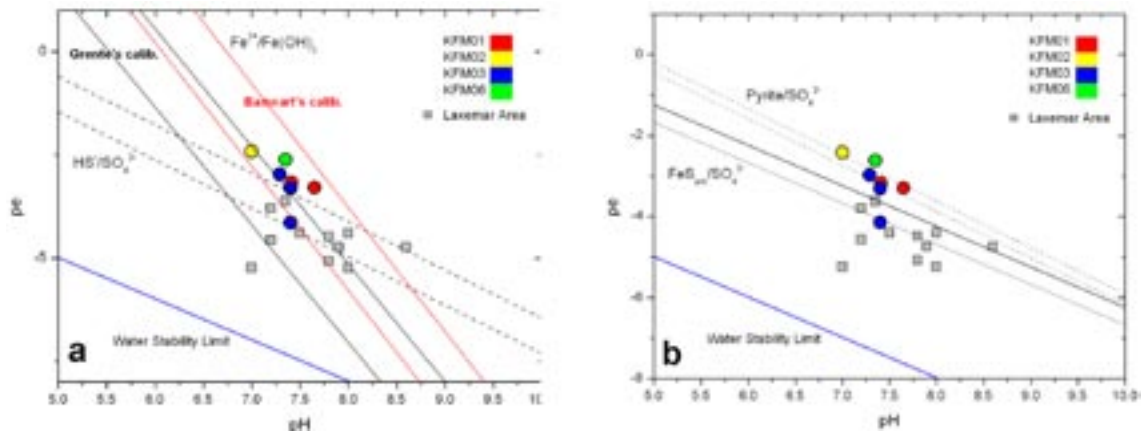


Figure C2-4. Eh-pH diagram showing the measured Eh and pH of the selected samples in Forsmark. Boundaries for $\text{Fe}^{2+}/\text{Fe}(\text{OH})_3$, $\text{SO}_4^{2-}/\text{HS}^-$ (panel a; solid black and red lines and dashed black lines, respectively) and $\text{SO}_4^{2-}/\text{FeS}_{(\text{am})}$ and $\text{SO}_4^{2-}/\text{pyrite}$ (panel b; dotted and solid black lines, respectively) are also shown for values of pH, Fe^{2+} , SO_4^{2-} and S^{2-} typical of Forsmark groundwaters. Data for the $\text{Fe}^{2+}/\text{Fe}(\text{OH})_3$ pair are from /Grenthe et al. 1992/ in black and from /Banwart 1999/ in red; data for the $\text{SO}_4^{2-}/\text{HS}^-$, $\text{SO}_4^{2-}/\text{pyrite}$ and $\text{SO}_4^{2-}/\text{FeS}_{(\text{am})}$ pairs are from the WATEQ4F database (last one corrected as explained in section C2.4.1) included in PHREEQC /Parkhurst and Appelo 1999/.

Table C2-3. Eh values for the selected samples in the Forsmark area. The potentiometrically measured values (column Chem) are shown for comparison with the values calculated with the different redox pairs. The last four rows show the four samples from taken from the next datafreeze and used in this work.

Borehole	Sample	Depth (m) (elevation secmid)	pH	Eh	SO_4/HS^-	$\text{SO}_4/\text{Pyrite}$	$\text{SO}_4/\text{FeS}_{\text{am}}$	CO_2/CH_4	$\text{Fe}^{2+}/\text{Fe}(\text{OH})_3$	
									/Grenthe et al. 1992/	/Banwart 1999/
KFM01A	4538	-112	7.65	-195	-200	-195	-235	-	-315	-221.8
	4724	-173	7.41	-188	-	-178	-221	-217	-257	-164.6
KFM02A	8016	-503	6.93	-143	-	-149	-193	-194	-221	-128.7
	8017	-442	7.29	-176	-186*	-170*	-212*	-	-253	-160.51
KFM03A	8273	-632	7.48	-196	-	-181	-225	-230	-235	-158.0
	8281	-931	7.4	-245	-214	-187	-229	-241	-236	-142.8
	8152	-978	8.0	-	-254	-232	-273	-282	-286	-193.1
	8267	-197	7.36	-	-	-173	-213	-	-285	-192.6
KFM06A	8808	-302	7.35	-155	-	-177	-218	-	-268	-174.9
	8785	-645	8.31	-	-263	-253	-290	-294	-355	-261.5
KFM07A	8879	-760	8.04	-	-253	-229	-267	-277	-358	-244.3
KFM02A	12002	-418	7.36	-	-191	-174	-215	-	-274	-182
	12004	-495	7.19	-	-180	-161	-203	-	-258	-166
KFM03A	12001	-631	7.49	-	-209	-185	-226	-	-290	-198
	12005	-969	-	-	-	-	-	-	-	-

* The calculations for this sample have been performed using the value of 0.031 as it is indicated in Table C2-4.

Eh values obtained by the pyrite/ SO_4^{2-} redox pair are also in agreement with the measured values in brackish groundwaters, but not with the value measured in the deepest sample (Table C2-3; Figure C2-4, panel b). The results obtained with the $\text{FeS}_{\text{am}}/\text{SO}_4^{2-}$ redox pair do not show as good an agreement as the previous one, in contrast with what happens in Laxemar /SKB 2006b/, where the Eh values derived from this pair are, in general, in better agreement (Figure C2-4, panel b) than the values calculated with the pair pyrite/ SO_4^{2-} .

Finally, Eh values obtained with the non-electroactive pair CH_4/CO_2 are in fairly good agreement with the measured ones (inside a range of ± 50 mV), as values obtained with the sulphur pairs are /as in Laxemar, SKB, 2004, 2006a/. However, very few data on the activity of methanogenic bacteria are available in Forsmark so far.

C2.3.2 Discussion

The redox potential measured in the deepest groundwaters in Forsmark, has only one data point (KFM03A, at 930 m depth, Table C2-3) but is the most reducing in the system and is in agreement with the value obtained in the calibration by /Grenthe et al. 1992/. This suggests that the Eh value of these groundwaters is in equilibrium with a crystalline iron oxyhydroxide such as goethite or, more probably, hematite. This is consistent with the reducing character and long residence times of these groundwaters, where low crystallinity phases are not expected /SKB 2004 and references therein/.

The remainder of the Eh values have been determined in brackish groundwaters at depths between 110 and 646 m. These seem to be controlled by the occurrence of an iron phase with an intermediate crystallinity (Figure C2-5) such as the one considered by /Banwart 1999/ in the Äspö large-scale redox experiment. This finding has important consequences.

The natural occurrence of an iron oxyhydroxide with this degree of crystallinity is difficult to justify in groundwaters with a long residence time. The brackish groundwaters with a high percentage of the Littorina end member may indicate the existence of pockets isolated from the hydrogeological system and, therefore, with an estimated residence time of, at least, thousands

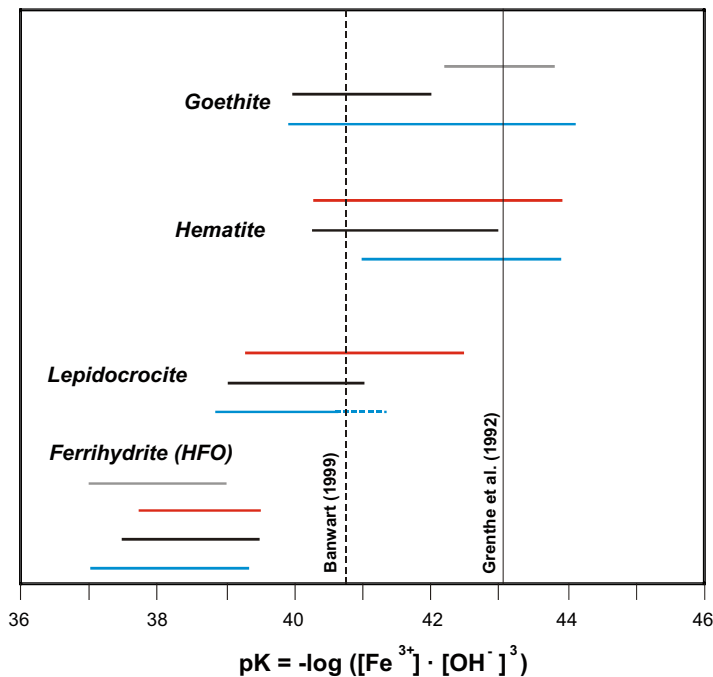


Figure C2-5. Reported solubility ranges at 25°C for the main ferric oxyhydroxides. Blue lines represent the ranges obtained by /Langmuir 1969, 1997/; black lines correspond to the values suggested by /Appelo and Postma 2005/ from an analysis of /Cornell and Schwertmann 2003/ data; red lines represent the ranges reported in /Bonneville et al. 2004/; and, finally, grey lines represent the range of values proposed by /Nordstrom et al. 1990/. The most recent solubility ranges obtained by /Majzlan et al. 2004/ for 2-line and 6-line ferrihydrite (HFO: hydrous ferric oxyhydroxides; values between 37.5 and 39.5) coincide with the ranges shown in the plot for this phase. The values reported by /Macalady et al. 1990/ for goethite ($pK=44.15$) and hematite ($pK=44.0$) are in agreement with the less soluble extreme of the range shown in the plot for these minerals. Empirical values deduced by /Grenthe et al. 1992/ ($pK=43.1$) and /Banwart 1999/ ($pK = 40.8$) for different Swedish groundwaters are also indicated.

of years. The recrystallization kinetics of poorly crystalline ferric oxides, towards the more crystalline and stable phases, can be very fast, in the order of days to years, when the groundwaters are alkaline, reducing /Houben 2003, Schwertmann and Murad 1983, Stipp et al. 2002/ and have high contents of Fe²⁺ /Pedersen et al. 2005/.

However, oxygen intrusion in reducing media usually induces the precipitation of amorphous phases³ (ferrihydrites or hydrous ferric oxides, /Langmuir 1997/), with a pK between 37 and 39 (Figure C2-5). As it has previously been pointed out, these phases quickly recrystallize to less soluble and more stable phases when the reducing conditions return.

Therefore, as /Banwart et al. 1994/ reported in the Äspö large-scale redox experiment, the presence of an intermediate iron oxyhydroxide with higher solubility than a crystalline phase is possible in these brackish groundwaters if there is a brief oxidizing disturbance.

All this would support the occurrence of oxygen intrusion, already suspected in some of the P-reports on the borehole hydrochemical characterization /e.g. KFM03A; Wacker et al. 2004b/ in spite of the absence of measurable oxygen concentrations in the Chemmac loggings. Moreover, the occurrence of an oxyhydroxide of intermediate crystallinity would indicate that the system is still evolving and compensating for the effects of the intrusion of oxygen.

There is no clear and systematic relationship between high drilling water contents in the brackish groundwater samples and the Eh control by intermediate-crystallinity oxyhydroxides (Appendix C). Therefore, the perturbation of the system could be also related to atmospheric air contamination. However, independent to the mechanism, this perturbation seems to affect only the brackish groundwaters⁴. This fact suggests that the original conditions of these waters and/or the lithological-hydrogeological system with which they are associated, must have some characteristic that makes them more susceptible.

In summary, it is difficult to assess the effects that oxygen contamination could have had on the redox system which, moreover, seems to be re-equilibrating and compensating for its effects. Dissolved sulphide could have also been affected; in fact, its contents in most of the Forsmark groundwaters are very low, notwithstanding the good results obtained with sulphur redox pairs.

C2.4 The sulphur system in Forsmark groundwaters: solubility calculations

The study of groundwater saturation states with respect to the more soluble iron monosulphides (amorphous and crystalline) can be used as an indicator of the intensity of SRB activity. The formation of these phases could be represented by the reaction



considering HS⁻ as the dominant species in waters with pH values higher than 7. Formation of monosulphides requires a source of iron and sulphate-reducing activity to supply the dissolved sulphide.

³ This is what happened in the Äspö underground laboratory when reducing groundwaters were put in contact with the oxygen-rich atmosphere of the tunnel. There, *bacteriogenic iron oxides* (BIOS) formed by ferrihydrite are precipitated /Ferris et al. 1999, Martínez et al. 2004/. It has also been observed by /Trotignon et al. 2002/ in an experiment carried out in the framework of the REX Project on the effect of oxygen intrusion in a reducing media, where they deduced a pK value of 38 for the precipitated oxyhydroxide.

⁴ The single saline sample with a representative Eh value (8281, Table C2-2) has 8.75 percent of drilling water, but the redox potential is controlled by a crystalline oxyhydroxide such as the one deduced by /Grenthe et al. 1992/ for a wide set of deep groundwaters in Sweden.

Accepting the occurrence of a source of iron, the intensity of the sulphate reduction process can be qualitatively determined using the specific monosulphide that is precipitated. The amorphous monosulphide is the first phase that typically precipitates in most natural aqueous systems. It is the most soluble of the iron sulphides ($\log K = -3$ for reaction 3), but its precipitation kinetics is very fast /seconds; Rickard 1989, 1995/ when waters reach oversaturation with respect to it. Mackinawite (the crystalline monosulphide) is slightly less soluble ($\log K = -3.6$) and its precipitation kinetics is also fast /days; Rickard 1989/. It is also common to find this crystalline phase as a result of the recrystallisation of amorphous monosulphides, which is also a very fast⁵ process, and affects the composition of the solution in contact.

Therefore, the identification of equilibrium states with respect to amorphous monosulphides (as happens in some subareas from Laxemar; /SKB 2006b/) indicates a continuous supply of H_2S to the system, enough to put waters over the solubility product of this phase and to produce its fast precipitation. Moreover, it indicates that the supply of H_2S , and therefore the sulphate-reducing activity, is taking place at present: if the dissolved sulphide supply finishes, the already formed amorphous monosulphides would quickly recrystallise to mackinawite and waters would reequilibrate to the activity product of mackinawite /Chen and Liu 2005/.

Previous results in Forsmark groundwaters indicated the occurrence of an equilibrium situation with respect to monosulphides /SKB 2005/. However, during the Site Investigation Program at Laxemar /SKB 2006b/ several errors were detected in the solubility constants of amorphous iron monosulphides and mackinawite in the PHREEQC.dat and WATEQ4F.dat databases distributed with PHREEQC /Parkurst and Appelo 1999/ and in the WATEQ4F code /Ball and Nordstrom 2001/.

Therefore, in this section the analysis of the saturation state of the groundwaters with respect to monosulphides (amorphous and crystalline) is revisited in order to check with the new solubility constants whether monosulphide precipitation is feasible in Forsmark.

C2.4.1 Methodology for monosulphide solubility calculations

The samples selected for calculations were those with a continuous logging of temperature, pH and Eh. Several additional samples were also selected with analytical data of dissolved S^{2-} and Fe^{2+} and in situ pH value, including some samples taken from the next data freeze (to be delivered in September 2006) with the highest S^{2-} concentrations found so far (Table C2-4). All the selected samples have a charge balance lower than 5%.

The samples belong to two types of waters: sulphidic and non sulphidic. Obviously, the more interesting for modelling purposes are those with a sulphidic signature, indicated by a total dissolved sulphide concentration ($S^{2-}_{(tot)} = S^{2-} + H_2S + HS^- +$ polysulphides, hereinafter S^{2-}) above the detection limit. This point has been carefully managed. Special attention has been paid to the detection limits and analytical uncertainties associated to dissolved Fe^{2+} and S^{2-} , as they are fundamental in the evaluation of the saturation state of the waters with respect to iron monosulphides.

In the more recent SKB's P-reports the detection limit for S^{2-} is 0.01 mg/l although usually a reporting limit of 0.03 mg/l is recommended. The reporting limit for Fe^{2+} is 0.02 mg/l. In the sulphidic samples iron concentration is well above detection limit. There are only three clearly sulphidic samples (samples 8879, 12001 and 12005, with high S^{2-} concentrations; Table C2-4), several samples with low but significant S^{2-} concentrations, and another group of samples whose S^{2-} concentration are in the 0.01–0.03 mg/l range. For these last samples a concentration of 0.03 mg/l has been used for calculations (Table C2-4).

⁵ This recrystallisation starts in few days and can be completed in two years /Rickard 1995, Wilkin and Barnes 1997ab/. More recent works suggest that the recrystallisation time is shorter. For instance, the ripening experiments performed by /Benning et al. 2000/ on amorphous monosulphides indicate that mackinawite transformation occurs in less than three months and waters in contact reach a solubility product of $\log K = -3.7$.

Table C2-4. Redox information for sulphur, uranium and manganese system analysis. pH and Eh values correspond to Chemmac values. Measured sulphide (S²⁻) concentrations are indicated together with the values used for calculations (S²⁻ for calc.). Column “Water type” classifies waters as sulphidic (S) or non-sulphidic (N S; see the text). SRB and MRB contents (MPN in cell/ml) have been taken from Hallbeck (this volume).

Bore-hole KFM	Depth (m) (elevation secmid)	Sample	pH	Eh	Fe ²⁺	Mn	U (·10 ⁻³)	S ²⁻	S ²⁻ (for calc.)	Water type	δS ³⁴	SRB (MPN)	MRB (MPN)	% Drilling water
01A	-112	4538	7.65	-195	0.953	0.691	1.51	0.014	0.03	S	25.5	1.2	3,000	0.76
	-173	4724	7.41	-188	0.475	1.02	14.9	bdl	0.03	N S	25.6	0.2	< 0.2	4.80
02A	-503	8016	7.0	-143	1.84	2.16	88.6	bdl	0.03	N S	24.9	1.4	< 0.2	6.77
03A	-442	8017	7.29	-176	0.919	1.17	2.21	bdl	0.031	S	25.4	17	70	0.25
	-632	8273	7.48	-196	0.223	0.319	46.1	bdl	0.03	N S	27.8	30.0	1.7	4.35
	-931	8281	7.4	-245	0.208	0.144	0.7	0.06	0.06	S	27.3	5,000	1.2	8.75
	-978	8152	8.0	-	0.026	0.01	0.45	0.033	0.033	S	29.6	24.0	< 0.2	3.85
04A	-197	8267	7.36	-	2.12	2.81	62.0	bdl	0.03	N S	24.5	-	-	7.45
06A	-302	8808	7.35	-155	1.1	0.621	9.6	bdl	0.03	N S	27.5	0.8	13	7.0
	-645	8785	8.31	-	0.051	0.08	-	0.022	0.03	S	38.4	0.4	0.2	1.55
07A	-760	8879	8.04	-	0.162	0.127	0.184	0.171	0.171	S	22.4	< 0.2	4.9	0.35
02A	-418	12002	7.36	-	1.36	1.84	25.9	0.058	0.058	S	22.5	-	-	2.85
	-495	12004	7.19	-	2.26	2.07	122.0	0.066	0.066	S	21.9	-	-	3.80
03A	-631	12001	7.49	-	1.06	0.51	45.2	0.71	0.71	S	25.1	-	-	5.27
	-969	12005	-	-	1.36	0.089	0.27	0.84	0.84	S	29.1	-	-	2.80

Some non-sulphidic waters are included in the calculations to test their equilibrium situation with respect to iron monosulphides. A value of 0.03 mg/l of dissolved S²⁻ has been also used (Table C2-4) in order to obtain a maximum estimation of the saturation index.

As mentioned above, during the Site Investigation Program at Laxemar /SKB 2006b/ several errors were detected in the solubility constants of amorphous iron monosulphides and mackinawite in the PHREEQC.dat and WATEQ4F.dat databases distributed with PHREEQC /Parkurst and Appelo 1999/ and in the WATEQ4F code /Ball and Nordstrom 2001/. The dissolution reaction for the two phases included in these databases is in the same form as reaction (3) with an equilibrium constant of log K = -3.91 for amorphous FeS and log K = -4.648 for mackinawite. /Ball and Nordstrom 2001/ indicate that these values come from the work by /Berner 1967/. /Chen and Liu 2005/ have demonstrated that the value included in these databases is the consequence of an error in the conversion of the reactions and thermodynamic data from /Berner 1967/ to the format accepted by the databases (reaction 3). The correct value for amorphous FeS, as deduced from Berner's data, is log K = -2.98, that is, almost an order of magnitude larger.

The same error affects the equilibrium constant of mackinawite /SKB 2006b/. Manipulating the reactions and the thermodynamic values proposed by /Berner 1967/ to obtain the equilibrium constant of reaction (3), the resulting value is log K = -3.6, and not log K = -4.648 as the database reflects⁶.

⁶ This error is also found in the MINTEQ.dat database distributed with PHREEQC /Parkhurst and Appelo 1999/. However, the newest version of this database, MINTEQ.v4.dat, has the correct values for FeS(ppt) and mackinawite (log K = -2.95 and log K = -3.6 respectively). Note, however, that along with MINTEQ.v4.dat, the older version of the database is also distributed with PHREEQC, and there the solubility values are not corrected!

Therefore, the log K values for these phases have been corrected in the WATEQ4F database ($\log K = -3$ for amorphous iron monosulphide and $\log K = -3.6$ for mackinawite) in order to perform the solubility calculations. The uncertainty value used for the SI value of these phases is ± 0.4 units /SKB 2006b/.

C2.4.2 Results of solubility calculations

The results of saturation indexes are shown in Figure C2-6. They indicate a clear undersaturation of most studied waters with respect to the amorphous monosulphide (Figure C2-6, panels a, b), except for sample 12001 at 630 m depth, which is in equilibrium with this phase. The saturation state in the sample with the highest S^{2-} content (sample 12005 at 969 m depth; Table C2-4) has not been calculated due to problems with the pH value. However, as its Fe^{2+} and S^{2-} contents are similar to the ones of sample 12001, it would probably be in equilibrium with respect to the same amorphous phase.

Waters are also in general undersaturated with respect to mackinawite (Figure C2-6, panels c and d), although equilibrium situations are slightly more frequent than before. The equilibrium state obtained for some waters above 300 m depth (Figure C2-6, panel c) is not real, as these waters have a dissolved sulphide concentration below 0.02 (inside the reporting limit or below the detection limit) but the value used in calculations is 0.03 mg/l. The samples in “real” equilibrium with mackinawite are those with a sulphidic signature (sample 8879, at 760 m depth in KFM07A borehole $-S^{2-} = 0.17$ mg/L) and samples 12002 and 12004 in KFM02A at

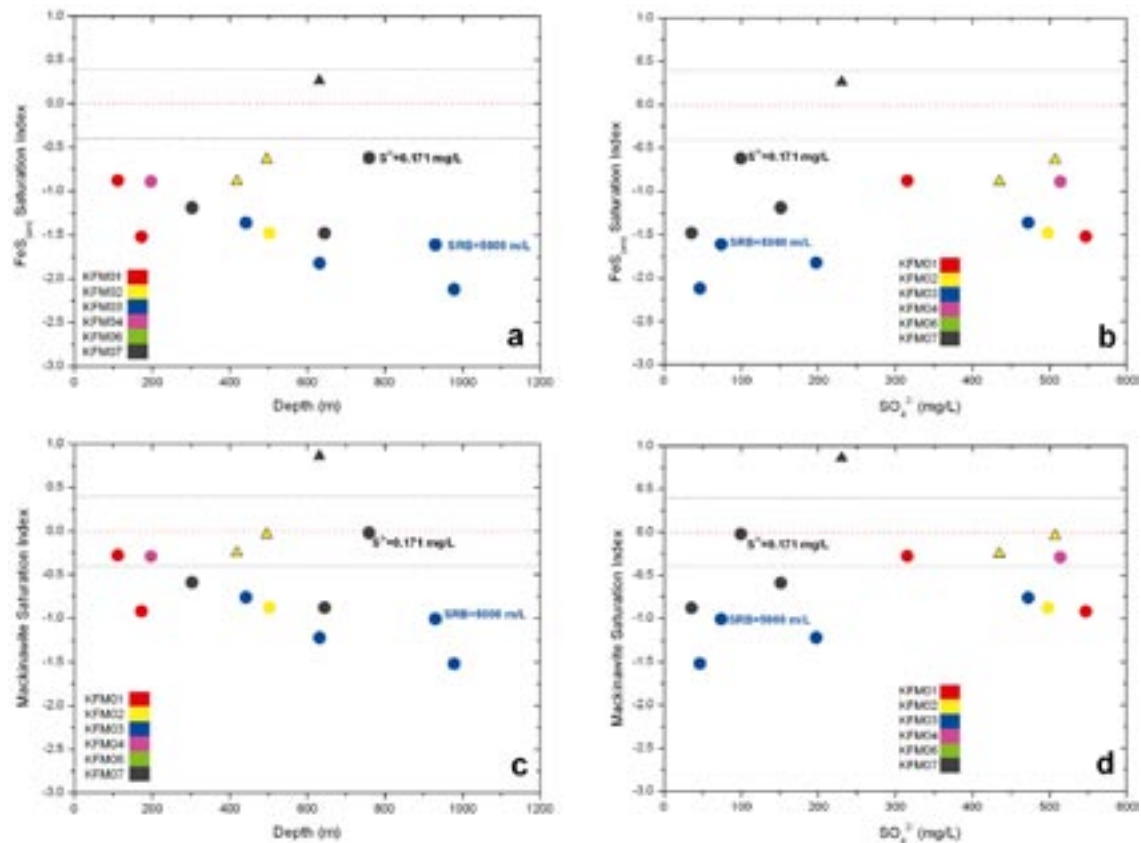


Figure C2-6. Saturation indexes for amorphous monosulphide (FeS_{am}) and mackinawite in the Forsmark groundwaters as a function of depth (a and c) and sulphate content (b and d). Triangles represent samples from the next data freeze (12001, 12002, 12004). The SRB in the only sample with significant values, are also indicated. The red dashed line and the shadow zone represent the $SI=0$ and the uncertainty range (± 0.4 for the $\log K$ indicated in the text).

418 and 495 m respectively; Figure C2-6, panels c and d). The occurrence of these equilibrium situations does not seem to be conditioned by the concentration of sulphate in waters (Figure C2-6, panels b and d).

This general situation is clearly different from what is observed in Laxemar /SKB 2006b/, where equilibrium with monosulphides is much more frequent in all the sampled depths. The occurrence of this equilibrium indicates a continuous (active today) supply of H_2S by SRB activity in agreement with the microbiological data. When dissolved Fe^{2+} (or a source for this component) is also present, waters become oversaturated with respect to the amorphous iron monosulphides and they can precipitate maintaining the equilibrium in the system (the precipitation rate is very fast in general, even instantaneous in neutral-alkaline conditions once its solubility product is attained; /Rickard 1989, 1995/). Therefore, the equilibrium observed in Laxemar waters corresponds to an iron monosulphide precipitation process active at present /SKB 2006b/.

The results obtained in Forsmark indicate, in contrast, that the active precipitation of iron monosulphide is much less important, mainly at depths between 100 and 600 m. This situation could be the result of: (1) a lower SRB activity, (2) the absence of a source of iron, or (3) the alteration of the pristine conditions in the groundwater system.

SRB activity together with the presence of an iron source has been demonstrated in many low temperature natural systems with active precipitation of sulphides. The predominance of one or the other is the responsible of the development of waters with high or low dissolved sulphide contents in spite of the SRB activity /Wilkin and Barnes 1997ab, Hurtgen et al. 1999 etc/. That is, SRB activity in an iron-poor medium leads to waters with high sulphide content; on the other hand, SRB activity in iron-rich environments could lead to waters with low sulphide contents due to iron monosulphide precipitation.

In most cases iron concentrations in Forsmark groundwaters are not specially low (Table C2-4). Moreover, there are evident and abundant sources of iron in the fracture fillings, mainly Fe-chlorites and hematite /Sandström et al. 2004, Sandtröm and Tullborg 2005/. Hematite has been identified in many of the studied fracture fillings. It appears in contents detectable by XRD or, more frequently, as micrograins in fracture fillings and is the responsible of the strong reddish colour /Sandström et al. 2004, Petersson et al. 2004, Sandstrom and Tullborg 2005/.

Therefore, as iron availability is not a limiting factor, it can be concluded that the frequent undersaturation with respect to the iron monosulphides is due to the low activity, or absence, of SRB or even to sampling problems. We will go into more detail in the following sections.

C2.4.3 SRB activity and geochemistry in Forsmark groundwaters

SRB microbiological results in Forsmark groundwaters are summarised in Table C2-4 (as the most probable number –MPN- of these micro-organisms). The number of boreholes and borehole sections studied here is high and it is noticeable the very low amounts of SRB detected so far: except in one case, the MPN for the SRB are lower than 30 cells/ml. This fact also indicates that, in general, sulphate-reduction activity is very low at present in Forsmark.

However, some interesting exceptions must be noticed in saline groundwaters. In sample 8281 at 931 m depth in borehole KFM03A, the MPN value for the SRB is significant (5,000 cell/ml; Table C2-4). However dissolved S^{2-} is very low (0.06 mg/l, sample 8281) and therefore the waters are undersaturated with respect to iron monosulphides (amorphous and microcrystalline; Figure C2-6). This behaviour can be related to the fact that this sample contains an important percent of drilling water (8.75%) which may have modified its original characters. But, more interestingly, sample 12005 (taken a year later in the same borehole several metres below, at 969 m depth) shows the highest S^{2-} concentrations measured in Forsmark groundwaters (see Table C2-4). No microbiological data are still available for this section nor for the samples taken from the next data freeze.

Sample 8879 in KFM07A at 760 m depth has a clear sulphidic character and is in equilibrium with mackinawite although SRB have not been detected in this section (Table C2-3). SRB expected here may be located elsewhere at these depths. Moreover, equilibrium with mackinawite would be related to the decrease of an intense SRB activity (enough to create amorphous iron monosulphides) and the later reequilibrium with mackinawite.

These facts are an additional evidence of the technical difficulties encountered during borehole sampling. They clearly indicate the need of independent estimations based on microbiology and geochemistry to detect this kind of problems. But, as a whole and in spite of the difficulties, both the geochemical and microbiological data indicate the presence of an important SRB activity at depths between 800 and 1,000 m in Forsmark. In the Laxemar area these depths are also the maximum where bacterial activity of this type has been detected.

Microbiological studies in brackish groundwaters with an important *Littorina* component indicate low or very low amounts of SRB. These studies, performed in samples from 2.1 data freeze, are in perfect agreement with the corresponding geochemical signatures: low S^{2-} concentrations and undersaturation with respect to monosulphides. But some samples of the next data freeze could modify this point.

Samples taken in KFM02A (12002 and 12004) between 400 and 500 m depth are in equilibrium with mackinawite. This suggests the presence of a present or recent SRB activity. More important, sample 12001 at 630 m depth in KFM03A is the only one in equilibrium with amorphous iron monosulphides, which would indicate a present and intensive SRB activity, although no microbiological data are still available for this section.

$\delta^{34}S$ is another parameter frequently used to indicate SRB activity. The activity of the SRB produces a noticeable fractionation of the sulphur isotopes. During sulphate reduction, the lighter isotope (^{32}S) is enriched in the sulphide and the heavier (^{34}S) in the remaining sulphate /Clark and Fritz 1997/, increasing the $\delta^{34}S$ value in sulphates.

The $\delta^{34}S$ values analysed in the studied groundwaters (Table C2-4) range from 22.4 to 34.8‰, clearly higher than the present values of the Baltic Sea in Forsmark (17.2 to 21.7 ‰). Some of the highest values have been determined in the deepest saline groundwaters (770–990 m; Table C2-3). This seems to support the already mentioned, currently active, sulphate reducing bacteria activity at these depths. However, the isotopic values determined in the brackish groundwaters also suggest the presence of SRB, which *apparently* is in disagreement with microbiological and geochemical data.

However, these isotopic values can be the trace of previously developed sulphate-reduction processes /SKB 2004, 2005/. During the *Littorina* stage, when the waters infiltrated through marine sediments into the basement, an important sulphate-reduction activity with iron sulphides precipitation was taking place in the seafloor rich in organic matter /e.g. Böttcher and Lepland 2000, Alvi and Winthelhalter 2001/. Then, after mixing with the previous groundwaters, the chemical signature of this sulphate-reduction process became diluted or modified, as the nutrients supply was not enough to keep the activity of SRB or as the colonization of other microorganisms inhibited the sulphate-reduction activity up to the present time.

The interpretation of $\delta^{34}S$ requires caution as, although it can be indicative of SRB activity, it does not indicate neither the moment nor the place in which it took place. In the waters with an important *Littorina* component, the isotopic values may reflect the occurrence of sulphate-reduction processes in the sea floor during the *Littorina* stage, instead of a present activity.

C2.4.4 Sulphides and its relation to system perturbations during sampling

In spite of the reasonable agreement between the geochemical and microbiological characteristics presented above, we can not forget that samples are probably not in an undisturbed state due to changes brought about during sampling, and that conclusions may also be affected by the relatively small number of samples analysed in a structurally and hydrologically complex system.

For instance, sample 8273 (KFM03A at 632 m depth) was analysed in 2004 and its S^{2-} concentration was below the detection limit. However, sample 12001 (taken from the next data freeze) from a similar depth in the same borehole (631 m depth) was analysed in 2005 and, in spite of similar contents of major elements (chloride and sulphate) and percentage of drilling water, it has a S^{2-} concentration of 0.71 mg/l (one of the highest detected up to now in Forsmark), the Fe^{2+} content is also higher and it is in equilibrium with respect to amorphous iron monosulphides. It is obvious that neither drilling water content (Table C2-4) nor major ion chemical composition are the cause of this temporal variation.

Something similar happens in samples 8152 (at 978 m depth) and 12005 (taken in 2005 at 969 m depth) from KFM03A borehole. Major compositional characters (Cl^- , SO_4^{2-} , alkalinity) are similar in both samples but again S^{2-} and Fe^{2+} concentrations are notably higher in the latest sample (12005, Table C2-4). In this case the drilling water percentage decreases from 3.85 to 2.85% but it is not evident that this decrease could justify the observed variation.

The same situation can be seen in borehole KFM02A for samples 8016 (503 m depth) and 12004 (495 m depth) although this time the change in S^{2-} and Fe^{2+} contents is smaller: S^{2-} is below detection limit in the first sample and has low but significant contents (0.066 mg/l) in the second, enough to make the water be in equilibrium with crystalline iron monosulphide.

Even taking into account these temporal variations some differences are still clear in the system above and below 600–700 m depth. At greater depths, temporal variations seem to confirm the presence of higher S^{2-} contents and more frequent equilibrium situations with respect to amorphous iron monosulphides. Shallower waters do not show a stronger enough sulphidic character to surpass equilibrium with mackinawite.

C2.4.5 Discussion and conclusions

The number of groundwater samples with sulphidic character is lower in Forsmark than in Laxemar. The same is valid for sulphide concentrations, lower in Forsmark than in Laxemar. This fact could be a simple question of sampling bias as there are important differences in the number of available samples in the two areas. This problem will be solved as more samples are available in the following data freezes. In fact, some of the samples taken from the next Forsmark data freeze show a more marked sulphidic character.

With the data available up to now, the agreement between geochemical and microbiological results on the presence or absence of SRB activity is very successful. Both sets of data indicate the active occurrence of these bacteria at depths between 900 and 1,000 m in Forsmark, which is in agreement with the maximum depth with bacterial activity of this type in Laxemar /SKB 2006b/.

The same agreement between geochemical and microbiological data is found for the brackish groundwaters at depths between 100 and 600 m; waters undersaturated with respect to iron monosulphides have very low concentrations of SRB. However, new data from datafreeze 2.2 suggest the presence of a slightly more intensive SRB activity in some waters that are in equilibrium with mackinawite. In any case, all the brackish samples show a lower SRB activity than found deeper in Forsmark or in general in the Laxemar area. Therefore, brackish groundwaters in this depth range (waters that are characterised by having an important *Littorina* proportion) should correspond more or less, to isolated pockets with a very low nutrients supply (see Hallbeck, this volume).

A result that may be significant is the equilibrium with respect to amorphous iron monosulphides found in sample 12001 (data freeze 2.2) one of the deepest brackish groundwater sampled up to now (at 630 m depth). This could indicate the active precipitation of amorphous iron monosulphides and, although not available yet, the presence of an important SRB activity at shallower depths than previously believed. Moreover, this depth is especially important as many

other redox elements undergo severe modifications in their concentrations (see section C2.2). On the other hand, this fact suggests that some high-Littorina waters have indeed a supply of nutrients and therefore, that not all of them occupy isolated pockets.

Sampling problems (oxygen intrusion, high contents of drilling water, etc) could have modified the original Fe^{2+} and S^{2-} groundwater contents and, consequently, some of the results of their saturation state with respect to the iron monosulphides. However, new data from the 2.2 data freeze do not change the conclusion of a very low SRB activity in the brackish groundwaters between 100 and 600 m depth.

C2.5 Uranium System analysis

The elevated dissolved uranium concentrations found in some Forsmark groundwaters between 200 and 650 m depth (Table C2-4) has aroused considerable interest due to their potential environmental implications and effects on the safety case for a high level waste repository.

The occurrence of these elevated uranium levels has been linked to sampling-related disturbances (oxygen intrusion, high drilling water content, corrosion of the drilling tools, etc). Any of these disturbances could have produced a more or less important contamination or alteration of the original physicochemical conditions in the system.

Five is the number of packed sections with elevated uranium content ($> 10.0 \mu\text{g/l}$) in the Forsmark 2.1 dataset (Table C2-4), and only four of them have an accompanying representative Eh value (essential parameter to carry out uranium speciation-solubility calculations). This is a small number of samples to get a comprehensive understanding of the problem. In order to increase the number of samples, several new samples from the next data freeze have also been included in this study. However, some other key parameters are still scarce or unavailable, such as the oxidation state of dissolved uranium oxidation state in groundwaters, its association with colloidal phases (not indicated up to now in the few available measurements), the nature of the U mineral phases in the fracture fillings, and U-series isotopes in fracture coatings and waters.

In the present state of affairs it is almost impossible to address all the questions that seem to be involved in the occurrence of the anomalously elevated uranium content. Therefore, the results and conclusions presented here must be considered as preliminary, subject to further refinement in successive iterations.

The first issue that must be confronted is the *magnitude* of the detected uranium levels. Are the concentrations really “high” or “anomalous”? and if so, In which context can they be qualified as “anomalous”? Answering these questions can give important clues on the meaning and origin of the uranium “anomaly”.

C2.5.1 Uranium concentrations in Forsmark and other crystalline rock environments

Groundwaters with a elevated concentration of uranium in the Forsmark area are located at depths between 170 and 632 m, with values between 14 and 122 $\mu\text{g/l}$ U. For shallower groundwaters only data at 115 m are available, and there uranium contents are low (1.5 $\mu\text{g/l}$). For deeper waters (up to 1,000 m) uranium contents are also low, not being higher than 1 $\mu\text{g/l}$ (Table C2-4). The potentiometrically measured Eh in the elevated uranium waters is between -140 and -200 mV while in the low uranium waters it is between -200 and -250 mV.

Available data for surface waters (lakes and streams) and near-surface groundwaters in Forsmark indicate uranium values not higher than 40 $\mu\text{g/l}$ in spite of being in a mainly oxic environment.

Surface and near surface groundwaters

Uranium contents in surface and near surface waters are well inside the range for similar waters (oxic and/or superficial waters) in other Swedish or Scandinavian sites. Maximum uranium contents in the Laxemar subarea do not surpass the value of 14 $\mu\text{g/l}$; they are below 8 $\mu\text{g/l}$ in the Äspö subarea, and up to 90 $\mu\text{g/l}$ in the case of Stripa (shallow groundwaters < 60 m depth) /Nordstrom et al. 1985/ (Figure C2-7).

Uranium analysed in 328 samples of Swedish drinking water from drilled bedrock wells have a geometric mean value of 14.3 $\mu\text{g/l}$ and can reach a maximum value of 427 $\mu\text{g/l}$ /Isam et al. 2002/.

Shallow groundwaters in Olkiluoto, Finland, (up to 100 m depth) with Eh values around +100 mV show uranium contents up to 18 $\mu\text{g/l}$ /Pitkänen et al. 2004/. Surface and overburden groundwaters in Palmottu (Finland) show uranium concentrations lower than 11 $\mu\text{g/l}$, while deeper groundwaters (from 100 to 150 m depth), with Eh values between 0 and +450 mV, can reach values of almost 900 $\mu\text{g/l}$ U /Blomqvist et al. 2000/ (Figure C2-8, panel a). Although the occurrence of uranium mineralizations in this area could justify these elevated dissolved uranium contents, they do not represent the maximum values found in Finland. /Salonen and Huikuri 2002/ reported a uranium mean value of 32 $\mu\text{g/l}$ for 7,000 drinking waters samples in Finland, with maximum contents up to 20 mg/l; and /Asikainen and Kahlos 1979/ found uranium concentrations up to 14.9 mg/l in a drinking water well from a uraniferous granitic bedrock near Helsinki.

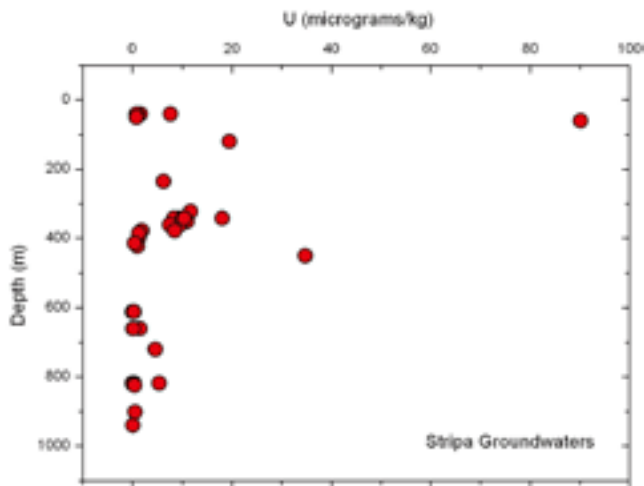


Figure C2-7. Uranium vs depth contents in the Stripa groundwaters.

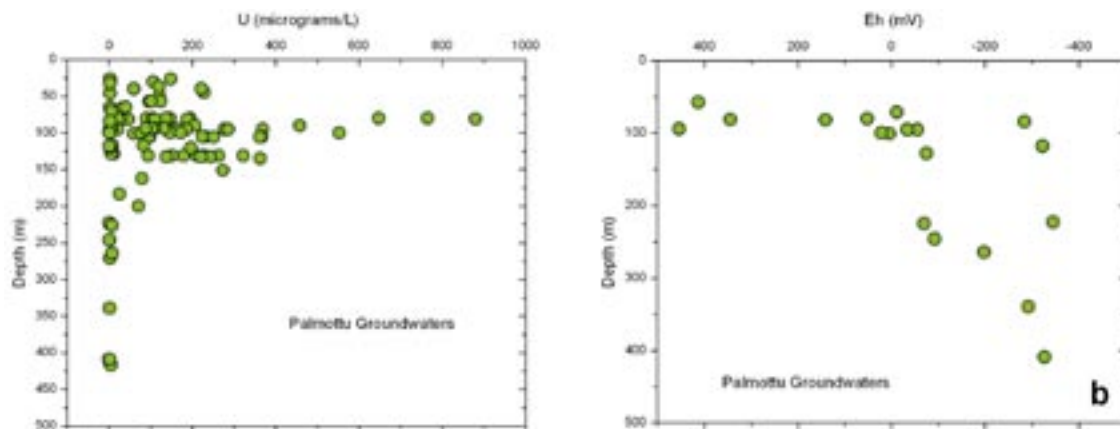


Figure C2-8. Uranium contents and Eh values vs depth in the Palmottu site groundwaters.

In the Norwegian crystalline bedrock, some studies have recorded up to 170 µg/l /Banks et al. 1995ab/ and approximately 2 mg/l in waters associated to granitic rocks /Reimann et al. 1996/. The most recent work from /Frenstad et al. 2004/, who analysed 476 groundwater samples from boreholes in the Norwegian crystalline bedrock, indicates maximum contents of 750 µg/l with mean values up to 16 or 34 µg/l depending on the lithology of the bedrock.

Elevated uranium concentrations are also frequent in the near surface groundwaters from other crystalline-rock environments such as the ones studied in the Canadian Shield. For instance, 100 µg/l U are common in the Lac du Boneth batholith groundwaters and even maximum values of up to 1 mg/l have also been reported. In the Eye-Dashwa Lakes pluton uranium contents can reach 50 µg/l /Gascoyne 1989, 1997/.

Uranium is a highly mobile element over a wide pH range in oxidising waters. Under these conditions, dissolved uranium concentrations can be as variable as has been shown above, depending on the type of complexing agents, the redox state, the occurrence of uranium ores (or anomalies), and/or the specific lithological characteristics and uranium contents in the materials in contact with the waters /Banks et al. 1995b, Gascoyne 1997, Frenstad et al. 2004/.

Therefore, uranium contents in the surface and near surface groundwaters in Forsmark are well inside the mean values reported in similar environments in the Scandinavian Shield, and even the maximum values found in Forsmark are far below the ones indicated in the studies mentioned above.

Groundwaters

Uranium contents in Forsmark groundwaters between 170 and 630 m are in contrast with the values found in the Laxemar area, where groundwaters between 200 and 1,000 m have uranium concentrations lower than 1 µg/l. However, the potentiometrically measured Eh in the Laxemar groundwaters are between -210 and -310 mV, that is, much lower than the corresponding values for the Forsmark groundwaters; only the deepest groundwaters (900–1,000 m) in Forsmark show uranium and Eh values similar to the ones found in Laxemar.

Uranium concentrations in the deepest groundwaters from Stripa (below 150–200 m) are variable (Figure C2-7), probably due to disturbances in the original conditions. Groundwaters below 600 m depth have uranium values always lower than 10 µg/l, while waters between 300 and 450 m have values up to 35 µg/l. However, uranium contents in the granitic rocks in this site are 10 times higher than the mean for granitic rocks. Moreover, the Eh values ($32 \text{ mV} \pm 112 \text{ mV}$ for 47 samples; /Glynn and Voss 1999/) are much more oxidising (and unrealistic) than any of the reported in Forsmark.

Finnsjön groundwaters between 70 and almost 400 m depth have uranium contents up to 16 µg/l, but most of them are below 8 µg/l. Eh values at these depths are lower than -250 mV.

Olkiluoto groundwaters (Finland) deeper than 200 m show uranium contents lower than 4 µg/l /Pitkänen et al. 2004/. In the Palmottu area (Finland), groundwaters below 200 m and far from the uranium ore show dissolved uranium contents between 1 and 10 µg/l /Blomqvist et al. 2000/ (Figure C2-8, panel a). Eh values for these waters are mainly between -200 and -350 mV (Figure C2-8, panel b). Groundwaters with redox potentials between -100 and -198 mV at depth greater than 200 m show uranium contents between 1.26 and 7.03 µg/l.

Finally, 90% of the groundwaters analysed in the Lac du Boneth batholith (Canada) up to 1,000 m depth show uranium concentrations higher than 1 µg/l because the measured Eh is always higher than -225 mV /Gascoyne 1997, 2004/. Groundwaters between 200 and 400 m depth show uranium contents between 1 and 300 µg/l with Eh values between +150 a -90 mV /Gascoyne 1997/. Groundwaters deeper than 600 m show uranium contents lower than 10 µg/l, and are associated with more reducing Eh values (usually between -100 mV and -225 mV).

Discussion

Uranium contents in surface waters and groundwaters from the Forsmark area are not specially high when compared with the values reported from other crystalline-rock groundwater systems. The highest uranium values found in Forsmark are even far below the maximum values measured in drinking waters from the Scandinavian Shield⁷.

Eh values measured in the waters with elevated uranium contents are not particularly reducing, between –140 and –200 mV. U solubility is high in oxidising conditions but also in mildly reducing conditions depending on the effects of other factors such as carbonate complexation /Langmuir 1997/. This influence will be described below. However, as it has been showed, groundwaters from other sites with similar Eh values (and similar or even higher alkalinity than the Forsmark groundwaters) show uranium concentrations noticeably lower.

In many cases uranium contents in more oxidising groundwaters (and higher alkalinity) are lower than in Forsmark groundwaters, as it happens with many of the surface or near surface groundwaters in the same area.

Drawing back the possible external contamination of U in these waters (see below), all the above data suggest that the origin of the elevated uranium contents in Forsmark is related to the occurrence of uranium mineralisations or anomalies in contact with the groundwaters. Uranium ores are found at several localities in Uppland: pitchblende vein fillings in skarn have been documented only some kilometres from the Forsmark site /SKB 2005/. The more recent works performed on the fracture fillings in the Forsmark area seem to support this fact (see below).

The reducing character of the waters with elevated uranium contents suggests that the uranium phases must be specially soluble, as it has been already reported in /SKB 2005/ from a comparison of the ²²⁶Ra/²³⁸U ratio in the Forsmark and Äspö groundwaters. The kind of mineral phases present and the factors conditioning U mobilisation need a more in-depth study of the Forsmark groundwater system.

C2.5.2 Uranium and general characters of Forsmark groundwaters

Forsmark groundwaters with uranium contents higher than 10 µg/l are located at four different depths: between 180 and 200 m (U contents up to 60 µg/l); between 425 and 433 m (U contents in the range 14–26 µg/l); between 495 and 503 m (U contents from 90 to 122 µg/l); and at 632 m depth, where 45 µg/l U have been reported (Figure C2-9, panel a). Shallow groundwaters have U contents always below 40 µg/l (Figure C2-9, panel a). Most of the surface waters show uranium contents not higher than 5 µg/l and only locally values of 25 a 30 µg/l have been measured (not plotted).

The low uranium concentrations found in surface and near surface groundwaters exclude them as the origin of the higher levels found at depth (as opposed of what happens, for instance, in some of the groundwaters studied by (/Gascoyne 1997, 2004/, in the Canadian Shield).

⁷ This is only to point out a fact and we do not pretend to evaluate the quality of the drinking water. This question can change depending on the limits for each country. As far as we know, there is no drinking water limit for uranium in the European Union. However, USA operate with a limit of 30 µg/l (/EPA 2001/; Directive n° 9283.1–14), the World Health Organisation's recommendation for U is 15 µg/l, the Canadian limit is 100 µg/l /Health Canada 1996/, value also used in Sweden. Following any of these criteria some of the Forsmark groundwaters will not be good for drinking, and the same would apply to some of the surface or near surface groundwaters. However, all the waters analysed in Forsmark 2.1 would be inside the limits considered by Canadian and Swedish and only one from the next data freeze would exceed them.

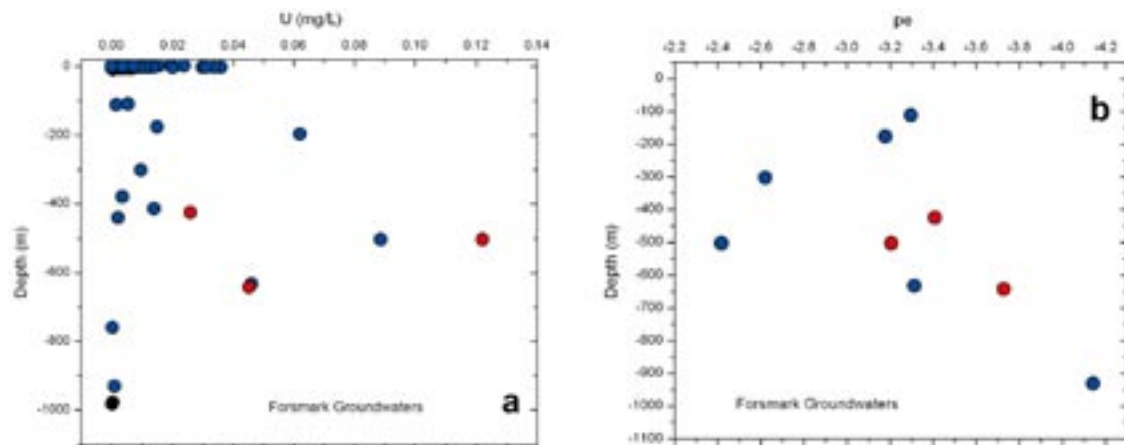


Figure C2-9. Uranium contents and pe values with respect to depth in all the representative Forsmark shallow and deep groundwaters.

In general, an increase in uranium content is observed from the surface to 500 m depth, followed by a noticeable decrease up to 1000 m depth (Figure C2-9, panel a). The trend is different from the one found in other crystalline basements such as Stripa /Nordstrom et al. 1985/ (Figure C2-7), Palmottu /Blomqvist et al. 2000/ (Figure C2-8, panel a), Olkiluoto /Pitkänen et al. 2004/ or the waters studied by /Gascoyne 2004/ in the Canadian Shield. In all these cases uranium concentrations decrease with depth.

The different behaviour can be related or magnified by the already mentioned alteration of original conditions in the system. However, it is more probably related with the complexity of the hydrological system and the paleohydrogeology of the Forsmark area, with the presence of both sub-vertical and sub-horizontal hydraulic structures, pockets and lenses of old sea water mixtures in the bedrock (waters with elevated uranium content show a clear Littorina signature; see below) and obviously, with the occurrence of uranium anomalies in the bedrock. There are still no detailed data but Molinero and Rasposo (this volume) show that the maximum concentrations of uranium correspond to water samples collected at two major water-conducting deformation zones, ZFMNE00A2 and ZFMNE00B1.

The number of potentiometrically measured Eh data in Forsmark groundwaters is still scarce, especially for the waters with elevated uranium contents (Table C2-4 and C2-6). However, some results can be advanced on the possible correlation between U content and Eh.

In general, the Eh distribution with depth (expressed as pe in Figure C2-9, panel b) does not clearly define the expected trend of progressively more reducing values with depth found in other groundwater systems in crystalline rocks such as Palmottu (Figure C2-8, panel b) or the Lac du Boneth batholith /Blomqvist et al. 2000, Gascoyne 1997, 2004, respectively/. Nor it is completely devoid of any depth trend as in the Laxemar area. Eh evolution with depth in Forsmark follows a more or less anti-parallel trend to the uranium concentration: less reducing values at 300–500 m depth (with elevated U contents; see Figure C2-9), and more reducing values at higher and lower depths (with low U contents).

This relation between Eh and Uranium concentration is shown in Figure C2-10. Inside the narrow range defined by the available Eh values in Forsmark (between –143 and –250 mV) there is no clear correlation between Eh and U content. However groundwaters with Eh values lower than –210 mV (pe = –3.6) show low uranium concentrations, similar to the values found in the Laxemar groundwaters. Groundwaters with the highest uranium contents have the less reducing Eh values (pe less than –3.4). This rough correlation suggests that redox potential is *one* of the factors conditioning dissolved uranium concentrations. But it also suggests the important effects of additional factors besides Eh.

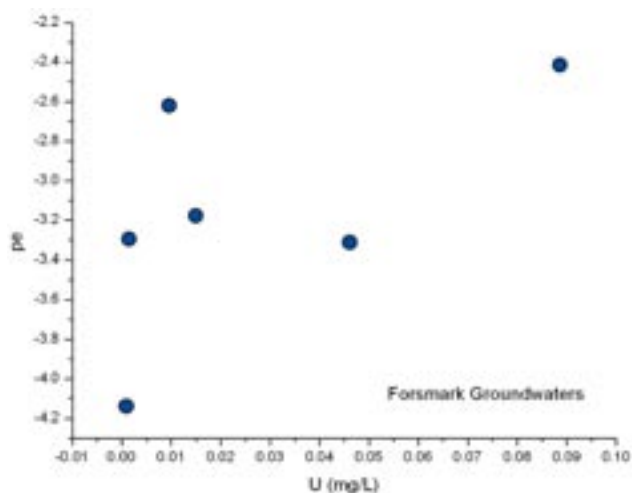


Figure C2-10. *U and pe relation in the Forsmark groundwaters.*

In other groundwater systems in crystalline rocks such as Stripa or the systems studied by /Gascoyne 2004/ in Canada, alkalinity has been recognised as an important controlling factor of U concentration through the formation of anionic species of U(VI) with CO_3^{2-} in oxidising and mildly reducing conditions. Correlation of uranium and alkalinity in the Forsmark groundwaters (Figure C2-11, panel a) does not show however the decrease of uranium concentration with the decrease of alkalinity that has been found in other systems.

This behaviour is nevertheless seen in the groundwaters that show a horizontal distribution in Figure C2-11, with variable and elevated uranium concentrations in a narrow range of alkalinity (90–130 mg/l). Considering the correlation only to that range of alkalinity, the trend of increasing uranium with alkalinity is more clearly seen (Figure C2-11, panel b) which would imply the influence of carbonate complexation on the dissolved uranium concentration. This issue will be analysed in more detail in the speciation section.

A plot of uranium concentration versus chloride concentration show a very noticeable particularity (Figure C2-12): the extreme variability of uranium contents at an almost constant chloride concentration of 5,300–5,600 mg/l. This behaviour is reinforced by the data collected for the next data freeze (sample 12004 from borehole KFM02A; Tables C2-4 and C2-6). This variability is related to waters characterised by a high proportion of the Littorina end-member, which are frequently found in the above-mentioned major water-conducting deformation zones (ZFMNE00A2 and ZFMNE00B1). This is also important in the discussion on the possible anthropic contamination as responsible of these elevated and unexpected uranium contents.

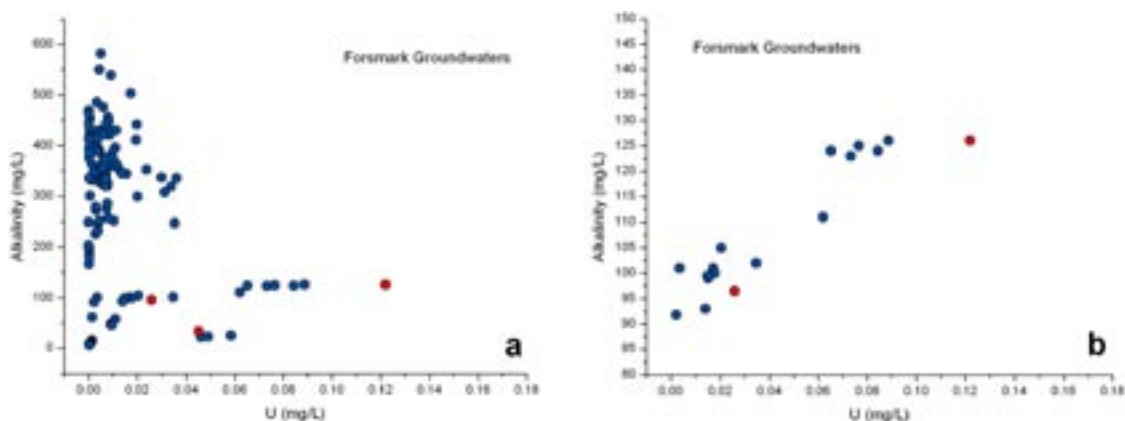


Figura C2-11. *Alkalinity vs uranium concentrations in Forsmark groundwaters. Panel (b) shows only the value of alkalinity between 80 and 150 mg/l.*

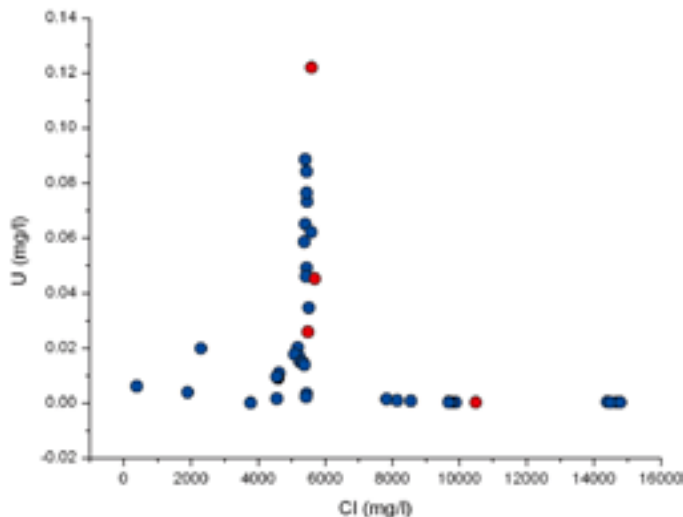


Figure C2-12. Uranium content with respect to chloride in the Forsmark groundwaters.

Alterations of the pristine geochemical conditions in the Forsmark groundwaters

As already pointed out in section C2.3.2, several problems have been detected during the sampling and analysis of the Forsmark groundwaters. These problems suggest the possibility of modifications of the original groundwater composition and physicochemical conditions of the system. They also could affect the interpretation of the elevated uranium contents in some of the samples. Several alteration hypothesis have been discussed as possible causes of the elevated uranium contents. They are presented below.

The external input of uranium to the groundwaters, coming through the drilling waters or the bentonite used during the boreholes drilling tasks, could be one of the causes. However it is difficult to justify how this kind of contamination can systematically only affect groundwaters with 5,500 mg/l Cl, in different boreholes and at different depths.

Detailed studies performed by Buckau and Gascoyne (both in this volume) indicate that the elevated uranium content in Forsmark could be the result of an alteration of the original conditions in the groundwater system due to:

- oxygen intrusion, probably associated with the high drilling water contents found in some of the groundwaters with elevated uranium,
- corrosion effects in the borehole equipment due to the presence of Fennoskan HVDC (High Voltage Direct Current) cable in the vicinity of the Forsmark area /Nissen et al. 2005/.

The presence of corrosion processes in the downhole equipment, already indicated by /Wacker et al. 2004a/ in the KFM04A borehole, can develop local oxidising conditions which enhance the mobilization of the uranium present in the fracture fillings. Oxygen intrusion in a reducing environment would have a similar effect.

The high drilling water contents in some groundwater samples from Forsmark has already been acknowledged in previous reports /SKB 2006a/. With respect to the uranium concentration, the correlation between elevated values of the element and high percent of drilling water in the sample is by no means perfect (Figure C2-13; Table C2-4), although waters with elevated uranium contents tend to also have high drilling water contents.

The occurrence of waters with low uranium contents and very high percent of drilling water (even higher than waters with elevated uranium concentrations) suggest that the alteration produced by the presence of drilling water is only effective in those zones where uranium mineral phases are available to be mobilised (see Buckau, this volume, for a more detailed analysis).

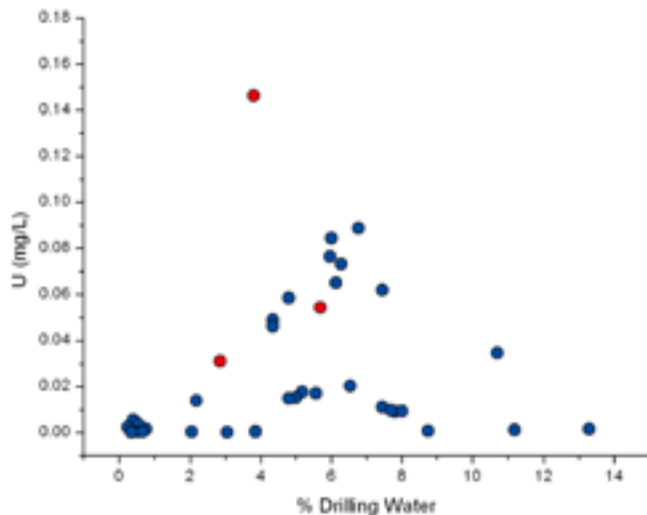


Figure C2-13. Uranium content with respect to the percent of drilling water present in the Forsmark groundwaters.

The hypothesis of the alteration of the original groundwater system, and specifically in the redox conditions, is also supported by the crystallinity of the ferric phase that seems to be controlling the measured Eh in most of the studied boreholes (Chapter C1 and section C2.3.2). The occurrence of this kind of phase suggest the existence of an oxidising alteration temporally developed in the system and compatible not only with the absence of oxygen traces during the Chemmac loggings, but also with the reducing Eh measured in the boreholes.

All these hypothesis assume the presence of uranium mineral phases locally distributed in the system. Data available up to now point to the real presence of these phases, as next section summarises.

Uranium in rocks and fracture fillings in Forsmark

The study of the occurrence of uranium mineral phases in the bedrock and fracture fillings is an ongoing work. However, several interesting observations are already available, which are very useful in the understanding of the uranium geochemical behaviour in Forsmark.

The different igneous rocks present in the Forsmark area have uranium concentrations around 4–5 ppm (only locally higher contents, 10–30 ppm, have been found in some pegmatites). These contents are in agreement with mean values reported for this element in granitic rocks (4 ppm; /Reimann and Caritat 1998/) and are similar to values in the Äspö subarea /Tullborg et al. 1991/ and the Canadian shield granites /Gascoyne 1989/. That is, the bedrock in Forsmark does not show anomalously elevated uranium contents.

However, the analysis performed, up to now, in the fracture coatings of this area show a different scenario (Table C2-5). Uranium contents are almost always higher than in the bedrock and particularly elevated at depths of 423, 516, 686 and 644 m where associated groundwaters also have elevated concentrations of this element.

The highest uranium contents are located in the fracture fillings at 644 and 686 m depth (KFM03A and KFM08A boreholes) with values between 164 a 2,200 ppm. In comparison, uranium enrichment in the altered rocks associated with fracture zones in the Lac du Bonnet and Eye-Dashwa Lakes plutons (Canada) do not exceed 20 ppm /Gascoyne 1997 and references therein/; and the highest uranium concentrations reported in 29 analysis of fracture fillings in the Äspö subarea are always below 80 ppm (and in most cases lower than 10 ppm; /Tullborg et al. 1991, Glynn and Voss 1999/).

Table C2-5. Uranium contents in fracture coatings /taken from Sandström and Tullborg 2005, Tullborg et al. 2008/.

Borehole	Depth (m)	U (ppm)
KFMO1A	127.4	6.7
KFMO1A	179.35	12.1
KFMO2A	118.25	4.5
KFMO2A	423.65	39.7
KFMO2A	516.09	20.9
KFMO3A	644.17	2,200
KFMO6A	357.81	14.9
KFMO7A	896.68	2.9
KFMO8A	686.67	164

Therefore, the elevated U-levels found in some of the Forsmark fractures could be considered as anomalies indicative of the presence of a more or less disseminated uranium mineralisations. In fact, /Sandström and Tullborg 2005/ have recently pointed out the occurrence of pitchblende (Figure C2-14) in fracture fillings at 644 m depth in the KFM03A borehole, where waters with elevated uranium concentrations have been sampled.

All these data support the occurrence of uranium mineralisations or enrichments in the external zones of the fracture fillings, the most accessible for the groundwaters. The ongoing studies will be essential to confirm the importance of this correlation between the occurrence of uranium phases, the uranium content in the filling coatings, and the uranium content in the groundwaters.

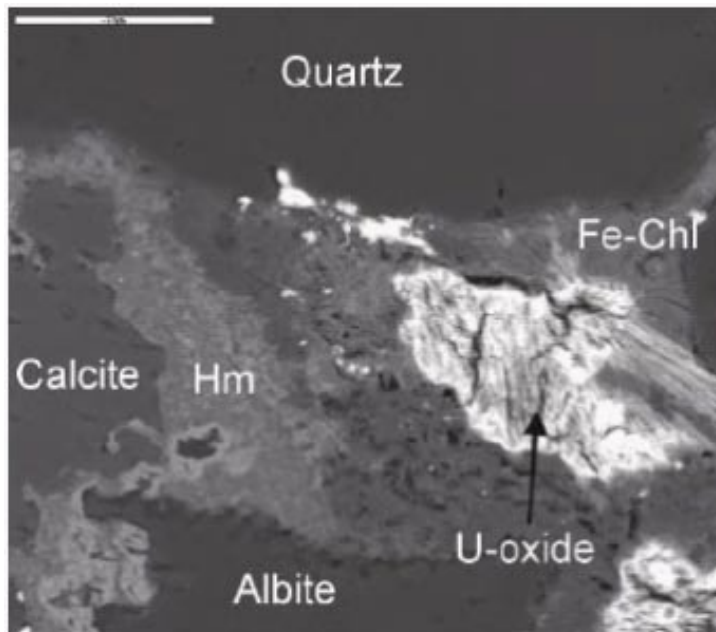


Figure C2-14. Altered U-oxide (Pitchblende) together with chlorite (Fe-Chl), hematite (Hm) and calcite. Backscattered electron image, the bar is 50 μm . KFM03A 643.8–644.17 m /taken from Sandström and Tullborg 2005/.

C2.5.3 Uranium speciation-solubility calculations

Uranium speciation-solubility calculation have been performed using PHREEQC /Parkhurst and Appelo 1999/ and three different thermodynamic databases: WATEQ4F /Ball and ordstrom 2001/, SKB-TDB (June, 2005; /Duro et al. 2005/) and NAGRA⁸ (Nagra/PSI TDB 01/01; /Hummel et al. 2002/).

SKB-TDB derives directly from the NAGRA database (Nagra/PSI TDB 01/01) with some modifications or extensions for elements of special interest for Performance Assessment: Sm, Ho, Pa, Am, Np, Pu, Th, U, Cs, Sr, Ra, Sn, Se, Zr, Nb, Tc, Ni, Pd and Ag /Duro et al. 2005/. Thermodynamic data for species and minerals for the carbon, sulphur and silica systems are identical to the ones included in NAGRA which, in turn, come from the review performed by /Nordstrom et al. 1990/ for these systems /Pearson and Berner 1991, Pearson et al. 1992, Hummel et al. 2002/ and are the ones included in WATEQ4F database /Ball and Nordstrom 2001/. Therefore, the differences in the speciation schemes and saturation states for the uranium system obtained using the three databases will be only related to the different thermodynamic data considered for this compositional system.

The number of samples from packed sections with elevated uranium content (> 10.0 µg/l) in the Forsmark 2.1 data freeze is only five (Table C2-6). Moreover, as the speciation-solubility calculations highly depend on the Eh, it is also important to have this parameter available (only four of the five samples have it, Table C2-6). In order to increase the number of samples with enough data we have included a series of samples from the next data freeze (samples 12001, 12002 and 12004, Table C2-6), all of them with elevated uranium content. For those samples with no Chemmac Eh, it has been calculated from the redox pairs Fe(OH)₃/Fe²⁺ and SO₄²⁻/S²⁻ (Tables C2-3 and C2-6) as all the previous studies in Forsmark and Laxemar have show the good empirical agreement between the values calculated by these pairs and the potentiometrically measured Eh /SKB 2004, 2005/.

Table C2-6. Forsmark groundwater samples used in the speciation-solubility calculations for uranium. Concentrations are expressed in mg/l. Eh values indicated in bold+italics have been estimated using the SO₄²⁻/S²⁻ and Fe(OH)₃/Fe²⁺ redox pairs(see text); the rest correspond to potentiometrical measurements with Chemmac.

Borehole	Sample	Depth	pH	Eh (mV)	Cl	Alk	SO ₄ ²⁻	S ²⁻	U
KFM01A	4538	-112	7.65	-195	4,562.8	61.0	315.6	0.014	1.51e-3
	4724	-173	7.41	-188	5,329.5	99.0	547.0	bdl	14.9e-3
	8016	-503	6.8	-143	5,410.0	125.0	489.0	bdl	88.6e-3
KFM02A	12002	-418	7.36	-191	5,440.0	96.5	435	0.058	25.9e-3
	12004	-495	7.19	-180	5,540.0	126.0	507.0	0.066	122e-3
	8273	-632	7.38	-196	5,430.0	22.0	197	bdl	46.1e-3
	8281	-931	7.4	-245	8,560.0	9.0	73.9	0.06	0.7e-3
KFM03A	8152	-978	8.0	-254	9,690.0	6.0	46.7	0.033	0.45e-3
	8017	-442	7.29	-176	5,430	91.8	472.0	0.031	2.21e-3
	12001	-631	7.49	-209	5,640.0	33.7	230.0	0.701	45.2e-3
KFM04A	8267	-197	7.36	-192	5,580	111.0	514.0	bdl	62.0e-3
KFM06A	8808	-302	7.35	-155	4,850.0	47.7	157.0	bdl	9.6e-3
KFM07A	8879	-760	8.05	-253	14,800	6.19	99.3	.171	0.184-3

⁸ WATEQ4F is distributed with the PHREEQC code. The other two databases have been formatted for their direct use with PHREEQC.

Eh values obtained by the $\text{SO}_4^{2-}/\text{S}^{2-}$ redox pair (section C2.3) have been used for elevated uranium samples. For these samples the use of the constant proposed by /Banwart 1999/ for the $\text{Fe}(\text{OH})_3/\text{Fe}^{2+}$ redox pair does not show differences higher than 14 mV with respect to the values obtained with the sulphur redox pair. In order to have a more comprehensive image of the system, two samples with low uranium content (samples 8152 and 8879, at more than 900 m depth; Table C2-2) have also been included and their redox potential have been calculated with the $\text{SO}_4^{2-}/\text{S}^{2-}$ redox pair (Tables C2-3 and C2-6).

Table C2-6 shows the samples selected for the detailed analysis of uranium speciation-solubility. However, in the first calculation all samples with uranium data were included in the calculations (i.e. all samples from the same depths taken over a period of time, both representative and not representative). The results obtained with the whole set of samples do not show significant differences with respect to the ones obtained using only the representative ones.

Uranium speciation results

Speciation calculations using the WATEQ4F database /Ball and Nordstrom 2001/ indicate that uranium speciation is controlled by U(IV) complexes, with $\text{U}(\text{OH})_4^0$ as the dominant species. Only in samples with the less reducing Eh (Figure C2-15) U(VI) carbonate complexes in the form of $\text{UO}_2(\text{CO}_3)_3^{4-}$ or $\text{UO}_2(\text{CO}_3)_2^{2-}$ appear in significant proportions.

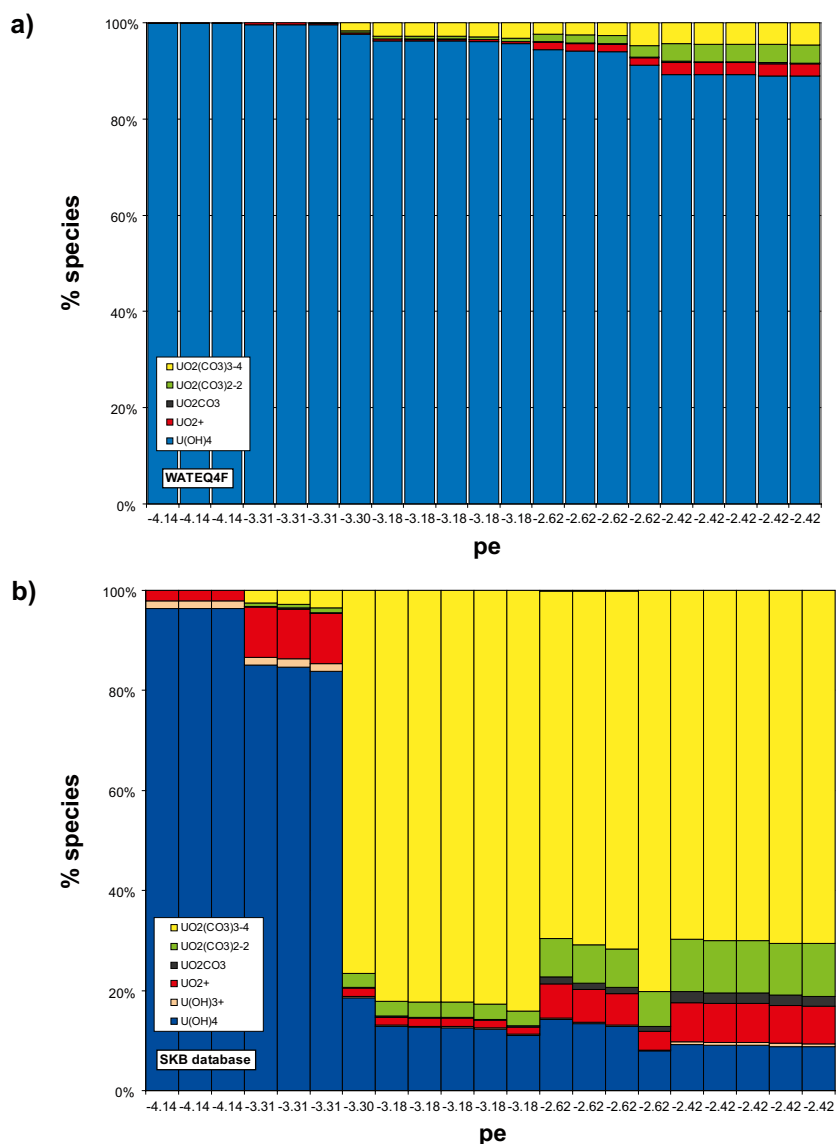


Figure C2-15. Speciation results with WATEQ4F (a) and SKB (b) thermodynamic databases.

Using the SKB-TDB database /Duro et al. 2005/ the speciation scheme is different. The dominant species are still the U(IV)-hydroxide complexes ($U(OH)_4^0$) and the U(VI)-carbonate complexes (as $UO_2(CO_3)_3^{4-}$ or $UO_2(CO_3)_2^{2-}$). However the ratio between these two sets of species is different from the previous one. $U(OH)_4^0$ is the dominant species only in the case of waters with redox potential lower than -190 mV. When the Eh value is more oxidising, the carbonate complexes $UO_2(CO_3)_3^{4-}$ and $UO_2(CO_3)_2^{2-}$ dominate over the $U(OH)_4^0$. Moreover, with the SKB-TDB database the U(V) complex UO_2^+ appears in a significant proportion.

The results obtained using the NAGRA database /Hummel et al. 2002/ are more or less similar to the one obtained with the SKB database and have not been plotted.

In spite of the fact that uranium speciation are quantitatively affected by the species and thermodynamic values included in the different databases, all of them indicate *qualitatively* that the redox potential in these groundwaters is not low enough to prevent the formation of hexavalent carbonate uranium complexes. This complexation process could affect the total uranium contents in the waters as a function of other parameters related with the carbonate system such as pH or alkalinity.

In order to test these effects on the uranium speciation, a sensitivity analysis have been performed. We have calculated the uranium species distribution in sample 8016 for different ranges of pH (between 6.8 and 7.5), Eh (between -140 and -250 mV; pe between -2.4 and -4.46) and alkalinity (between 22 and 125 mg/l). These ranges correspond to those defined by the set of samples with elevated uranium content (higher than 10 $\mu\text{g/l}$). Figure C2-16 shows the results obtained using the SKB-TDB, the more updated database up to now.

The effects of a variation in pe (keeping pH and alkalinity constant) are noticeable (Figure C2-16, panel a). Around a value of $pe = -3.2$ a drastic change in the concentration of the dominant species occurs, increasing the values of the carbonate complexes towards the less reducing potential and decreasing towards the more reducing ones. The range of pe values of the samples with the highest uranium contents is -2.55 to -3.57 , that is, just in the range where the more pronounced change in the uranium speciation is seen.

Something similar happens with alkalinity (Figure C2-16, panel b): in the range of alkalinity values associated with the waters with the highest uranium contents, the dominant species change from a hydroxide complex to a carbonate complex. The variation of pH in the analysed range do not produce important modifications in the speciation and has not been plotted. These calculations also indicate that the effect of alkalinity on the uranium speciation are negligible when pe values are lower than -4.2 , when the dominant species are the U(IV) hydroxides.

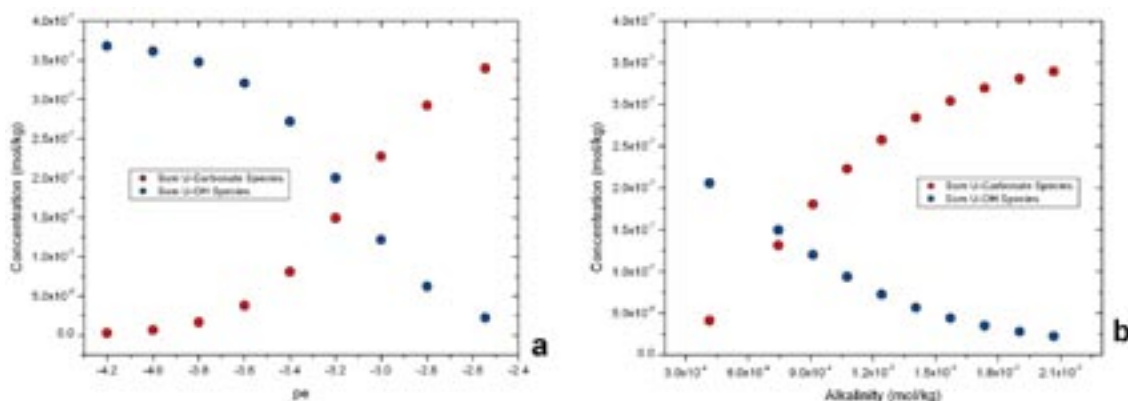


Figure C2-16. Sensitivity analysis of uranium speciation to pe and alkalinity using SKB-TDB.

These results indicate that waters with elevated uranium contents belong to a particularly critical range of Eh and alkalinity values in which the U-carbonate species can drastically change in content, affecting the solubility of the uranium phases present in the system (such as uraninite or pitchblende) whose stability would be enhanced due to the reducing Eh values. U(VI)-carbonate complexation in slightly reducing conditions, in which some UO_2 is still stable, has been reported in other natural systems /e.g. Bruno et al. 2002/.

Uranium saturation indices

Under reducing conditions in crystalline systems, different uraninites or pitchblendes⁹ (of general stoichiometry UO_{2+x} with x varying from 0 to 0.33) and crystalline coffinites (USiO_4) are usually the responsible phases for the dissolved uranium control /Pearsson et al. 1991, Langmuir 1997, Moll et al. 1997, Bruno et al. 2002/.

The results obtained for Forsmark groundwaters show that they are very oversaturated with respect to the crystalline uraninite (SI between +4.5 and +8.5 for all the waters; Figure C2-17, panel a), and with respect to the uranium oxides with mixed valences, $\text{UO}_{2.25}$ and $\text{UO}_{2.33}$ (SI for both phases between +3.0 and +6.0 with SKB database and between +8.0 and +20.0 for $\text{UO}_{2.25}$ with WATEQ4F, Figure C2-17, panel b).

Crystalline coffinite (USiO_4 , in WATEQ4F with $\log K = -7.67$ and in SKB with $\log K = -8.06$ for the same reaction) is also oversaturated, with SI between +4 and +8 (Figure C2-17, panel d), even in waters with low uranium content.

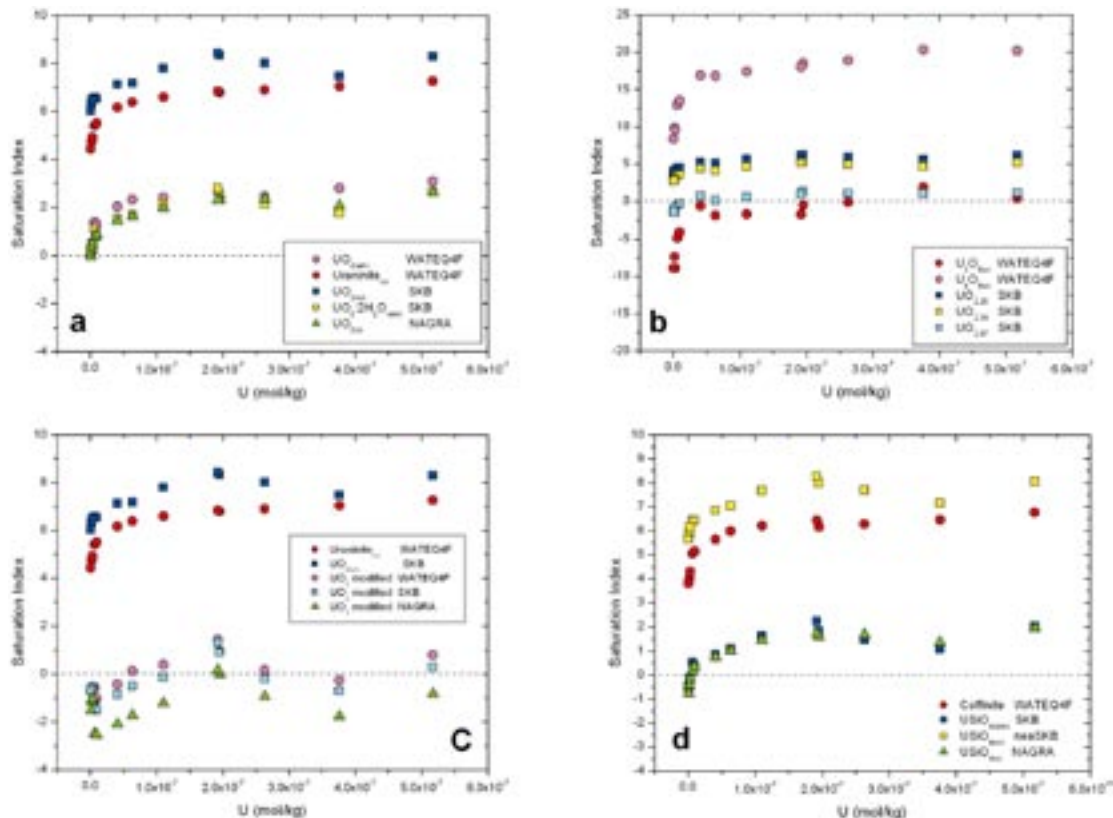


Figure C2-17. Saturation indexes for the different uranium oxides and coffinite using the three different databases. Circles for WATEQ4F database, squares for SKB TDB, and triangles for NAGRA database

⁹ Pitchblende is roughly amorphous UO_2 /Langmuir 1997/ or UO_{2+x} with x varying from 0.25 to 0.67 /e.g. Pérez del Villar et al. 2002/.

The only phases that could be in an apparent equilibrium situation in the groundwaters with elevated uranium contents are $\text{UO}_{2.66}$ and the amorphous phases of the previous minerals ($\text{UO}_{2(\text{am})}$ and $\text{USiO}_{4(\text{am})}$). With the WATEQ4F database and specially with the SKB¹⁰ database there is a set of groundwaters in equilibrium with $\text{UO}_{2.66}$ (U_3O_8). Assuming an uncertainty range for the SI not higher than ± 1.0 (Figure C2-17, panel b), most of the waters with uranium concentrations higher than $4 \cdot 10^{-9}$ M (1 $\mu\text{g/l}$) would be in equilibrium with this phase using the SKB database. With the WATEQ4F database the dispersion of results is higher for these groundwaters and the equilibrium situation has an uncertainty range of ± 2.0 SI units. Considering the important thermodynamic uncertainties for these mixed oxides and the uncertainties associated with the sampling or the pH and Eh measurements in groundwaters, these results can be considered quite successful.

The results obtained for amorphous coffinite (included in the SKB and NAGRA databases with $\log K = -1.5$ and -2.98 , respectively) indicate a very stable oversaturation state (SI between $+1.8$ and $+2.0$; Figure C2-17, panel d) for elevated uranium waters ($5 \cdot 10^{-8}$ M; 12 $\mu\text{g/l}$). Something similar happens with respect to $\text{UO}_{2(\text{am})}$ (or $\text{UO}_2 \cdot 2\text{H}_2\text{O}_{(\text{am})}$), a constant oversaturation state (between $+2.5$ and $+3$) is obtained for the waters with the highest uranium concentrations (Figure C2-17, panel a). Forsmark groundwaters with the lowest uranium concentration would be “strictly” in equilibrium with respect to these phases (inside a range of values of ± 1.0 SI units), as it happens with the most reducing Laxemar groundwaters with uranium concentrations lower than 1 $\mu\text{g/l}$ (similar to this subset of Forsmark waters).

The fact that the oversaturation is relatively constant with respect to the amorphous solids $\text{UO}_{2(\text{am})}$ and $\text{USiO}_{4(\text{am})}$ suggests that high-U (10–120 $\mu\text{g/l}$) groundwaters at Forsmark can be in equilibrium with amorphous U phases but with a higher solubility than the one considered in the databases. Taking into account the special problems associated with the solubility of these phases this issue has been analysed in more detail below.

Ionic activity products for amorphous UO_2 and amorphous coffinite

The experimental solubility values for coffinite are very scarce and the ones for $\text{UO}_{2(\text{am})}$ have been subject to controversies related with experimental problems or with the own degree of crystallinity of the studied phases (amorphous-microcrystalline; /Langmuir 1997 or Hummel et al. 2002/. At this point it is recommendable to employ Langmuir’s approach /Langmuir 1978, 1997/ and use the groundwaters to calculate the solubility product of these phases¹¹.

In this way, the ionic activity product has been obtained for the following reaction:



using the same three database as above. The results are shown in Figure C2-18. The stable $\log \text{IAP}$ obtained for the waters with uranium concentrations higher than 20 $\mu\text{g/l}$ is 4 with SKB database and ranges between 2.5 and 3 when using NAGRA and WATEQ4F databases. These differences are due to the different uranium speciation system included in each database. However, considering the extreme values, there is a good agreement with the more recent value proposed for the solubility product of $\text{UO}_{2(\text{am})}$.

From the /Langmuir 1997/ review, a range of solubility values for the $\text{UO}_{2(\text{am})}$ between 2.6 and 4.1 (expressed as $\log K$ for reaction 4) can be obtained depending on the degree of crystallinity (amorphous-microcrystalline) of the solids used in the experiments. /Rai et al. 1990, 1997/ reported experimental values of $\log K = 4.0$ and $\log K = 2.55$, respectively, for this kind of amorphous phases. They indicate that the second value ($\log K = 2.55$) is reflective of the solubility product for relatively aged $\text{UO}_{2(\text{am})}$ and, therefore, associated with an increase in crystallinity with respect to the other value $\log K = 4.0$.

¹⁰ Uranium oxides with mixed valences are not included in the NAGRA database /Hummel et al. 2002/.

¹¹ The NEA guidelines propose to use this approach as a guide for the estimation of the stability of coffinite and the equilibrium constant enclosed in the SKB database comes from this kind of estimation /Duro et al. 2005/.

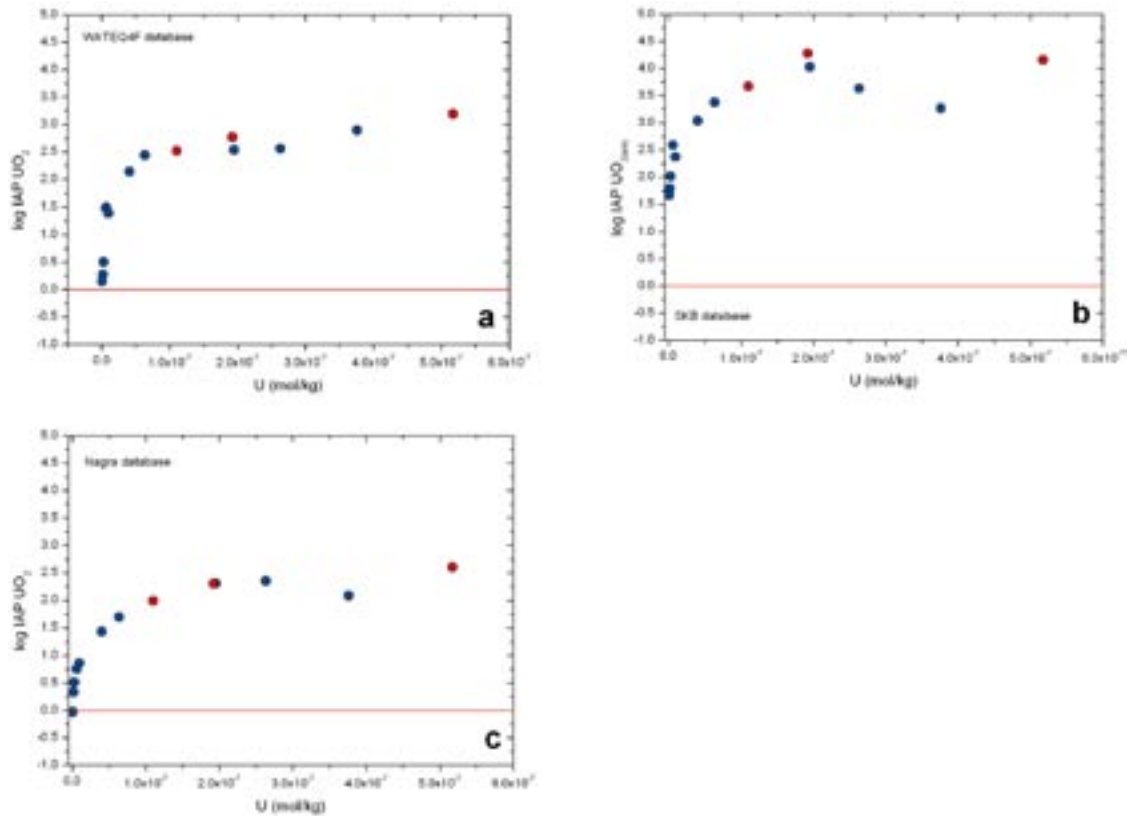
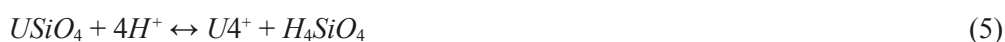


Figure C2-18. Log IAP for the UO_2 phase using the three databases. (a) WATEQ4F, (b) SKB, and (c) Nagra.

The solubility values for the $UO_{2(am)}$ obtained from the Forsmark groundwaters (between 2.6 and 4.0) are higher than any of the values included in the thermodynamic databases used in our work ($\log K = 0.1, 1.5$ and 0.0 in WATEQ4F, SKB and NAGRA databases, respectively). Nevertheless, the range of variation is conditioned by the different uranium speciation systems implemented in each database and, mainly, by the values included for reaction (4) and for the complexation reaction of $U(OH)_4^0$ /Hummel et al. 2002, Duro et al. 2005/.

Several scoping calculations have been performed including the value proposed by /Rai et al. 1990/ for reaction (4) ($\log K = 4.0$) and modifying the value for the $U(OH)_4^0$ formation reaction (proposed by /Langmuir 1997/) in the different databases¹². The saturation states obtained for the $UO_{2(am)}$ under these conditions (Figure C2-17, panel c) indicate an equilibrium state (with an uncertainty range of ± 1.0 SI units) with the three databases and for almost all the samples with uranium contents higher than $10 \mu\text{g/l}$.

In the case of amorphous coffinite, SI results obtained with the SKB and NAGRA databases (Figure C2-17, panel d) suggest that Forsmark groundwaters with the highest uranium contents could be in equilibrium with this phase if its solubility is two orders of magnitude higher than reported in the databases. The solubility product for this amorphous phase included in SKB-TDB comes from an estimation by /Langmuir 1978, 1997/ from several reducing groundwaters in contact with amorphous coffinite /Duro et al. 2005/. /Langmuir 1978, 1997/ obtained a value of $\log K = 0.5$ for the reaction



¹² Obviously and for consistency reasons /e.g. Hummel et al. 2002, Duro et al. 2005/, the definite input of these value in the database would require to make much more modifications in the uranium speciation system included in each database. But this is not the aim of this work and, moreover, the results obtained for the Forsmark groundwaters are still very preliminary.

as a mean value of the maximum IAP in three groundwaters from Cigar Lake and Palmottu and considering a value of $\log K = -12.0$ for $U(OH)_4^0$. The value for this species in SKB-TDB is $\log K = -10$ and consistently the $\log K$ for reaction (5) is -1.5 . However, the solubility value obtained from the IAP values in the Forsmark groundwaters with the highest uranium concentrations and using this database is 0.5 (or 2.5 with the data originally used by /Langmuir 1978, 1997/), that is, with the already mentioned difference of two orders of magnitude.

Discussion

The elevated uranium contents in the Forsmark groundwaters seem to be controlled by equilibrium situations with respect to amorphous phases such as $UO_{2(am)}$, $UO_{2.67}$ or $USiO_4$. These phases are more soluble than the ones suggested up to now as responsible for the uranium control in reducing groundwaters: $UO_{2.25}$ (U_4O_9), $UO_{2.33}$ (U_3O_7) or $USiO_4$ crystalline /Ahonen et al. 1993, Duro et al. 1999, Blomqvist et al. 2000/. Only recently /Iwatsuki et al. 2004/ have reported the control by $UO_{2(am)}$ (with a solubility value of $\log K = 2.6$ for reaction (4)), on the dissolved uranium content in a set of groundwaters from Tono Mine with Eh values higher than -260 mV.

The studies of the occurrence of uranium mineral phases in the fracture fillings are on going and the available observations are still scarce. However, the presence of a mineral phases reported as “altered U-oxides” (pitchblende) has already been demonstrated in some of the examined sections /Sandström and Tullborg 2005, Figure C2-14/. This finding would support the control of the dissolved uranium content by some of the amorphous phases of UO_2 (that is, $UO_{2(am)}$, or $UO_{2.67}$) identified in this work.

In most natural systems, uraninite and pitchblende appear as oxides with mixed valences (U_4O_9 , U_3O_7 and U_3O_8 ; /Langmuir 1997/ formed by gradual oxidation of uraninite. On the other hand, amorphous UO_2 can be fairly insoluble and persistently metaestable over a broad range of environmental conditions /Iwatsuki et al. 2004 and references therein/. Therefore, both kinds of solids could have been present originally in the fracture fillings in Forsmark.

However, the alterations induced in the natural system could have conditioned different kinds of reequilibria. Oxygen intrusion could have enhanced the development of more oxidised surfaces in the previously existing UO_2 phases leading to a reequilibrium with respect to $UO_{2.67}$. These alterations could also be the cause of the remobilisation of uranium, important enough to reach saturation with respect to $UO_{2(am)}$ and to provoke its precipitation (amorphous UO_2 precipitates rapidly over experimental time scales; /Rai et al. 1990, 1997/).

In any case, the two key observations to justify the dissolved uranium concentration in Forsmark groundwaters are (1) the occurrence of amorphous U-phases in fracture fillings and (2) the mildly reducing Eh values, which allow for uranium-carbonate complexation.

The solubility of crystalline and amorphous UO_2 increases due to uranium-carbonate complexation, that is, depending on the pH, alkalinity or CO_2 partial pressure conditions /Bruno et al. 1997, Iwatsuki et al. 2004/. In the Forsmark groundwaters the range of alkalinity although narrow (22–125 mg/l), is in the specially critical values for the Eh measured in these waters. The increase in alkalinity produces a very important increase in the carbonate species, enhancing the dissolution of U solid phases, increasing the dissolved uranium concentrations and thus justifying the observed correlation between dissolved uranium and alkalinity in the groundwaters of Forsmark (Figure C2-11, panel b).

The important modifications that uranium speciation has inside the examined ranges of Eh, pH and alkalinity, could have conditioned different uranium mobilisation and fixation processes over the paleohydrogeological history of the system and the successive mixing processes that have taken place. In fact, variation in alkalinity due to a higher or lower Littorina proportion in the groundwaters, even under reducing conditions such as the ones used in the calculations, could justify the mobilisation of important amounts of dissolved uranium as a function of the induced reequilibria. As it was already introduced in /SKB 2005/ as a hypothesis, this kind of situation could explain the observed association between waters with an important Littorina

signature and the elevated uranium contents; however more data are needed to confirm this hypothesis.

In this context, it would be very interesting to find groundwaters with a more saline character and elevated uranium concentrations. This fact would imply that the relationship found between elevated uranium content and high *Littorina* proportion is not bijective (one-to-one correspondence); moreover, it could help to confirm $\text{UO}_{2(\text{am})}$ as the dissolved uranium controlling phase in these waters. Theoretically, if this phase is also in equilibrium in the more saline waters, dissolved uranium concentrations can also be elevated (even in more reducing conditions) depending on the carbonate system /see for example, Iwatsuki et al. 2004/.

The high sensitivity of uranium speciation to small variations in Eh or alkalinity can be even more important if we consider the modifications of the natural conditions undergone by the groundwater system. The alteration of an originally more reducing environment due to oxygen intrusion or drilling water could be the cause of an increase in the degree of carbonate complexation, thus enhancing the dissolution of uranium phases and increasing the amount of dissolved uranium. But even assuming that the redox potential had been unaffected, variations in the carbonate system (alkalinity) due to drilling waters could have significant effects in the mobilization of uranium from mineral phases.

The participation of coprecipitated uranium in iron(III) oxyhydroxides on the control of dissolved uranium content has been reported in other natural systems /Bruno et al. 2002/. This possibility has not been analysed here as there are no available data and the uranium control in Forsmark groundwaters seems to be related with the occurrence of “simple” uranium phases. Nevertheless, the common presence of hematite as coatings in the fracture fillings makes possible the occurrence of additional uranium adsorption-desorption processes in the waters with elevated uranium contents.

This association of uranium with iron(III) oxyhydroxides could be a new interesting line of study in the system mainly if it is analysed together with the microbial activity. Hallbeck (this volume) points out that iron/manganese oxyhydroxide dissolution by iron- or manganese reducing bacteria may cause dissolution of the uranium associated in these phases. But the opposite could also be true.

For example, one of the few samples with low uranium content but compositional characters similar to those with elevated concentrations (KFM01A at 112 m depth; sample 4538, Table C2-4) presents very elevated IRB (and MRB) populations (MPN = 4,000 ml⁻¹; see Hallberck, this volume) while the population of these microorganisms is very low in the rest of samples with elevated uranium content.

Reduction of soluble U(VI) by IRB and SRB activities (both by direct enzymatic reduction or by indirect effects in the redox environment) are relatively well known process and they are considered in the bioremediation studies of U-containing groundwaters /Anderson and Lovley 2002, Neal et al. 2004 and references therein/ and in the studies related with the safety assessment /e.g. Haveman and Pedersen 2001/. The important bacterial activity detected in this section could be the cause of the low uranium content of the groundwaters. Moreover, the efficiency of these processes is very well related with the occurrence of iron oxyhydroxides in the system and with the uranium complexation reactions.

Reduction of U(VI) under iron-reducing conditions in presence of Fe(III) oxyhydroxides is an effective process in uranium immobilisation. However, the enzymatic reduction of U(VI) by the IRB and the abiotic surface catalyzed U(VI) reduction could be dramatically inhibited due to uranium carbonate complexation /Behrends and Van Capellen 2005/. Moreover, under sulphate-reducing conditions, SRB mediated reduction of soluble U(VI) to insoluble U(IV) is also effective as long as a suitable electron donor is available. Depletion of the electron donor may result in partial reoxidation of the U(IV) when surfaces of crystalline iron oxyhydroxides are incompletely reduced /Sani et al. 2004/.

All these evidences indicate that the efficiency of the microorganisms in the immobilisation of uranium depends on other factors or processes whose occurrence or extent has been independently identified in the system. The influence of alkalinity on the inorganic uranium complexation has just been mentioned. Moreover, a low crystallinity iron oxyhydroxide (associated with the oxygen intrusion in the system) has been identified as responsible for the potentiometrically measured Eh. IRB activity could have been magnified in section 110.1–120.8 m (KFM01A at 112 m depth) due to the formation of this oxyhydroxide as these organisms prefer low crystallinity (or high surface area) oxyhydroxides for their metabolism /Roden and Zachara 1996, Roden 2003 and references therein/.

Obviously, these hypothesis must be verified in following iterations as the amount of available data increases (e.g. it is also possible that the low uranium contents in the brackish groundwater at 112 m depth be only conditioned by the absence of uranium phases at that point.) Nevertheless they highlight the interest of keeping studying the system as it offers exceptional characters (waters with elevated uranium contents, iron oxyhydroxides and bacterial activity) to understand the efficiency of the microbial processes in the uranium mobilisation-retention.

C2.5.4 Implications for Performance Assessment

The relatively elevated uranium contents found in some Forsmark groundwaters seem to be the result of two factors: (a) the control exerted by an amorphous uranium phase (and, therefore, specially soluble) present in the system and (b) the mildly reducing Eh of the waters. Only under these conditions groundwaters are able to mobilize the detected uranium contents (assuming that these waters participate in the flow paths and do not correspond to more or less stagnant “pockets”).

An important conclusion can be drawn: these waters will not be able (from a thermodynamic point of view) to dissolve a hypothetical spent fuel in contact with them. These waters are in equilibrium with uranium amorphous phases and therefore they are also strongly oversaturated with respect to crystalline uraninite ($\log K = -4.85$ for reaction 1) or to the spent fuel material ($\log K = -1.6$; /Bruno and Puigdoménech 1989, Casas et al. 1998/). That is, the uranium mobility in some Forsmark groundwaters is controlled by phases more soluble than crystalline uraninite or spent fuel.

As it has been presented above, the original conditions of these groundwaters (mainly the redox state) seem to have been modified by drilling water and the external input of oxygen. The extent of the induced alteration is difficult to quantify but, as it has already been stated, the solubility of these amorphous phases is very sensible to small variations in pH, Eh and the carbonate system, in the ranges found in the natural system. Therefore the elevated uranium concentrations found in some waters could have been magnified with respect to the ones existing under unaltered conditions.

The confirmation of this hypothesis before the Forsmark area is evaluated as a possible candidate for a high-level waste repository is critical. Therefore, it is also essential to continue this study. However, independently of the selection of this area as a repository, we think that Forsmark has other interesting merits from the Performance Assessment point of view.

The physicochemical conditions of the groundwaters with elevated uranium contents seem to correspond to a system that has re-equilibrated after an alteration of its redox state. Therefore, a detailed monitoring of the system can be useful:

- to study the geochemical evolution of a system altered by oxygen intrusion, mixture of waters or corrosion, frequent elements considered (separately or together) in the main PA scenarios;
- to analyse the particular evolution of the active redox systems: uranium, iron and sulphur.

Moreover, future studies could help to delimitate the uranium phase or phases responsible for the control of this element in the waters and check their solubility values. The preliminary calculations performed here suggest that the solubility values for $\text{UO}_2(\text{am})$, an especially problematical phase in the bibliography, are closer to the ones determined by /Rai et al. 1990, 1997/ and, therefore, higher than the values included in the most commonly used thermodynamic databases.

It is very important to test this findings as $\text{UO}_2(\text{am})$ is usually used to obtain the conservative values (maximum concentrations) in the solubility limits estimations in PA exercises such as H-3 /PNC 1992/, Kristallin-I, /Berner 1995/ or SITE-94 /Arthur and Apted 1996/. Depending on the solubility values used, the results may be not so conservative. Something similar happens with USiO_4 also used, occasionally, for the calculation of solubility limits (e.g. in SR 97; /Bruno et al. 1997/).

Finally, the special characters found in the system (elevated uranium contents in groundwaters, reducing conditions with uranium carbonate complexation, occurrence of iron oxyhydroxides and bacterial activity) can help in the study of the interest of microbial processes in the uranium mobilisation-retention processes.

C2.6 Manganese in Forsmark Groundwaters

Manganese contents in surface waters and groundwaters in Forsmark span a very wide range, reaching values as high as 3 mg/l in some groundwaters (Tables C2-2 and C2-4). High-uranium waters at Forsmark have usually (but not always) a high Mn content (between 1.7 and 3 mg/l)¹³. As the presence of Mn^{2+} is a strong indicator of reducing conditions, the U-Mn association in Forsmark groundwaters is, to say the least, striking.

The hypothesis formulated in the previous section can explain the elevated uranium concentrations in some Forsmark groundwaters but it cannot explain the elevated Mn concentrations nor its association with waters of a very specific Cl content (around 5,500 mg/l).

The detailed geochemical behaviour of Mn has not been addressed in Forsmark yet, nor in other granitic groundwater systems. As a result, and in light of the apparent relationship with uranium, a detailed study has been carried out here, framing the discussion in the broader picture of other granitic systems in the Scandinavian Shield.

C2.6.1 Manganese concentrations in Forsmark and other granitic groundwater systems

Manganese concentrations in surface waters, near-surface groundwaters and deep groundwaters in the Forsmark area vary from very low (below detection limit) to 3 mg/l. As already said, the highest values are found in groundwaters with chloride contents around 5,500 mg/l (Figures C2-2 and C2-3, panels b). Deeper and more saline groundwaters have lower manganese concentrations (< 0.5 mg/l).

In the Laxemar area (Figure C2-19 panel a), maximum Mn contents in representative groundwater samples are similar (around 3 mg/l in Ävrö subarea). These maximum concentrations are associated with low-Cl near surface groundwaters (< 100 m). Deeper groundwaters, with Cl contents around 5,000 mg/l, have variable but relatively high Mn concentrations (from 0 to 1.6 mg/l), similar to, but not as marked as in Forsmark /SKB 2006b/.

¹³ The European Community /EC 1998/ has set the value 0.05 mg/l as the upper Mn limit in drinking waters.

In the Finnsjön area, at depths between 100 and 700 m, maximum Mn concentrations reach 1.3 mg/l, and again, as in Forsmark and Laxemar, variable and relatively high Mn contents are associated with waters with a Cl content between 3,000 and 5,000 mg/l (Figure C2-19, panel b).

At Olkiluoto (Finland) the same behaviour is found, with highly variable Mn contents, together with high values (up to 1.2 mg/l), in waters with a chlorine concentration of 4,000–5,000 mg/l (Figure C2-19, panel c). In this system maximum Mn levels of 2.3–2.6 mg/l have been measured in near surface groundwaters and in two very saline samples (Cl = 44,000 mg/l) at 900 m depth /Pitkänen et al. 2004/.

Groundwaters from Palmottu (Finland) have maximum Mn contents of 1.2 mg/l in the near surface groundwaters (100–200 m depth), where Cl is very low (Figure C2-19, panel d). Deep groundwaters do not get beyond 0.2 mg/l of Mn in any case.

Stripa groundwaters have very low Mn levels, with maximum values of 0.05 mg/l, and often below the detection limit /Nordstrom et al. 1985/. And finally, groundwaters studied by /Gascoyne 2004/ in the Canadian Shield have low Mn concentrations, always below 0.7 mg/l.

From this short survey of Mn concentrations in granitic systems three important conclusions can be drawn. **First**, Mn levels at Forsmark groundwaters are higher than in most systems under comparison.

Second, there is no direct correlation between U and Mn in groundwaters in general; systems where Mn is high usually have low U contents (see previous section). For example, in Palmottu, where an uranium ore exists, maximum U levels (much higher than at Forsmark) have associated Mn contents of 0 to 0.6 mg/l, variable but not particularly high. High Mn²⁺ values in groundwaters (as in Forsmark and Laxemar) indicate a reducing environment where, as a rule, U contents are low. The presence of amorphous U phases, as those identified in Forsmark, is one of the very few geochemical situations where elevated dissolved Mn and U contents can occur simultaneously.

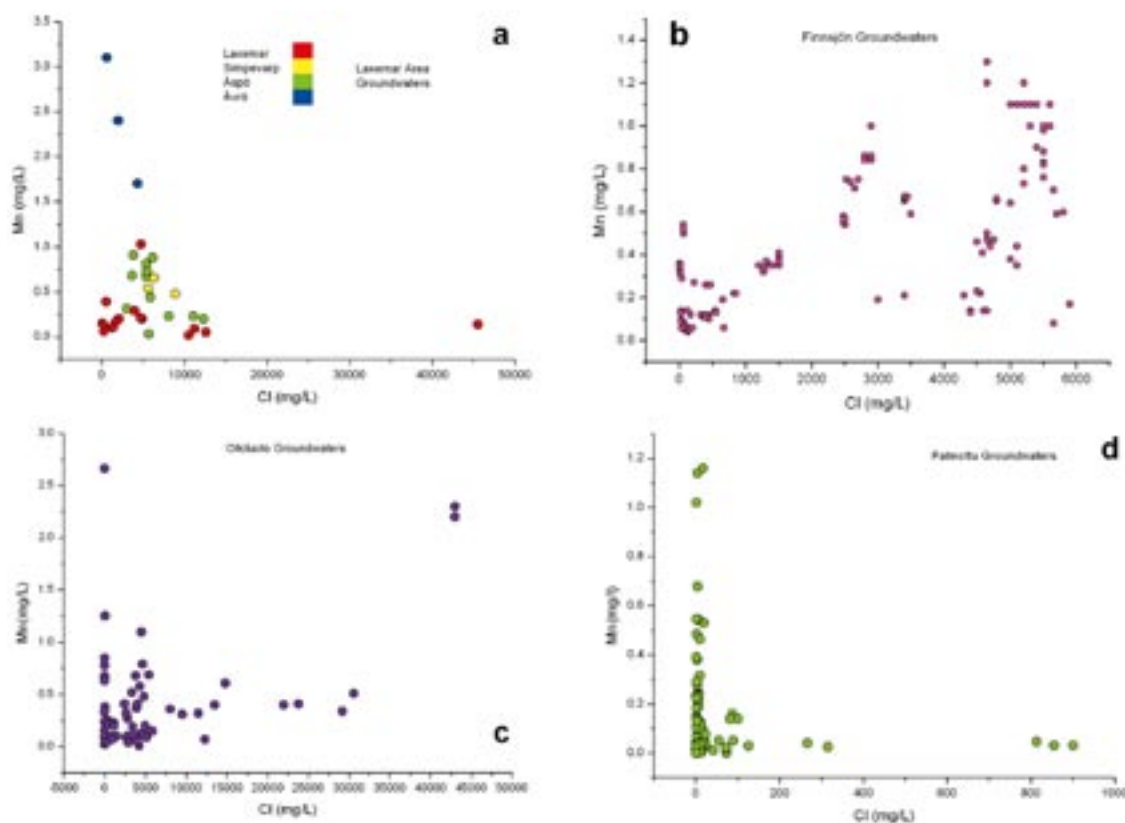


Figure C2-19. Manganese distribution with respect to chloride in different Nordic Sites. (a) Laxemar area (Sweden); (b) Finnsjön (Sweden); (c) Olkiluoto (Finland); and (d) Palmottu (Finland).

Third, the high variability of Mn concentrations in soil pipes and near surface groundwaters in all reviewed systems can be considered as normal, and is related to the intrinsic redox variability of the superficial environment and the different intensity in activity of Mn-reducing bacteria (MRB). More interesting is the Mn variability in deep groundwaters with Cl contents in the range 3,000–5,000 mg/l. In Forsmark and Finnsjön this variability is comparable to the one in the near-surface environment, with maximum Mn contents even higher than in the near-surface.

The deep groundwater Mn variability detected in Forsmark, Finnsjön, Olkiluoto and, in a lesser degree, Laxemar, can be related to their paleohydrogeological history: a Littorina recharge period, not detected in the other groundwater systems. Mixing calculations carried out in Forsmark and Olkiluoto /Pitkänen et al. 1999, 2004/ show the existence of waters with a high percentage of the Littorina end-member (see below).

C2.6.2 Manganese and general characters of Forsmark groundwaters

Divalent manganese occurs as a trace constituent in many minerals. In fracture fillings can be associated with iron minerals, usually iron oxyhydroxides or mixed Mn-Fe oxyhydroxides, or even in Fe²⁺-chlorites and clays /Sandström and Tullborg 2005/. Mn²⁺ is also known to substitute for calcium in calcite, although Mn contents in Forsmark fracture filling calcites are low or very low /Sandström et al. 2004, Sandström and Tullborg 2005/. All these minerals could have controlled (or be controlling) the concentration of Mn in the groundwaters.

As already indicated, dissolved manganese follows a similar trend with depth as iron, with variable and high values from the surface to 600 m in the brackish groundwaters, and very low values in the deeper, more saline waters (Figure C2-3, panels a and b).

This parallel behaviour is shown as a good correlation between the concentration of both elements in groundwaters (Figure C2-20, panel a), which could be an indication of their control by iron-manganese phases (oxyhydroxides, clays), or the operation of surface processes between dissolved manganese and iron oxyhydroxides.

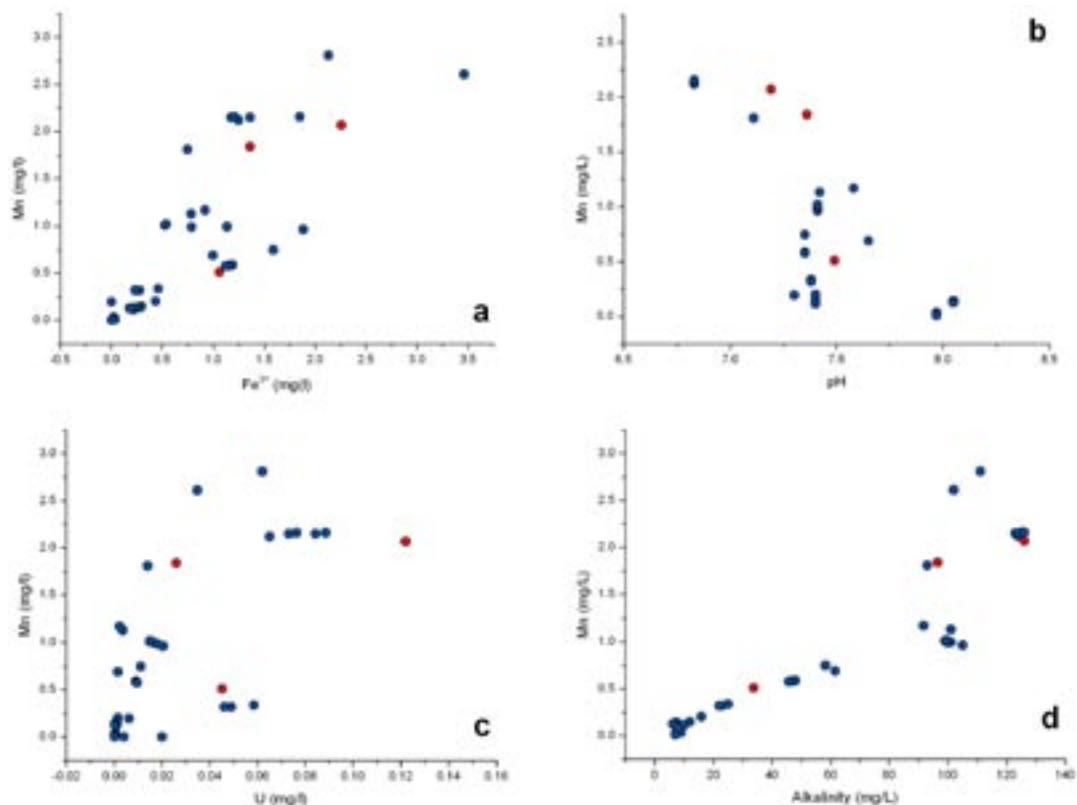


Figure C2-20. Manganese contents in Forsmark groundwaters with respect to different parameters. (a) Ferrous iron concentration; (b) pH; (c) Uranium content; and (d) Alkalinity.

Manganese concentrations decrease with increasing pH (Figure C2-20, panel b). As /Glynn and Voss 1999/ suggest for Laxemar groundwaters, this decrease resembles the standard inverted-integral sign profile in measurements of cation sorption as function of pH. Pristine points of zero charge for goethite and hematite are between 7 and 8.5 and both minerals, specially hematite, are usually found as fracture coatings /Sandström et al. 2004, Sandström and Tullborg 2005/. In any case, data available are still too scarce to reach any definitive conclusion.

With respect to other redox parameters (S^{2-} , uranium, Eh), dissolved Mn does not show clear correlations; only in the case of uranium a weak positive correlation can be inferred (Figure C2-20, panel c). There is also no clear correlation between Mn and Ca. On the other hand, Mn does show a positive correlation with respect to alkalinity (Figure C2-20, panel d): Mn and alkalinity increase together until this last parameter reaches values around 100 mg/l (brackish groundwaters). The known negative trend between alkalinity and depth (or chlorine), typical of these granitic systems, and the very low Mn contents in the more saline waters, strengthen the Mn-alkalinity correlation in the 0–100 mg/l alkalinity range. But this correlation could also be partially conditioned by the activity of Mn reducing bacteria (MRB) that produce Mn^{2+} but also HCO_3^- due to the oxidation of organic matter. However, there seems to be no generalised MRB activity in Forsmark groundwaters, as is explained in the next section.

C2.6.3 Manganese and Manganese Reducing Bacteria (MRB)

Microbiological studies carried out in Forsmark (see Hallbeck, this volume) detect, as a rule, a very low activity of MRB (Table C2-4). In the deeper and more saline waters (from 650 to 1,000 m) the absence of MRB is consistent with the low measured Mn^{2+} contents. In the rest of the studied groundwaters of the brackish type, manganese-reducing bacteria are present in very low amounts, with the exception of the 115 m depth section in borehole KFM01A, where MPN values reach $3,000\text{ ml}^{-1}$ (see Hallbeck, this volume) in groundwaters with a Mn concentration of 0.7 mg/l (not very high). Some borehole sections with high Mn contents, like at 173 m depth in KFM01A (sample 4724, 1.02 mg/l) and at 503 m in KFM02A (sample 8016 with 2.16 mg/l; Figure C2-21), have MRB numbers below the detection limit ($< 0.2\text{ ml}^{-1}$). In general, there is no definite correlation between dissolved Mn and MRB abundances /SKB 2005, 2006a/.

As a conclusion, MRB activity can influence Mn^{2+} concentrations in some near surface brackish groundwaters (e.g. KFM01A at 112 m depth), but it seems to have no effect on the variable and usually high Mn concentrations in most brackish groundwaters. This conclusion also implies that the observed Mn-alkalinity correlation has nothing to do with the present activity of manganese reducing bacteria.

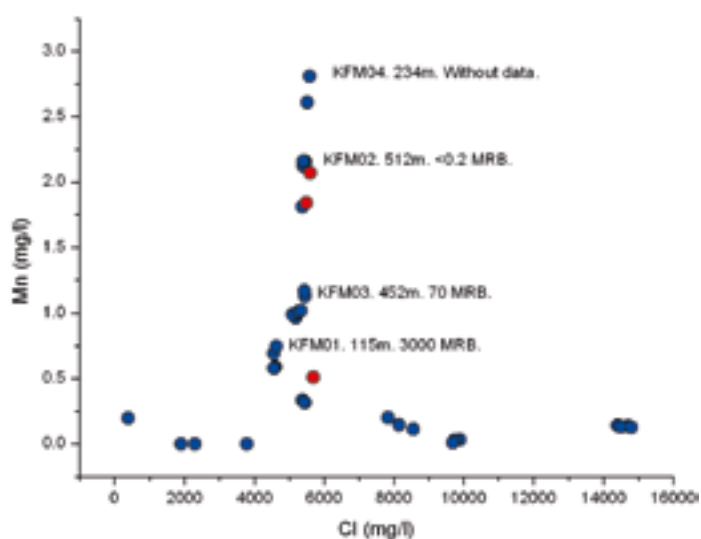


Figure C2-21. Manganese distribution with respect to chloride and most probable number of MRB in different Forsmark groundwater samples.

The activity of other microorganisms in the brackish groundwaters between 180 and 640 m depth seems also to be very low. Although the amount of data is scarce, it can be suggested that the sampled borehole sections correspond to isolated pockets without enough nutrient inflow to sustain a bacterial population (Hallbeck, this volume).

C2.6.4 Solubility calculations

Speciation-solubility calculations have been performed with PHREEQC /Parkhurst and Appelo 1999/ and the WATEQ4F /Ball and Nordstrom 2001/ database. Results indicate strong undersaturation states for all Mn oxides and oxyhydroxides included in that database. The only Mn mineral that reaches equilibrium in the studied groundwaters is rhodochrosite (MnCO_3 ; Figure C2-22, panels a and b), considering a SI uncertainty range of ± 0.5 ¹⁴.

Equilibrium with rhodochrosite can be observed in near surface groundwaters with low Mn and high alkalinity, but it is especially evident in deeper groundwaters with an important *Littorina* content, characterised by alkalinity values between 50 and 100 mg/l and Mn contents above 1 mg/l¹⁵. In both water types there are also samples undersaturated in rhodochrosite, reflecting their variable Mn contents.

Rhodochrosite has not been identified in the fracture fillings in Forsmark. However, the generalised equilibrium situation affecting groundwaters with a wide range of alkalinities and Mn contents suggests that this phase is an actual limiting factor in the dissolved concentration of Mn, at least in specific conditions.

Precipitation of rhodochrosite has long been described in marine sedimentary environments /Li et al. 1969, Suess 1978, Thompson et al. 1986, Gingele and Kasten 1994; etc/, including the Baltic Sea /e.g. Jakobsen and Postma 1989, Kunzendorf and Larsen 2002, Neumann et al. 2002, etc/. This mineral has also been suspected or identified as a possible Mn^{2+} -sink in sedimentary aquifer systems /Matsunaga et al. 1992, Mayer et al. 2001, Massmann et al. 2004/. Moreover, in laboratory studies on microbial organic carbon reduction of Mn(IV), /Lovley and Phillips 1988/ reported that the Mn^{2+} produced was quickly precipitated as MnCO_3 . More recently, /Amirbahman et al. 2003/ reach similar conclusions in column experiments designed to simulate the biogeochemical processes resulting from microbially catalysed oxidation of organic matter.

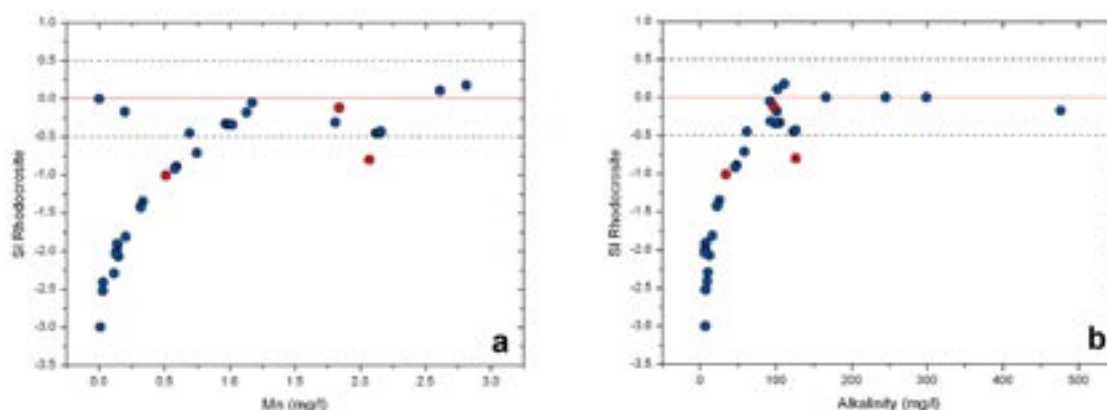


Figure C2-22. Rhodochrosite saturation index with respect to manganese (a) and alkalinity (b) contents in Forsmark groundwaters.

¹⁴ The solubility value of rhodochrosite used in the calculations is the one included in WATQ4F database /Ball and Nordstrom 2001/, $\log K = -11.13$. This value is very similar to the more recent values proposed by /Jensen et al. 2002/. The uncertainty range has been fixed in a 5% of the $\log K$ value.

¹⁵ Most waters with high U levels and in equilibrium with a UO_2 amorphous phase (previous section) are also in equilibrium with rhodochrosite.

However, the direct control of dissolved Mn by rhodochrosite has not been described in any granitic groundwater system, mainly because Mn is not one of the usually investigated elements and not much information about the saturation indices of its minerals is included. To overcome this deficiency, speciation-solubility calculations with groundwater samples from Laxemar, Olkiluoto and Palmottu have been carried out. Laxemar and Olkiluoto have a Littorina stage in their paleohydrogeological evolution.

Results for Olkiluoto (analytical data taken from /Pitkänen et al. 1999, 2004/) show that, as in Forsmark, only some of the groundwaters with a high proportion of the Littorina end-member (with Cl contents between 3,500 and 5,000 mg/l and Mn contents up to 1.2 mg/l; Figure C2-23, panel a) reach equilibrium with rhodochrosite, taken into account the uncertainty range of ± 0.5 IS units. The maximum percentage of Littorina in these waters is 40–60% /Pitkänen et al. 1999, 2004/, similar to Forsmark (30–50%). The rest of the deep groundwaters in Olkiluoto are clearly undersaturated with respect to rhodochrosite, even the most saline groundwaters with the maximum Mn contents (2.3 mg/l, Figure C2-19, panel c).

As for Laxemar, results suggest a similar situation (Figure C2-23, panel b) for the few samples with a Littorina signature (some of the samples from Äspö, Simpevarp and Laxemar, with Cl contents around 5,000 mg/l, 0.14 mol/kg; /SKB 2004, 2006b/). Groundwaters in Laxemar area with higher concentrations of Cl are again clearly undersaturated in rhodochrosite.

Finally, in Palmottu, a groundwater system where Littorina waters have not participate in its hydrological evolution, chloride concentration is very low in all the waters (Figure C2-23, panel c) and most of the available data correspond to shallow depths (up to 400 m depth). Some of these waters are in equilibrium with rhodochrosite (as it happens in Forsmark for the shallow groundwaters – up to 150 m) but they tend to undersaturation as the depth increases.

These results show that equilibrium with rhodochrosite is not common in deep and old groundwaters in granitic systems. Only those groundwaters with a high proportion of Littorina reach equilibrium.

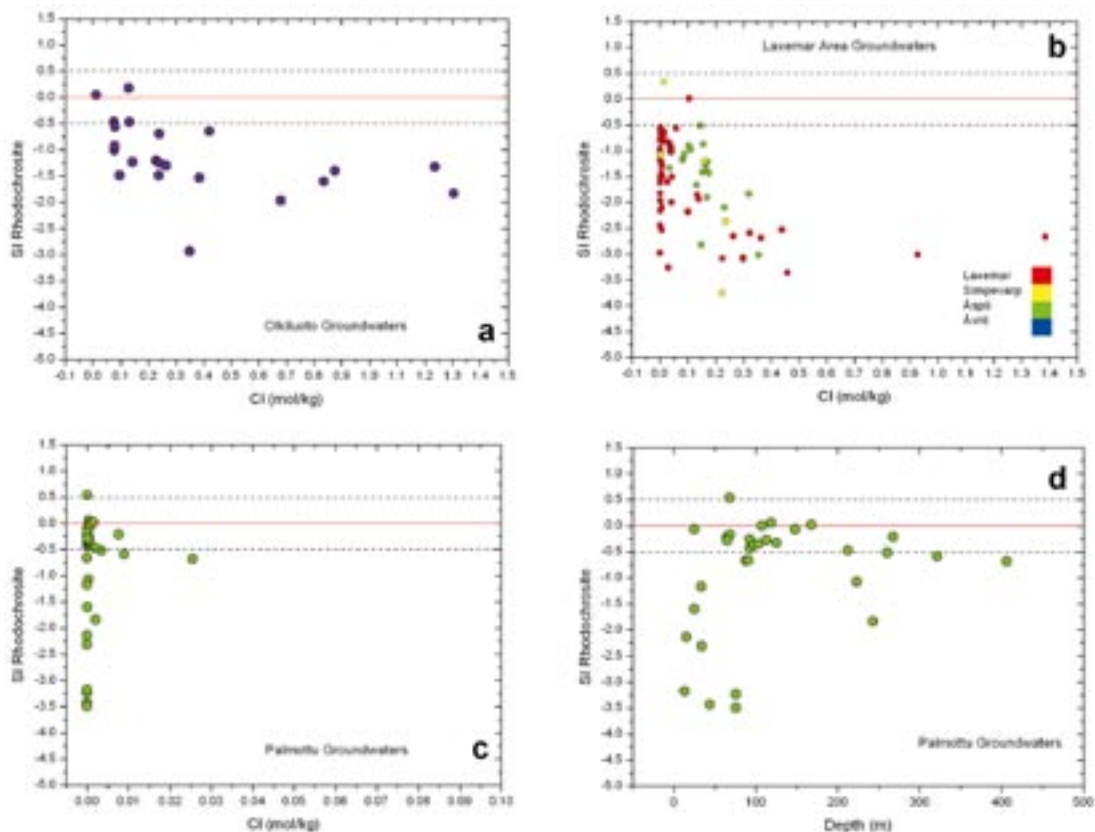


Figure C2-23. Rhodochrosite saturation indexes in the groundwaters from different sites. (a) Olkiluoto (Finland); (b) Laxemar Area (Sweden); and (c) and (d) Palmottu (Finland).

C2.6.5 Manganese, Rhodochrosite and Littorina

All the evidences put forward in the previous sections suggest a clear link between equilibrium with rhodochrosite and high proportions of Littorina in the groundwater. This relationship can be understood analysing the diagenetic history of the marine sediments related with the Littorina marine waters.

Sedimentary manganese carbonates, such as rhodochrosite and kuthnavorite¹⁶, occur in many organic-rich laminated marine sediments as the ones present in the Baltic Sea /Lepland and Stevens 1998, Burke and Kemp 2002, Kunzendorf and Larsen 2002/. In the Baltic Sea, Mn-carbonate formation has taken place for the last 7,000 yr (Littorina stage) leading, for example, to Mn concentrations of up to 10 wt.% in the bulk sediments of the Gotland Basin /Neumann et al. 2002 and references therein/.

Formation of these authigenic rhodochrosite laminae in the Baltic Sea has been related to the periodic renewal of deep waters by inflows of North Atlantic surface waters /Kulik et al. 2000, Heiser et al. 2001, Neumann et al. 2002, Burke and Kemp 2002/. During an inflow event, the anoxic water column is flushed by saline and oxic water, that rapidly reoxidizes the dissolved manganese present, and large quantities of particulate Mn-oxide are deposited at the sediment–water interface. These Mn-oxides supplied from oxic surface sediments are reduced at depth by manganese reducing bacteria when all the available oxygen is consumed. This process produces large in situ Mn²⁺ concentrations and, in combination with high carbonate alkalinity generated by mineralization of organic matter, leads to pore-water conditions in the sediments that are supersaturated with respect to rhodochrosite or to a mixed Ca and Mn-rich carbonate /Burke and Kemp 2002/.

This scenario of periodic authigenesis of rhodochrosite can easily justify the intrusion of marine waters with high (and variable) concentrations of dissolved Mn²⁺ into the groundwater system. During the mixing event, under reducing conditions, of marine waters with the original groundwaters occupying the hydrological system, the high Mn contents would act as a signature of their origin only in those situations where the proportion of marine water was high. Only in this circumstance the disequilibrium introduced by the mixing event would be small, and re-equilibrium easy. On the other hand, when the proportion of Littorina is small, the undersaturation state with respect to rhodochrosite, typical of the original groundwaters, would prevail. The absence of MRB activity in most Forsmark groundwaters would favour this undersaturation state.

Figure C2-24, panels a and b, shows the relationship between rhodochrosite saturation indices and Littorina proportion as calculated by M3 (n-PC mixing algorithm) for a representative set of Forsmark groundwaters. As is clear from the plots, saline waters with low Littorina proportion (< 14%) have low Mn contents and are clearly undersaturated with respect to rhodochrosite. When the Littorina proportion reaches 40–50%, waters start to be in equilibrium with rhodochrosite, together with high but variable Mn contents, perhaps related to inorganic re-equilibrium processes after the mixing event.

Nevertheless, a subset of samples with an important Littorina proportion (between 20 and 35%) have low Mn contents and are undersaturated with respect to rhodochrosite. Only one of these samples is in equilibrium with rhodochrosite; but also this is the only sample with a high amount of MRB, that could have increased the Mn²⁺ content, facilitating this way the equilibrium with rhodochrosite.

In summary, it seems that the proportion of Littorina in the groundwater is the key factor to understand equilibrium with rhodochrosite.

¹⁶ Kuthnavorite or (Mn_xCa_{1-x})CO₃ has been commonly described as Ca-rhodochrosite by other authors /Neumann et al. 2002, Burke and Kemp 2002/.

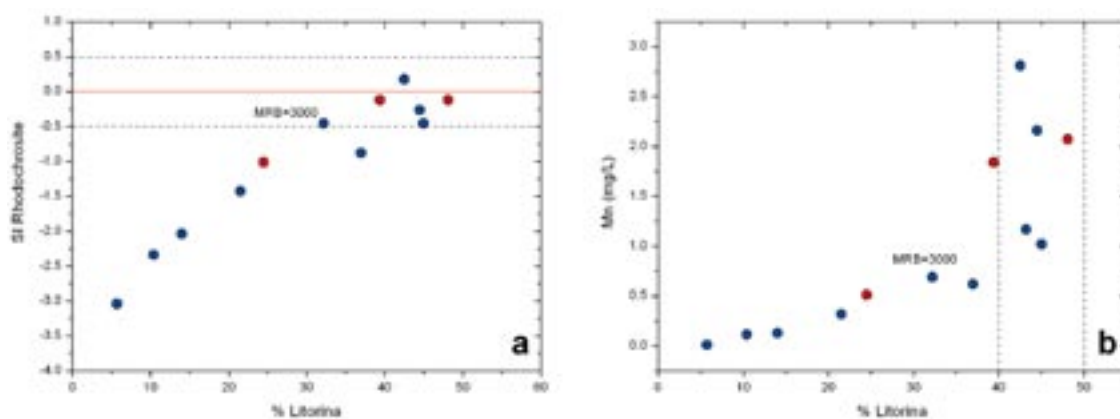


Figure C2-24. Rhodochrosite saturation indices in Forsmark groundwaters with respect to the Littorina proportion. Sample with the highest MPN for MRB are also indicated.

C2.6.6 Discussion and conclusions

Low Mn contents and undersaturation with respect to rhodochrosite in deep (> 700 m) saline Forsmark groundwaters is the common situation, in parallel with many other granitic groundwater systems. However, brackish groundwaters with an important Littorina contribution show high Mn concentrations and reach equilibrium with respect to rhodochrosite. This, of course, is a very uncommon condition in most other granitic systems in the Scandinavian Shield, unless the Littorina proportion happens to be in the same range.

All this suggests that Mn content and equilibrium with rhodochrosite in brackish groundwaters are characters imposed by the superficial marine environment prevailing during the Littorina stage. Authigenesis of Mn-carbonates is an active process in the Baltic Sea since 7,000–8,000 year ago /Kulik et al. 2000, Neumann et al. 2002 and references therein/.

Logically, the observation of this signature in Forsmark groundwaters requires the presence of waters with high Littorina proportions (higher than 40%) and has been probably favoured by the isolated character (pockets) of the analysed samples and by the lack of bacterial activity. Groundwaters with less (although relatively high) Littorina proportion (20–30%) seem to have lost this characteristic as they are undersaturated with respect to rhodochrosite. If an active presence of MRB would have been detected in these Littorina-rich groundwaters, the equilibrium with rhodochrosite could have been related with this activity at present instead of with an inherited character.

Therefore, the hypothesis suggested here (rhodochrosite equilibrium imposed by the superficial marine environment prevailing during the Littorina stage) is consistent with these singular hydrogeological and microbiological characteristics of Forsmark groundwaters (presence of pockets and absence of MRB). Nevertheless, it would be interesting to explore in more detail its applicability to other analogous granitic systems like Finnsjön or Olkiluoto.

The simultaneous presence of elevated U and elevated Mn contents in some Forsmark groundwaters seems to be fortuitous. High Mn contents are related to high Littorina proportions, but all other systems with high Littorina proportions (e.g. Olkiluoto), do not have an associated elevated U content (on the contrary, U levels are very low).

The anthropic perturbations to the system (oxygen intrusion, high drilling water proportion, etc), already mentioned in previous sections, could have introduced modifications in the concentration of dissolved Mn^{2+} . But, if this is indeed the case, they have not been strong enough to alter the equilibrium state with respect to rhodochrosite, a state that seems to be the “natural” one in other groundwater systems with high proportions of Littorina that have not suffer anthropic perturbations.

C3 A mixing hypothesis for the constant Cl value zone in the Forsmark groundwaters

In previous sections, the special characteristics of the group of brackish groundwaters with a similar chloride content of $5,500 \pm 300$ mg/L (0.15 ± 0.01 mol/kg) was investigated in terms of mixing. This group are located between 150 and 650 m depth in the Forsmark area and are characterised by an important Littorina signature (Figure C3-1). In spite of this constant chloride content, most of the other elements have a fairly broad range of values for this same depth interval. In other words, Cl content is constant but the concentrations of the other elements are not. This is especially the case for the redox elements (Chapter C2).

The question is if this is due to mixing or reaction or both. The hypothesis presented here proposes that this behaviour could be the result of pure mixing of different proportions of Littorina waters (with a chloride content of 6,500 mg/L) in a volume of rock where a previous mixture of Glacial + Brine (giving a similar Cl concentration) already existed.

Figure C3-2 plots those mixtures of Brine (Br), Glacial (Gl), Dilute Groundwater (DGw) and Littorina (Lit) that give a total Cl concentration of 5,500 mg/L. In the plot, the horizontal axis describes the proportion of Gl+DGw, and the vertical axis, the proportion of Brine. Black dotted lines give the proportion of Littorina and the continuous red line gives the combinations of Brine, Dilute Groundwater and Glacial that provide a Cl concentration of 5,500 mg/L.

As the fraction of Littorina in Forsmark groundwaters at 150 to 650 m depth varies from 20 to 60% (the dark blue rectangle with rounded corners enclosing the red line in Figure C3-2), that means that the expected values of the ratio (Gl+DGw)/Br compatible with this mixing hypothesis are between 8.5 (for 20% Litt) and 10 (for 60% Litt). These values are obtained from the plot as the ratio of the abscissa to the ordinate (light blue lines).

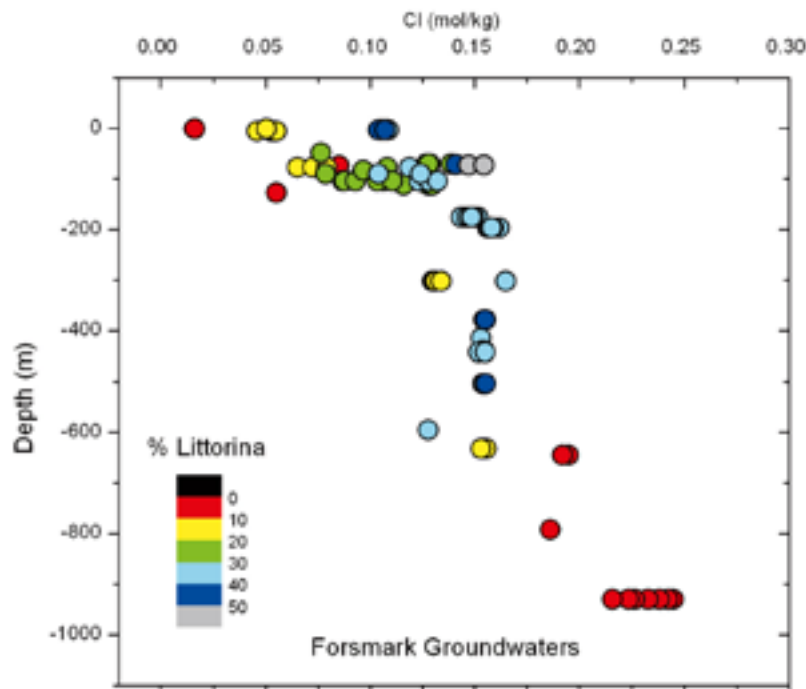


Figure C3-1. Chloride-depth distribution in the Forsmark groundwaters. The colour coding gives the percentage of Littorina in the mixture, and between 150 to 650 m depth varies from 20 to 60%.

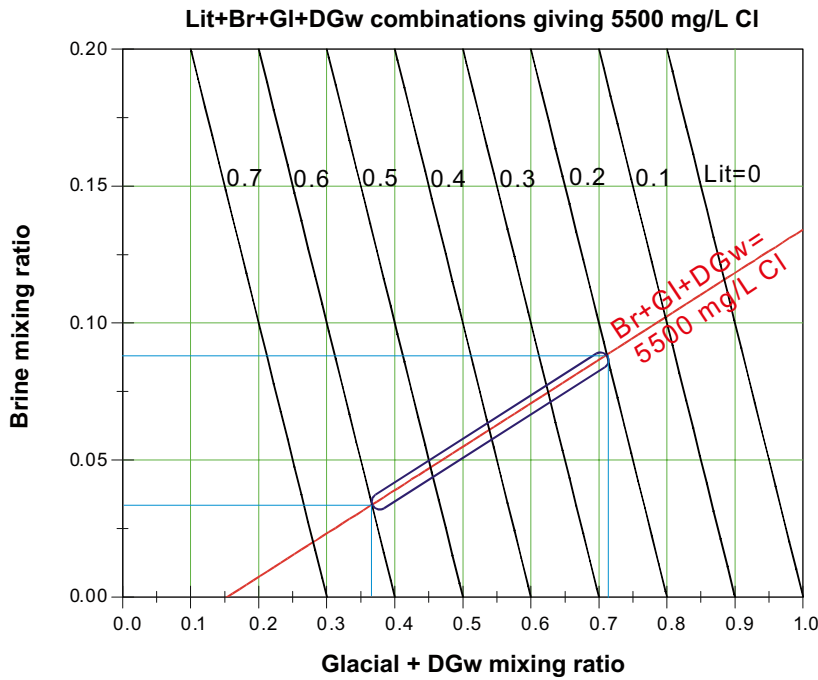


Figure C3-2. Mixtures of end-member waters Brine, Glacial, Dilute groundwater and Littorina that gives a final chlorine content of 5,500 mg/L.

Figure C3-3 shows that this is indeed the case. In this figure, depth increases to the right. Open black circles represent the chloride content in Forsmark groundwaters with the scale on the right. On the left, the ratio $(Gl+DGw)/Br$ of each sample is plotted as coloured squares, the colour giving the percentage of Littorina in the mixture.

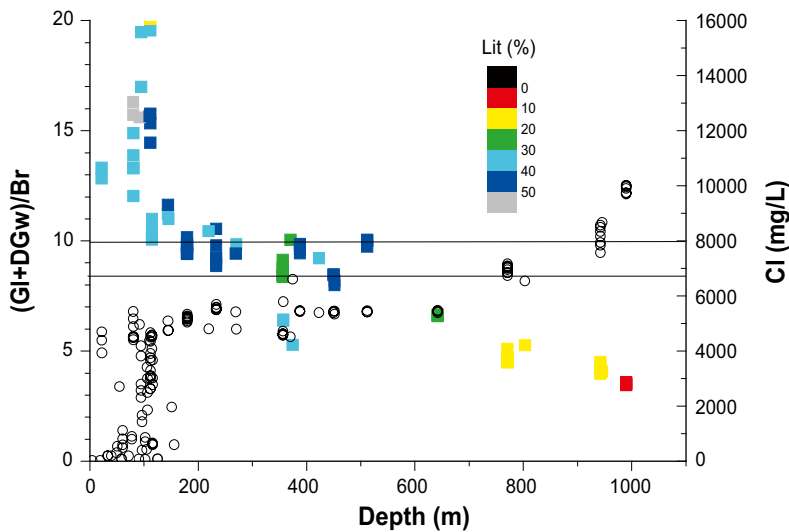


Figure C3-3. Ratio of Glacial+Dilute groundwater to Brine in waters between 0 and 1,000 m depth in the Forsmark area. Samples between 150 and 650 m depth have a constant Cl content of $5,500 \pm 300$ mg/L, a $(Gl+DGw)/Br$ ratio of 8.5–10 and a percentage of Littorina of 20–50%.

The two horizontal red lines show the (G1+DGw)/Br ratio between 8.5 and 10, as the above analysis indicates. It can be seen that samples between 150 and 650 m depth correspond to Littorina proportions of 20–50% and (G1+DGw)/Br ratios that fall inside the expected bracket.

The intrusion of variable amounts of Littorina (from 20% to around a maximum of 60%) with its $5,500 \pm 300$ mg/L of Cl, does not modify the Cl concentration of the previous Br+G1+DGw mixture, *but* it does modify the concentrations of all remaining elements.

To further investigate if the concentration of the other elements can also be explained by the mixing-only hypothesis, PHREEQC mixing calculations was carried out. Littorina mixing fractions of 20 to 60% (as computed by M3, n-PC algorithm for Forsmark samples) in steps of 10% were used to calculate the concentration of selected elements in waters composed of different mixtures of Lit+Br+G1+DGw, all with a chloride content of $5,500 \pm 300$ mg/L and a (G1+DGw)/Br ratio of 9. The results are summarised in Figure C3-4 for some major ions Na, Mg and SO_4^{2-} .

As can be readily observed, the calculations closely reproduce the observed ranges of these elements between 150 and 650 m depth. Black spheres are the result of the simulations, and coloured dots are the actual samples. The horizontal axis gives the chlorine content in mol/kg ($5,500$ mg/L = 0.15 mol/kg). In all cases the range of values of the synthetic samples matches the observed range, confirming that a simple mixing hypothesis can explain the geochemical behaviour of the constant-Cl depth range in Forsmark area.

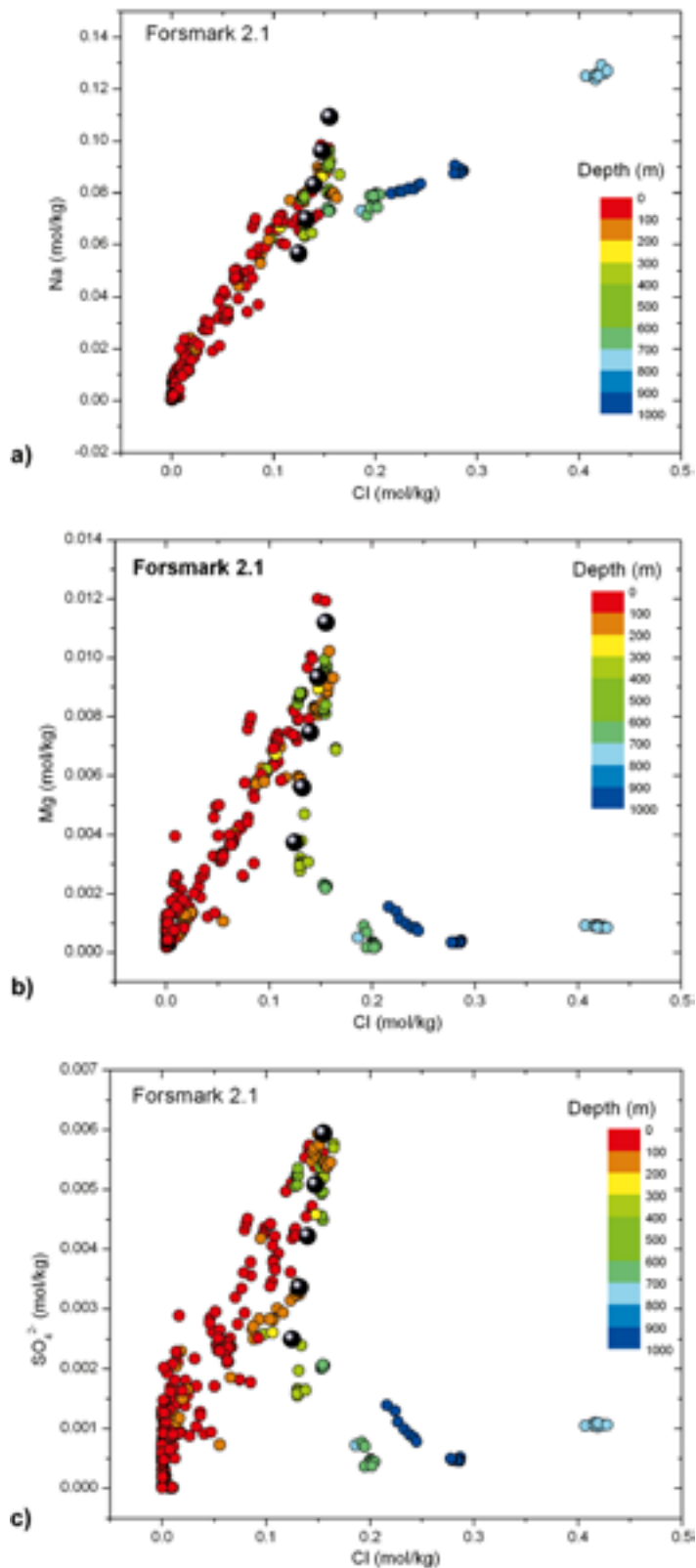


Figure C3-4. Computed concentrations (black spheres) of selected major ions (a: Na, b: Mg and c: SO_4^{2-}) in synthetic mixtures of Lit+Br+Gl+DGw with a Cl content of $5,500 \pm 300$ mg/L ($=0.15 \pm 0.01$ mol/kg). The different mixing proportions plotted as black spheres correspond to :3.2B+36.8(G+DGW)+60L, 4.0B+46.0(G+DGW)+50L, 4.8B+ 55.2(G+DGW)+40L, 5.6B+64.4(G+DGW)+30L and 6.4B+73.6(G+DGW)+20L. The computed range matches the observed range (coloured dots) in the 0.15 ± 0.01 mol/kg Cl interval. Real samples are colour coded according to depth. Note how all depths from 150 to 650 m (orange to green) are found around a Cl content of 0.15 mol/kg.

C4 Revision of conceptual models

The Forsmark area is characterised by a specially complex structural, hydrogeological and hydrogeochemical context. In fact, one of the main goals of this work has been to try and explain the most peculiar hydrogeochemical characters, many of them related to the redox behaviour. The completion of this study has come across several important problems:

1. the number of representative samples is still too low to define accurately the hydrogeochemical evolution of the system; this is even more problematic for the redox elements, specially sensitive to sampling problems;
2. in spite of the important efforts made by the Site Investigation Team, several sampling problems related to oxygen intrusion, high percent of drilling water in the water samples, corrosion processes, absence of water conducting fractures at depth, etc, have been reported in the corresponding P-reports; all this problems are probably due more to the special features of the system than to the methodology used by the site team (very good and successful in other sites as the Laxemar area, for example);
3. the number of complementary data for the study of uranium and its associated problems is still very low.

In spite of all these problems, an important effort has been made in the verification and update of the conceptual model proposed in previous phases and in the assessment of the existing uncertainties, specially with respect to the redox processes active in the system.

C4.1 Conceptual model

A special case of mixing processes

Between 150 and 650 m depth in the Forsmark area Cl content is roughly constant at $5,500 \pm 300$ mg/L (0.15 ± 0.01 mol/kg) and these waters show an important Littorina signature. On the other hand, most of the other elements at this same depth interval have a fairly broad range of values. In other words, Cl content is constant but the concentration of the rest of the elements is not. Considering that the Cl content in Littorina is around 6,500 mg/l, the hypothesis proposed here is that this behaviour could be the result of pure mixing of different proportions of Littorina waters in a volume of rock where a previous mixture of Glacial + Brine giving a very similar chloride concentration ($5,500 \pm 300$ mg/L) already existed. Calculations performed under this assumption reproduce the observed variability in the major ions dissolved contents.

Redox processes

The number of samples with representative and complete data for the analysis of the redox system (Eh values, Fe^{2+} , S^{2-} , Mn, U, microbial and mineralogical data) is not high enough to obtain definitive conclusions, even less considering the complexity of the system and the detected sampling problems. However, some preliminary conclusions have arose from the analysis presented in this work.

With respect to the general trends of the redox parameters

Eh values in Forsmark range from -140 and -250 mV, that is, a mildly reducing environment. Their distribution with depth do not seem to clearly show the trend observed in other crystalline systems (decreasing with depth). In this system the highest Eh values are found between 300 and 550 m depth, being more reducing both in shallower and deeper waters.

Iron, manganese, sulphide and uranium concentrations do not show a clear trend with chloride. This is mainly due to the wide range of concentrations of these elements in Littorina-rich groundwaters with 5,500 mg/L of chloride, where also the maximum concentrations are found.

With respect to depth Fe^{2+} and Mn^{2+} follow roughly similar trends, with variable but high concentrations between 100 and 600 m (in waters with a high Littorina proportion), and low concentrations in deeper and more saline waters. Also remarkable is the high Mn^{2+} content of some brackish groundwaters. S^{2-} contents from the surface to 600 m depth are very low (or below detection limit) and increase from there downwards. The inclusion of new samples from the next data freeze shows a change in the sulphide behaviour as very high S^{2-} contents are found at 650 m and near 1,000 m depth. As for uranium, it shows variable concentrations but usually high (up to 0.122 mg/l) at depth between 100 and 650 m, again in those waters with a high Littorina percentage. In deeper waters U concentrations decrease drastically.

All these observations suggest that there is a depth range, around 600–700 m, where an important change in the dominant species or the components that buffer the redox system occurs. This change coincides with the transition from brackish, high Littorina waters (Cl^- between 4,500 and 5,500 mg/l) to more saline groundwaters ($\text{Cl}^- > 7,000$ mg/l), which is an indication of the existence of groundwater layers with different hydrochemical characters and different geochemical evolution.

With respect to the iron system

The redox potential measured in the deepest groundwaters in Forsmark, although only one datum point is available (KFM03A, at 939.5–946.1 m depth), is the most reducing in the system and is in agreement with the value obtained with the calibration by /Grenthe et al. 1992/. This would indicate that the Eh value of these groundwaters is controlled by a clearly crystalline iron oxyhydroxide such as goethite or, more probably, hematite. This is coherent with the reducing character and long residence time of these groundwaters, where low crystallinity phases are not expected /SKB 2004 and references therein/.

The rest of the Eh values have been determined in brackish groundwaters at depths between 110 and 646 m. These seem to be controlled by the occurrence of an iron phase with an intermediate crystallinity like the one considered by /Banwart 1999/ in the Äspö large-scale redox experiment. The presence of this intermediate iron oxyhydroxide with higher solubility than a crystalline phase is possible in these brackish groundwaters if there exists a brief oxidizing disturbance. It also indicates that the system is still compensating (buffering) this disturbance.

With respect to the sulphur system

There is a surprisingly good agreement between the potentiometrically measured Eh and the values calculated with the *non-electroactive* $\text{SO}_4^{2-}/\text{HS}^-$ and pyrite/ SO_4^{2-} redox pairs in brackish groundwaters where the aforementioned oxygen intrusion and iron reequilibrium has taken place and there is no apparent SRB activity.

With the data available up to now, the agreement between geochemical (iron monosulphides saturation state) and microbiological results on the presence or absence of SRB activity is very successful. Both sets of data indicate the active occurrence of these bacteria at depths between 900 and 1,000 m in Forsmark, which is in agreement with the maximum depth with bacterial activity of this type in Laxemar /SKB 2006b/.

The same agreement between geochemical and microbiological data is found for the brackish groundwaters at depths between 100 and 600 m: undersaturated waters with respect to iron monosulphides and very low amount of SRB. However, new data taken from the next data freeze suggest the presence of a slightly more intensive SRB activity in some waters in equilibrium with mackinawite. In any case, all the brackish samples show a lower SRB activity than the one found deeper in Forsmark or in general in the Laxemar area. Therefore, brackish groundwaters in this depth range (waters that are characterised by having an important Littorina proportion) should correspond to more or less isolated pockets with a very low nutrients supply (see Hallbeck, this volume).

The equilibrium with respect to the amorphous iron monosulphides found in the deepest brackish groundwater sampled up to now (at 634–642.2 m depth) could indicate the active precipitation of amorphous iron monosulphides and, although not available yet, also the presence of an important SRB activity at shallower depths than thought before. Moreover, this depth is specially important as many other redox elements undergo severe modifications here. On the other hand, this fact suggests that some high-Littorina waters have indeed a supply of nutrients and therefore, that not all of them occupy isolated pockets as was discussed in /SKB 2005/.

With respect to the uranium system

The simplest explanation of the available data would indicate that the origin of the elevated dissolved uranium contents detected in the Forsmark brackish groundwaters are related with local U anomalies or mineralisations in contact with these groundwaters. Mineralogical data seem to confirm this point in the form of U-enriched zones (and presence of pitchblende) due to an early hydrothermal activity or a later alteration on major faults or deformation zones.

Speciation-solubility calculations support this view indicating that the elevated uranium contents are the result of two factors: (a) the control exerted by an amorphous (and very soluble) uranium phase present in the system, and (b) the not very reducing Eh values which allow uranium complexation and reequilibrium in more or less extent depending on Eh and dissolved carbonate.

Uranium minerals identified as potential controlling phases are amorphous phases such as $\text{UO}_{2.67}$, $\text{UO}_{2(\text{am})}$ or $\text{USiO}_{4(\text{am})}$. These phases are more soluble than those usually identified in other natural systems. Equilibrium with $\text{UO}_{2(\text{am})}$ (or $\text{USiO}_{4(\text{am})}$) has been defined with respect to an amorphous phase more soluble than the one considered in the thermodynamic databases but consistent with the values obtained from other natural systems or laboratory experiments. These circumstances highlight the need for and interest of keeping the ongoing work on fracture filling minerals in order to obtain a more specific and comprehensive mineralogical characterisation.

High-U waters in Forsmark have a range of uranium concentrations that span one order of magnitude. This variation could be easily justified by equilibrium situations under slightly different conditions. Inside the Eh and alkalinity ranges that characterise Forsmark waters, the speciation scheme of uranium is very sensitive to minor modifications in these parameters because they affect the extent of uranium carbonate complexation and therefore the solubility of the solids.

This last point is important considering the modification of the natural conditions possibly undergone by these waters. The alteration of an originally more reducing environment and/or the increase in dissolved carbonate (e.g. by mixing with drilling waters) could have been the cause of the increase of uranium-carbonate complexation, enhancing the dissolution of uranium phases and increasing the contents of dissolved uranium with respect to the originally present in the system.

With respect to manganese system

Low Mn contents and undersaturation with respect to rhodochrosite in deep (> 700 m) saline Forsmark groundwaters is the common situation, in parallel to many other granitic groundwater systems. However, brackish groundwaters with an important Littorina contribution show high Mn concentrations and reach equilibrium with respect to rhodochrosite. This, of course, is not a very common condition in most other granitic systems in the Scandinavian Shield, unless the Littorina proportion happens to be in the same range.

All this suggests that Mn content and equilibrium with rhodochrosite in brackish groundwaters are characters imposed by the superficial marine environment prevailing during the Littorina stage. Logically, the observation of this signature in Forsmark groundwaters requires the presence of waters with high Littorina proportions and has been probably favoured by the isolated character (pockets) of the analysed samples and by the lack of bacterial activity. The hypothesis suggested here is also consistent with the singular hydrogeological and microbiological characteristics of Forsmark groundwaters.

The simultaneous presence of elevated U and elevated Mn contents in some Forsmark groundwaters seems to be fortuitous. High Mn contents are related to high *Littorina* proportions, but all other systems with high *Littorina* proportions (e.g. Olkiluoto), do not have an associated elevated U content (on the contrary, U levels are very low).

In general terms, results support the conceptual model reported in Forsmark 1.2 /SKB 2005/. The specific hydrochemical characters analysed in this 2.1 phase also highlight a noticeable difference in the system below and above 600–700 m depth. Waters between 110 and 643 m depth (brackish groundwaters) have a very narrow chloride range, elevated and variable U, Mn and Fe concentrations, and very low sulphide contents (except in the transition zone at 643 m), and an important *Littorina* proportion. The deepest and more saline groundwaters (from 770 to near 1,000 m) have a higher chloride contents (from 6,000 to 16,000 mg/l), are low in U, Mn and Fe and high in sulphide, and have a more important brine component.

C4.2 Uncertainties

The analysis performed in this work has shown that the sampling problems reported in the Forsmark P-reports could have provoked more or less important alterations in the original redox conditions of the hydrochemical system. However, the extent of the induced alterations is difficult to quantify as it could be the result of several independent or combined processes (oxygen intrusion, high percent of drilling waters, corrosion of the drilling tools, etc). These processes could have affected the system in a different extent depending on its original characters.

Iron is the element most clearly affected. The Eh control by oxyhydroxides of intermediate crystallinity is in agreement with a disturbance due to oxygen intrusion. Besides, the occurrence of this phase would indicate that the system is still evolving and compensating the effects of the intrusion of oxygen. This situation has been detected in the brackish waters but not in the deeper saline groundwaters.

Perturbations in the original sulphide content have also been detected. Some of the samples analysed here but taken from the next data freeze correspond to previously sampled sections where very low sulphide contents (even bld) were found, but now they show high and significant dissolved sulphide. Although the number of samples is low (only three) they give a very interesting information: (a) high values found in saline groundwaters clearly indicate the sulphidic character of these deepest waters (between 640 and 1,000 m depth) supporting the agreement between the available geochemical and microbial data; and (b) detectable but still very low sulphide concentrations in brackish groundwaters seem to confirm that the generally non-sulphidic character of most of the brackish groundwaters and the associated low SRB population are “real” characters of the system, and not promoted by the alteration of the original conditions in the system; otherwise, the only possible explanation would be that both the geochemical and microbial data have been drastically modified by the alteration of the system.

These observations demonstrate two things: (a) we are still in a phase where the conceptual model and the associated uncertainties are dependent on the number of available samples; and (b) re-sampling campaigns are very important in order to decrease uncertainties and to better understand the studied system.

Uranium in another of the redox elements that may have been affected by disturbances in the system. The alteration of an originally more reducing environment due to oxygen intrusion or drilling water could be the cause of an increase in the degree of carbonate complexation, thus enhancing the dissolution of uranium phases and increasing the amount of dissolved uranium. Oxygen intrusion could have enhanced the development of more oxidised surfaces in the previously existing UO_2 phases leading to a reequilibrium with respect to $\text{UO}_{2.67}$. These alterations could also be the cause of the remobilisation of uranium, important enough to reach saturation with respect to $\text{UO}_{2(\text{am})}$ and to provoke its precipitation. But even assuming that the redox potential had been unaffected, variations in the carbonate system (alkalinity) due to drilling waters could have significant effects in the mobilization of uranium from mineral phases.

All these possibilities are of indubitable interest in understanding the system and for the safety case. However, they can not be readily evaluated due to the low number of samples with the necessary data and the absence of other key parameters such as the oxidation state of dissolved uranium, its association with colloidal phases, the nature of the U mineral phases in the fracture fillings, and U-series isotopes results in fracture coatings and waters.

In this complex framework an additional issue has arisen: the high manganese contents associated with the brackish groundwaters seem to not have been affected by disturbances in the system. In many cases, manganese contents seem to be conditioned by processes that took place when Littorina waters infiltrated through the marine sediments.

The most peculiar features of the Forsmark system are associated with the brackish groundwaters (special case of mixing, elevated uranium and manganese contents, low SRB populations, etc). However these peculiarities are too many and too different to accept that all of them are just the result of an alteration of the pristine conditions. Therefore, the question here is to assess how much of this “peculiar” behaviour is intrinsic and how much is extrinsic.

C4.3 Feedback to the Sites

Different observations indicate that the Forsmark system could have been disturbed during sampling. However, in most cases the special geological characteristics of the system could also explain these geochemical peculiarities, or they could even be the result of a combination of both.

The estimation of the real effects of both possibilities, a perturbation of the original system or intrinsic peculiarities of the system before the Forsmark area is evaluated as a possible candidate for a high-level waste repository is critical. Therefore, it is also essential to continue this study. However, independently of the selection of this area as a repository, we think that Forsmark has other interesting merits from the Performance Assessment point of view.

The physicochemical conditions of the groundwaters with elevated uranium contents seem to correspond to a system that has re-equilibrated after an alteration of its redox state. Therefore, a detailed monitoring of the system can be useful:

- to study the geochemical evolution of a system altered by oxygen intrusion, mixture of waters or corrosion, frequent elements considered (separately or together) in the main PA scenarios,
- to analyse the particular evolution of the active redox systems: uranium, iron and sulphur.

Moreover, future studies could help to delimitate the uranium phase or phases responsible for the control of this element in the waters and check their solubility values.

Finally, the special characters found in the system (elevated uranium contents in groundwaters, reducing conditions with uranium carbonate complexation, occurrence of iron oxyhydroxides and bacterial activity) can help in the study of the interest of microbial processes in the uranium mobilisation-retention processes.

Therefore, our suggestion to the site is to continue the studies in Forsmark, making special emphasis in the following:

Mineralogical studies:

1. Uranium concentrations in fracture fillings/coatings.
2. Presence of U-phases (and characterisation) in fracture fillings. Genetical relation with the rest of minerals (age?).
3. U in Fe-oxyhydroxides (concentrations, type of association, etc).
4. Presence of Ca-Mn carbonates in Littorina groundwaters.

Hydrochemical analysis:

1. Oxidation states of the dissolved uranium.
2. Uranium series disequilibrium analysis.
3. Re-sampling of sections (as it has been doing in this data freeze).

**3D-Terra, Montreal, Canada, Forsmark 2.1
issues report**

Ioana Gurban

March 2007

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D1 Introduction

This paper presents the results of the mixing modeling and 2D visualization of Forsmark 2.1 groundwater data. The focus is on updating the hydrochemical model, to make uncertainty tests and to present models that can be better integrated with the hydrodynamic models. The need for additional uncertainty tests was identified during the Forsmark 1.2 modelling phase. Issues like the use of tritium as variable in the PCA and the use of different end members are addressed. The code M3 was updated to a new version including hyperspace option calculations. The new M3 code was tested and compared with the old version, in 2D and in hyperspace. A feasibility DIS (Drilling Impact Study) evaluation was done for the section 353.5–360.62 m in KFM06. An attempt to use the electrical conductivity values, gathered during the DIFF (Differential flow measurements) measurements, as a hydrochemical variability indicator was made for the borehole KFM06.

Some issues, like the use of the tritium as a variable and the use of the meteoric (rain 60 with 168TU) end member, were already addressed in the Laxemar 2.1 exercise /SKB 2006b/. The alternative models and the experience from Laxemar 2.1 helped to clarify the different previously unsolved issues such as: the use of tritium as a variable (without correcting the age), the use of meteoric end member and the use of only groundwater data. These issues were integrated and a new bedrock model was built for Forsmark 2.1.

The different modelling issues are presented bellow and at the end of each paragraph the issues are commented.

Table D1-1. Modelling issues addressed.

(18) Investigation of the recharge end-member and it's effect on the mixing models and the site understanding	M3
(19) The proper use of Tritium in the models	M3
(20) Test of models including all elements and isotopes versus models with conservative constituents (D, O ¹⁸ , T)	M3/ Expert judgement
(21) Comparison of different models and the number of observations they can describe	M3/M4
(22) Inclusion of samples from large depth and how they affect the bedrock model	M3
(23) Evaluation of suitable data from SICADA and DMS to perform Drilling Impact Study (DIS) calculations	Expert judgement/calculations
(24) Evaluation of the Electric Conductivity for K boreholes and its use for understanding/validate the GW spatial variability	M3 and expert judgement

D2 M3 modelling; issues 18, 19, 20 and 22

The issues 18, 19, 20 and 22 listed above and concerning the M3 modelling are discussed in the following paragraphs(2.1, 2.2, 2.3, 2.4, 2.5, 2.6 and 2.7): data selection (19, 20, 22), the reference waters used (18), 2 D visualisation along the boreholes (22) and M3 hyperspace (21). The drilling impact study issue (23) and the use of Electric conductivity issue (24) are listed in the Chapters D3 and D4. The issues 18, 19 and 20 were addressed already in Laxemar 2.1, so they will be discussed briefly. Due to the new M3 hyperspace, the issue 21 (M3/M4 comparison) is exhaustively discussed.

D2.1 Data selection

The M3 method consists of 4 steps where the first step is a standard principal component analysis (PCA), selection of reference waters, followed by calculations of mixing proportions, and finally mass balance calculations (for more details see /Laaksoharju 1999a/ and /Laaksoharju et al. 1999b/).

The M3 2D version is being updated and hyperspace calculations are now possible. The new M3 hyperspace version, called here for simplification M3 n-PC (n principal components, where n is the number of end members of the model) was tested. The M3 calculations were compared with the new M3 2D results and with the M3 n-PC calculations. This helped to verify that the new M3 2D works exactly like the old M3 code, and then to compare and judge the benefits or limitations by using 2D or n-PC calculations.

For Forsmark 1.2 phase, 2 models were built: at regional scale and at local scale. 367 samples from Forsmark 1.2 met the M3 criteria (data for major elements and isotopes) and were used in the M3 modelling. These samples were from boreholes (core and percussion), soil pipes (shallow and near surface groundwater), lake water, sea water, running water and precipitation. From the 367 samples available, 182 were considered representative from hydrochemical point of view and 185 non representative.

The present Forsmark 2.1 modeling employs only groundwater data, from percussion and core boreholes, meaning 145 groundwater samples (from which 35 are considered representative).

The M3 code is applied to the bedrock data, using as variables the major elements and D, O¹⁸ and T and as end members, Littorina, Sea Sediment, Brine, Glacial and Meteoric (rain60 with 168TU)

The PCA applied on Forsmark 2.1 data is illustrated in Figure D2-1. A total of 145 groundwater samples from Forsmark 2.1 were used for this plot. The Laxemar 2.1 data are used as background information and for future comparison of the sites. The PCA in Figure 1 shows surface water affected by seasonal variation (winter – summer precipitation), a marine trend showing Baltic Sea water influence and for some samples a possible Littorina sea water influence. A glacial and finally a deep groundwater trend are also shown.

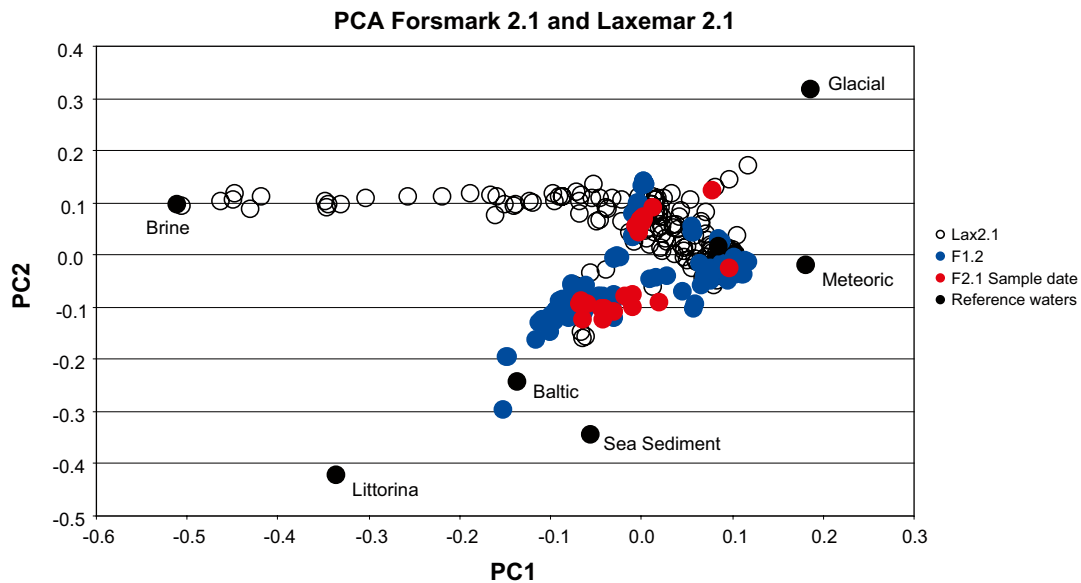


Figure D2-1. The picture shows the principal component analysis and the identification of the reference waters. First principal component: 0.42656, First and second principal components: 0.68578, First, second and third principal components: 0.81). All the major elements, O^{18} , D and Tritium are used as variables. The Sea sediment, Littorina, Brine, Glacial and Meteoric reference waters are used as end members for the modelling. The total data available for Forsmark 2.1 is 145 samples. After the Forsmark 1.2 data freeze (after May 2004), 25 new samples were obtained. In the PCA the red circles indicates the new data obtained after the F1.2 data freeze, the blue circles the F1.2 data and in unfilled circles the Laxemar 2.1 data.

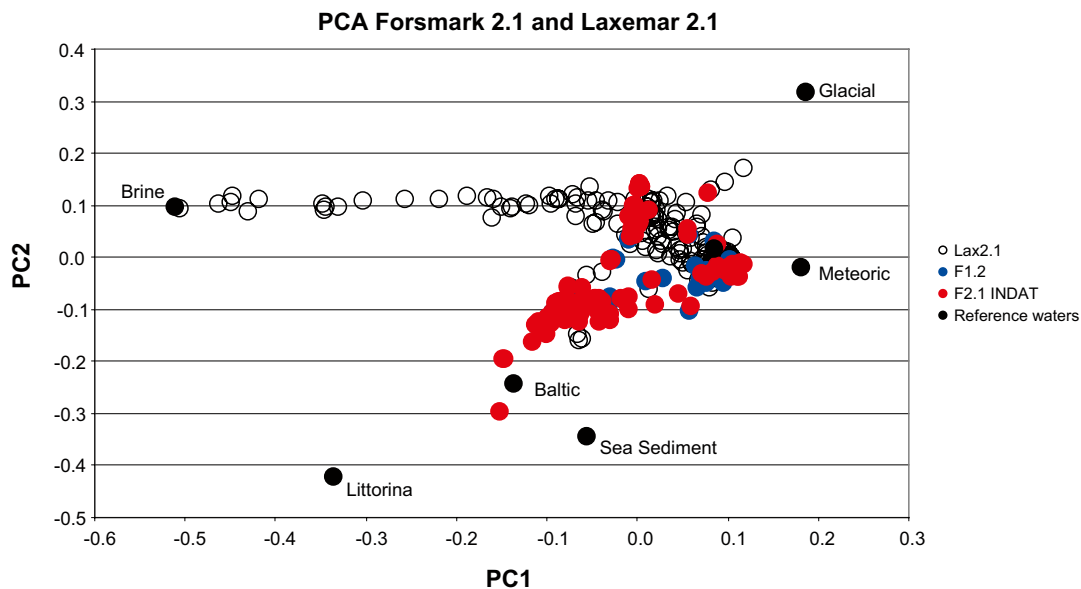


Figure D2-2. The picture shows the principal components analysis and the identification of the reference waters, identical to figure 1. The data selection is based on the date of the input of the last data in SICADA. After the Forsmark 1.2 data freeze (after May 2004), 104 new samples were included (or modified) in SICADA. In the PCA the red circles indicates the new data obtained after the F1.2 data freeze, the blue circles the F1.2 data and in unfilled circles the Laxemar 2.1 data. New entries in SICADA don't mean necessarily that the samples were changed; they may contain new information or validation of existing data. Therefore, the selection should be made based on the sampling date, as indicated in Figure D2-1.

Issues 18, 19 and 20 conclusions

The PCA analysis employing all groundwater samples with major elements (Na, K, Ca, Mg, SO₄, HCO₃, Cl) and isotopes the D, O¹⁸ and T (non corrected) and with the end members: Littorina, Brine, Glacial, Meteoric (rain60 age corrected) give the most suitable characterization of the Forsmark 2.1 and Laxemar 2.1 dataset, as following:

- more robust calculations and almost all the samples included in the PCA,
- the borehole data are not affected by the problems with the Tritium at the surface,
- the use of only conservative variables don't give unique solution, therefore the benefit of using also non conservative elements,
- returns mixing proportions including the same end members used by the hydrogeologists,
- the data is selected based on the sampling date; the new entries in SICADA are difficult to identify.

D2.2. The reference waters used

The following reference waters were used in the M3 modelling (for analytical data see Table C2-1):

- Brine type of reference water:** Represents the sampled deep brine type (Cl = 47,000 mg/L) of water found in KLX02: 1,631–1,681 m /Laaksoharju et al. 1995/. An old age for the Brine is suggested by the measured ³⁶Cl values indicating a minimum residence time of 1.5 Ma for the Cl component /Laaksoharju and Wallin 1997/.
- Glacial reference water:** Represents a possible melt-water composition from the last glaciation > 13,000 BP. Modern sampled glacial melt water from Norway was used for the major elements and the δ¹⁸O isotope value (–21 ‰ SMOW) was based on measured values of δ¹⁸O in calcite surface deposits /Tullborg and Larsson 1984/. The δ²H value (–158 ‰ SMOW) is a modelled value based on the equation (δH = 8 × δ¹⁸O + 10) for the meteoric water line.
- Littorina Water:** Represents modelled Littorina water (see Table C2-1).
- Sea sediment:** Represents Baltic Sea affected by microbial sulphate reduction.
- Age corrected Rain 1960:** Corresponds to infiltration of meteoric water (the origin can be rain or snow) from 1960. Sampled modern meteoric water with a modelled high tritium content was used to represent precipitation from that period. The age corrected value for the tritium was 168TU.

Table C2-1. Groundwater analytical or modelled data* used as reference waters in the M3 modelling for Laxemar 2.1.

	Cl (mg/L)	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	HCO ₃ (mg/L)	SO ₄ (mg/L)	³ H (TU)	δ ² H ‰	δ ¹⁸ O ‰
Brine	47,200	8,500	45.5	19,300	2.12	14.1	906	0	–44.9	–8.9
Glacial	0.5	0.17	0.4	0.18	0.1	0.12	0.5	0	–158*	–21*
Littorina sea*	6,500	3,674	134	151	448	93	890	0	–38	–4.7
Sea Sediment	3,383	2,144	91.8	103	258	793	53.1	0	–61	–7
Rain 1960	0.23	0.4	0.29	0.24	0.1	12.2	1.4	2,000	–80	–10.5
Age corrected Rain 1960	0.23	0.4	0.29	0.24	0.1	12.2	1.4	168	–80	–10.5

Issue 18 conclusions

The reference waters used are the Brine, Glacial, Littorina, Sea sediment and Meteoric (rain60, with the tritium age corrected to 168TU). These reference waters can explain most of the samples of Forsmark and Laxemar.

D2.3 2D visualization of the Cl, O¹⁸, T and mixing proportions along the K boreholes

The Figures D2-3 to D2-7 show the Cl, O¹⁸, tritium and mixing proportions calculated along the K boreholes with the old M3 code. The hydrogeologists use only one marine end member. In order to compare our model with the hydrogeologists, the marine mixing proportions are used in the following graphs. The marine is defined by being the sum of Littorina and Sea sediment mixing proportions.

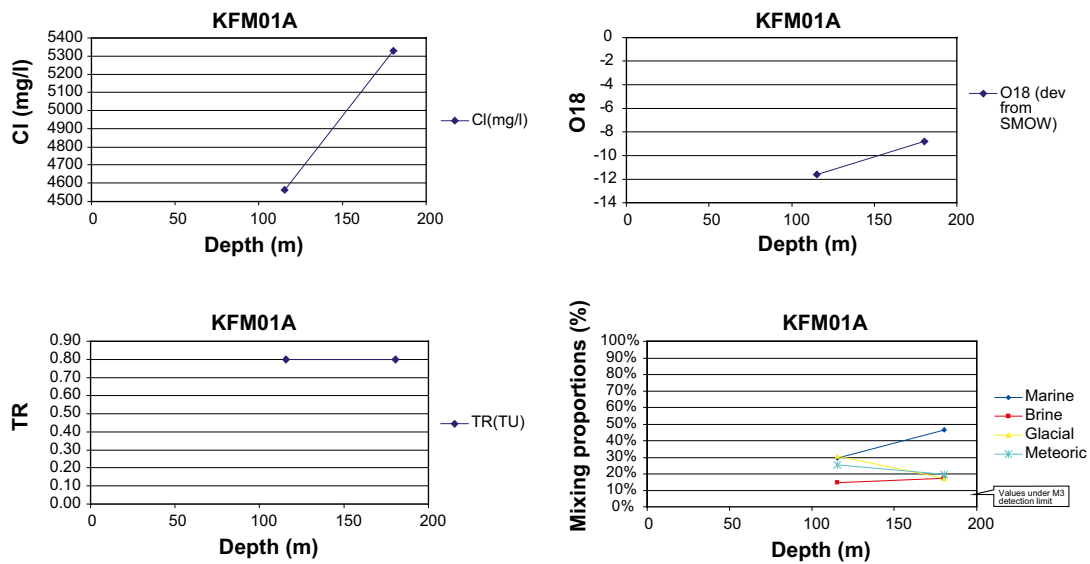


Figure D2-3. Cl, O¹⁸, T and mixing proportions along KFM01.

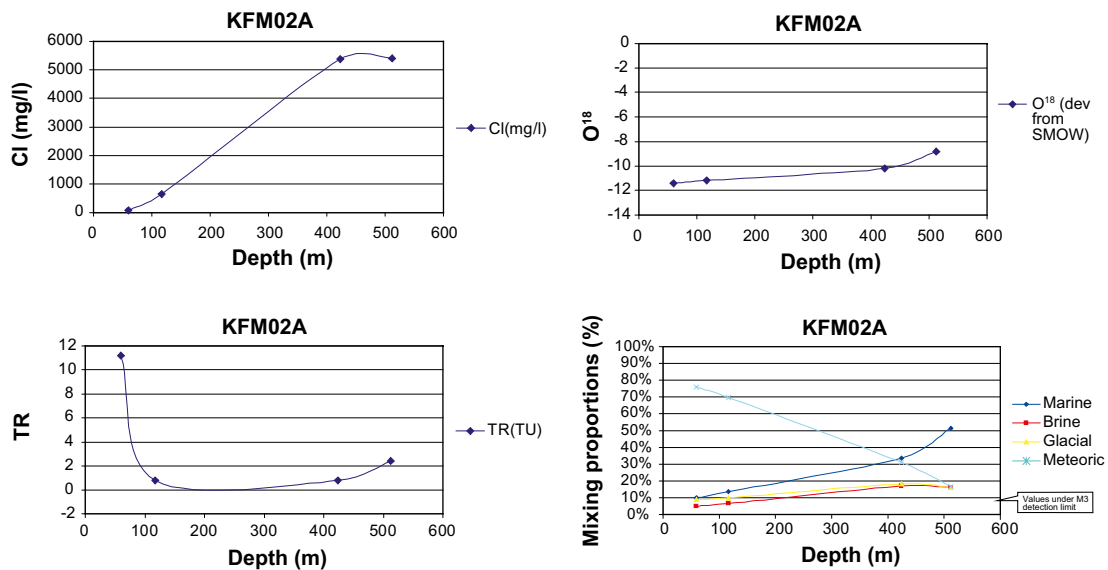


Figure D2-4. Cl, O¹⁸, T and mixing proportions along KFM02.

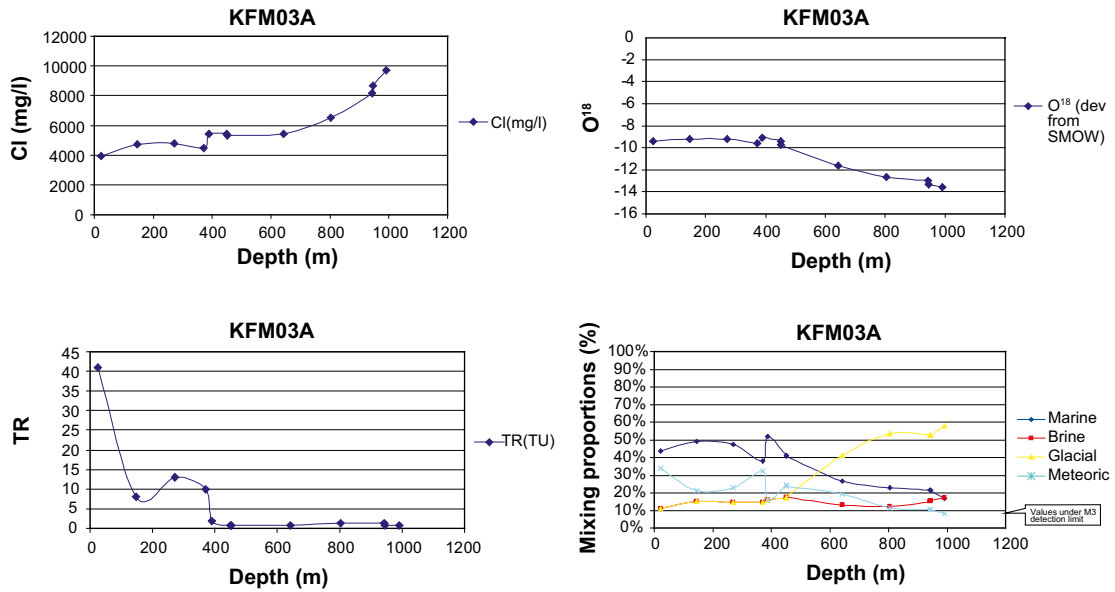


Figure D2-5. Cl, O¹⁸, T and mixing proportions along KFM03.

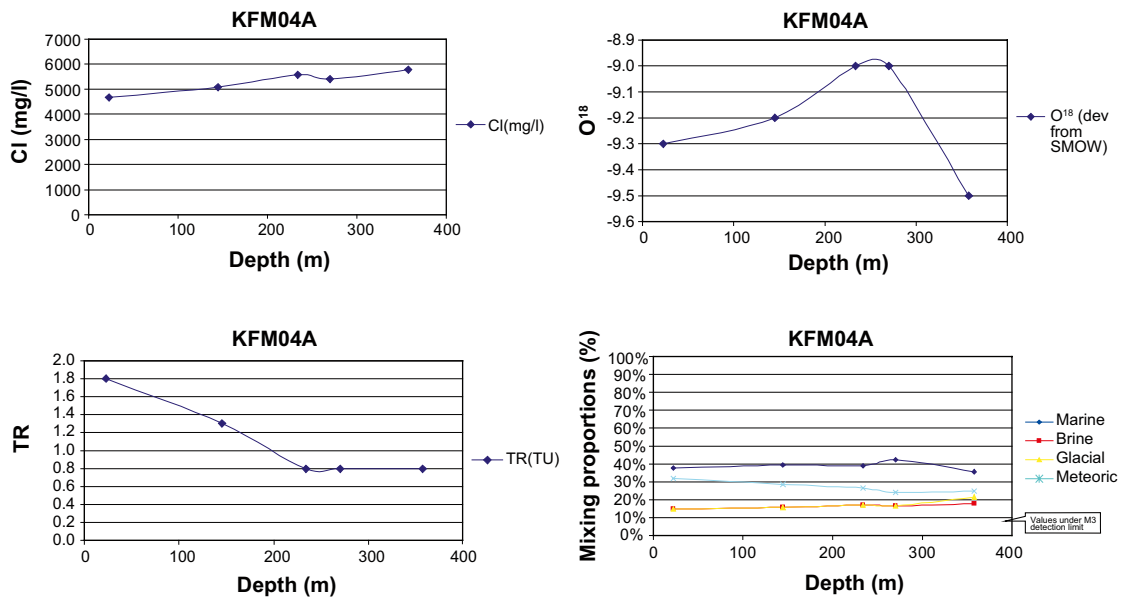


Figure D2-6. Cl, O¹⁸, T and mixing proportions along KFM04.

Issue 22 conclusions

The M3 modeling gives mixing proportions along the boreholes, which, together with the Cl, O¹⁸ and Tritium, can help the hydrogeologists for groundwater modeling calibration. The inclusions of samples from larger depth obtained from Forsmark 2.1 data freeze bring more understanding to the bedrock model. The Forsmark 2.1 model is very similar to 1.2, but samples from the depth give the opportunity to characterize also a deeper part of the bedrock. This can help to give more mixing proportions to the hydrogeologists for modeling calibration and verification.

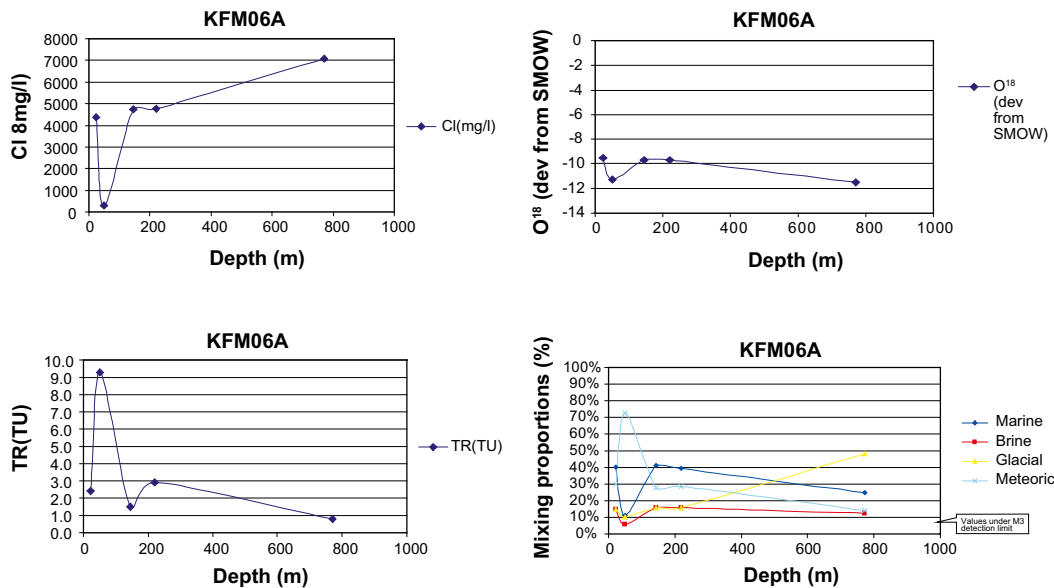


Figure D2-7. Cl, O¹⁸, T and mixing proportions along KFM06.

D2.4 M3 hyperspace: M3 2D and M3 n-PC modeling issues; allowance factor and coverage

In M3 2D the calculations include all the samples within the 2D polygon defined by the end members. In M3 n-PC the samples calculated should be included in the n space polyhedron defined by the end members. Fewer samples are included in the polyhedron and meet the M3 n-PC requirements. The coverage factor indicates how many samples (in %) are included in the polyhedron. In order to include more samples, the allowance parameter can be modified and more samples included in the calculations.

Some issues concerning the allowance factor are presented as following (J. Gomez, personal communication, April 2006):

- The allowance parameter value= 0 to 1, meaning that samples outside the polyhedron at distances from 0 to 10% of a side wall (with respect to the distance from the side wall to the end-member vertex) are considered as being just on the side wall (and included thus in the mixing calculations).
- The value of 1 (10%) is too big for most calculations and a value of 0 (0%) too small due to rounding errors. So, any value between 0.1 (1%) and 0.5 (5%) is reasonable.
- The Forsmark 2.1 dataset is typical of a dataset where most groundwaters are near one of the side walls of the polyhedron. In this case, changing the allowance parameter gives great variations in the sample coverage (because being most samples near the side walls, but many actually outside, slightly modifying their positions will put them inside). The indication is to not go beyond 5% but also never below 1%. The different sample coverage's with 1%, 2%, 3%, 4% and 5% are reported and the results are given with the 5% value.

For the Forsmark 2.1 data set, M3 2D gives coverage of 98.6%. The M3 n-PC gives the following coverage depending on the allowance factor:

- for an allowance factor 0.07, the coverage is 44%,
- for an allowance factor 0.1, the coverage is 48.2%,
- for an allowance factor 0.2, the coverage is 62.5%,
- for an allowance factor 0.3, the coverage is 69.5%,

- for an allowance factor 0.4, the coverage is 93.6%,
- for an allowance factor 0.45, the coverage is 98.9%,
- for an allowance factor 0.5, the coverage is 100%.

The Table D2-2 summarize for the different datasets (Laxemar and Forsmark 2.1 together, only Laxemar, only Forsmark, etc) the allowance factor used and the coverage of data obtained with a given allowance factor.

Several models were built based on different datasets (Forsmark and Laxemar 2.1 dataset, Forsmark 2.1 as a subset of Forsmark and Laxemar 2.1 dataset, only Forsmark 2.1 dataset) and different allowance factors and coverage.

In order to quantify the accuracy of the model, the RMSE (root mean square error) was calculated for the different M3 2D and M3 n-PC models. The best model is the one with the smallest error, as per the following calculations:

1. Calculate the difference between data and model = the “error” on the model with respect to the data: $y_{data} - y_{model}$.
2. Compute the signed variance of the errors: sigma (error) and the mean error to get rid of biases.
3. Get the RMSE (Root-mean-square error) = $SQRT(\sigma(\text{error}) + (\text{mean_error})^2)$.

The model with the smallest RMSE-ul gives the best predictions.

Issue 21 conclusions

The allowance factor helps to include more data in the calculations. However, the results of the modelling using too high allowance factors (higher than 0.1), can give erroneous calculations. The results of the modelling (predictions) should be compared with the conservative measured variables such as CI and O¹⁸. The model which predicts the best these values are the most accurate. For exemplification, the results of the modelling where the allowance factor used was 0.1 are presented bellow.

Table D2-2. RMSE, allowance factor and coverage for the CI predicted with different models.

	Forsmark 2.1 and Laxemar 2.1		Forsmark 2.1 (subset of the Lax2.1 and F2.1 dataset)		Laxemar 2.1		Forsmark 2.1	
	M3 2D	M3 n-PC	M3 2D	M3 n-PC	M3 2D	M3 n-PC	M3 2D	M3 n-PC
Allowance factor 0.5	3,467.4 (350 samples) Cover. 98.6%	4,771.7 (350 samples) Cover. 100%	3,543.1 (145 samples) Cover. 98.6%	3,895.1 (145 samples) Cover. 100%				
All. factor 0.255							2,289.5 (140 samples) Cover. 96.7%	1,364.2 (140 samples) Cover. 96.7%
Allowance factor 0.1	3,799.7 (166 samples) Cover. 98.6%	3,808.1 (166 samples) Cover. 48.2%	4,164.1 (83 samples) Cover. 98.6%	3,172.6 (83 samples) Cover. 48.2%	2,980.4 (204 samples) Cover. 97.6%	2,625.3 (204 samples) Cover. 99.5%	2,409.7 (115 samples) Cover. 96.7%	1,008.3 (115 samples) Cover. 80.3%

D2.5 M3 hyperspace: M3, M3 2D and M3 n-PC comparison

The old M3 code and the new M3 hyperspace, version 2D, are compared. As expected, the results are identical.

The Figure D2-9 shows the comparison between the M3 2D and M3 n-PC mixing proportions.

Issue 21 conclusions

The old M3 and the new M3 2D is identical and gives the same results. The M3 n-PC modeling gives similar trends, but the mixing proportions can vary. In M3 n-PC fewer samples are included in the polyhedron (as shown above, corresponding to the coverage factor and allowance parameter) but the results can be more accurate.

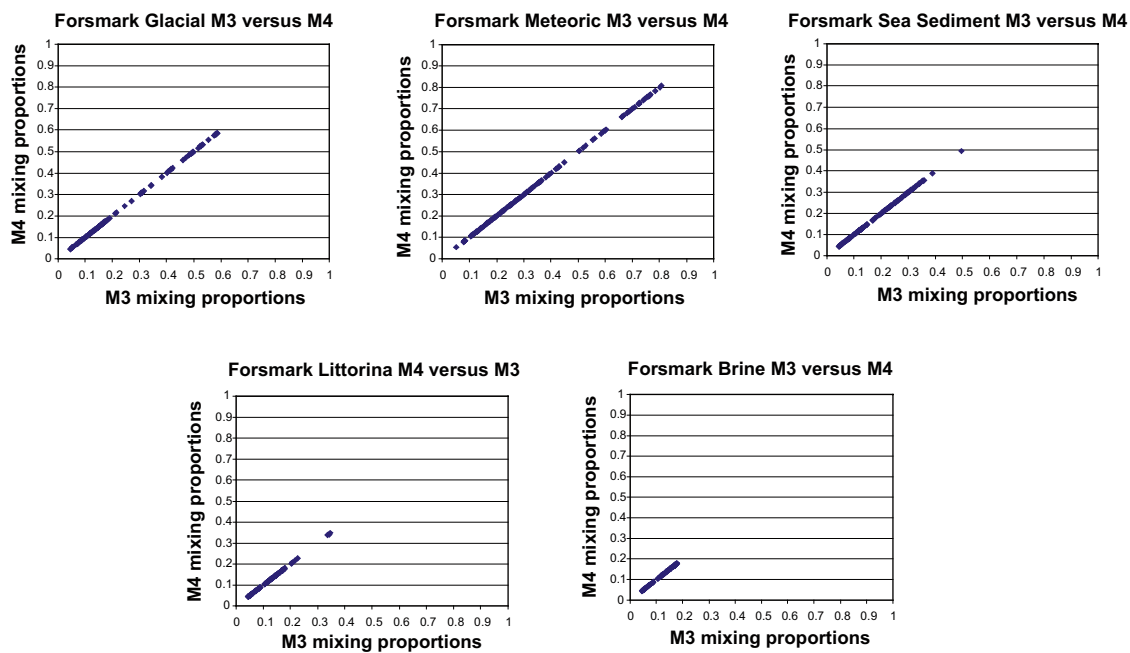


Figure D2-8. Comparison between the mixing proportions obtained with M3 (the old version) and M3 2D (previously called M4). The results show that the old M3 and the new M3 2D give the same mixing proportions when using the same dataset and the same reference waters. The old M3 and the new M3 2D are identical and give the same mixing proportions.

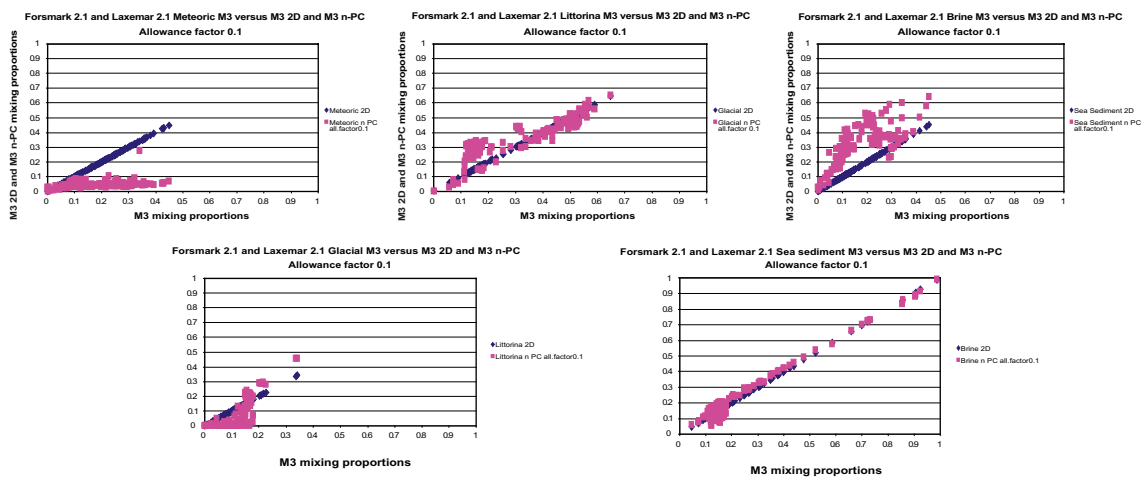


Figure D2-9. Comparison between the M3 2D and M3 n-PC mixing proportions. M3 2D and M3 n-PC calculate similar amount of Brine and glacial mixing proportions. M3 n-PC calculates higher values for the Sea Sediment mixing proportions and smaller values for Meteoric and Littorina mixing proportions.

D2.6 M3 hyperspace: M3, M3 2D and M3 n-PC verification; prediction of the conservative elements O¹⁸ and Cl

The model used should describe as well as possible the measured data. In order to check the accuracy of the model, the conservative variables Cl and O¹⁸ were used. Being considered conservative, the Cl and O¹⁸ should not be affected by reactions; therefore the values predicted by the models should be as close as possible to the measured data. As explained in the paragraph 2.4 the RMSE of the best model is the smallest. The Figure D2-10 shows the calculated values of the Cl and O¹⁸ versus the measured values.

For example, for the Cl, the RMSE M3 2d is 3,799.7 and RMSE M3 n-PC is 3,808.1. The Figure D2-11 shows the measured Cl values and the calculated Cl values with the 2 models. In this case, the RMSE values are very similar.

Issue 21 conclusions

The measured values should be compared with the predictions given by the different models. The best model is the one with the smallest error. The error of a model can be calculated by a statistic approach (RMSE, standard deviation, etc), but also by checking the consistency of the model according to the conceptual hydrogeologic and hydrochemical understanding.

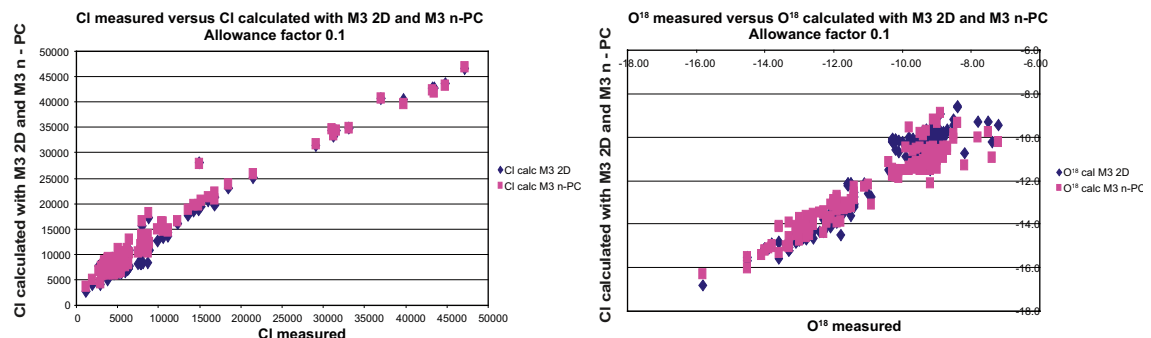


Figure D2-10. The Cl and O¹⁸ values predicted by the M3 2D and M3 n-PC models versus the measured data.

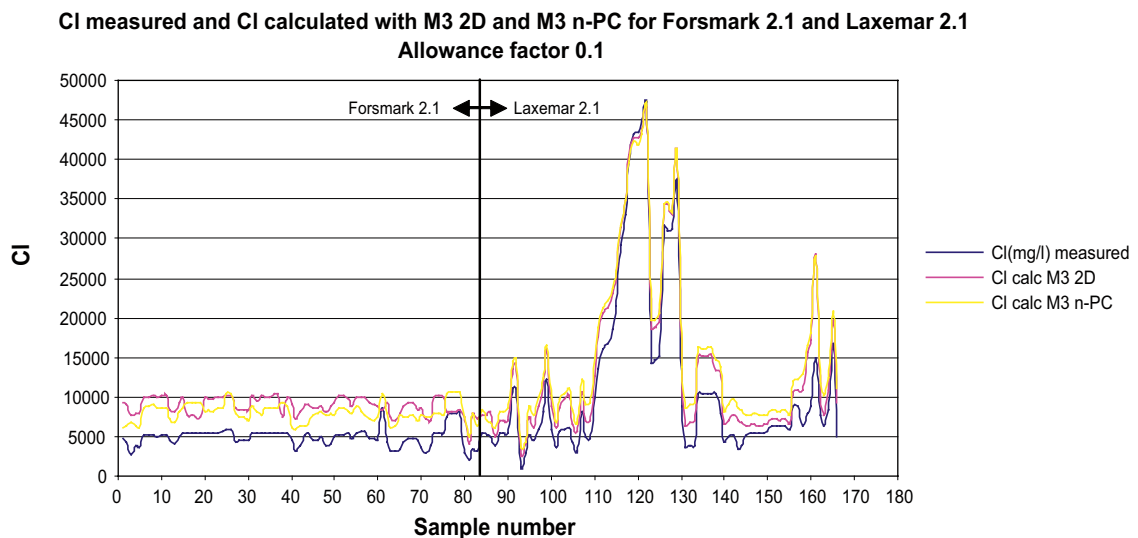


Figure D2-11. The Cl values measured and predicted by the M3 2D and M3 n-PC models. Both models predict well the measured data. However, for small Cl values, the M3 n-PC model seems to be more adequate.

D2.7 Mixing proportions along the core boreholes obtained with M3 2D, M3 n-PC

The Figures D2-12 to D2-16 show the Cl, O^{18} and mixing proportions along the K boreholes with 4 models: old M3 applied to the Forsmark and Laxemar 2.1 dataset, M3 2D applied to only Forsmark dataset, M3 n-PC applied to Forsmark 2.1 dataset with allowance factor of 0.255 and M3 n-PC applied to Forsmark 2.1 dataset with allowance factor of 0.1.

One should be very observant about the results from the calculations when the allowance factor was increased above the default. For example, for one sample point in KFM06A the n-PC calculations applied to onlt Forsmark 2.1 indicated that the point contains 60% marine water and the 2D indicated 83% meteoric. The last calculation was more realistic since the Cl concentration was 295 mg/l (see Figure D2-16, f and h). For the Laxemar and Forsmark datasets modeled together, the n-PC gave also 61% marine and the 2D indicated 72% meteoric (Figures c and e).

Therefore, for the future we will try to use the n-PC calculations where ever is possible. For Laxemar and Forsmark (together) dataset, the n-PC describes only 48% of the samples with the default allowance factor (M3 2D gives a coverage of 98.6%). For only Forsmark dataset the n-PC describes 80.3% of the samples with the default allowance factor (the M3 2D gives a coverage of 96.7%). However, as shown in the Figure d and g some samples can be lost.

One should be very careful when using the allowance factor. It may well be that we have to use a combination of n-PC and 2D when modeling the site data to be able to describe all the samples.

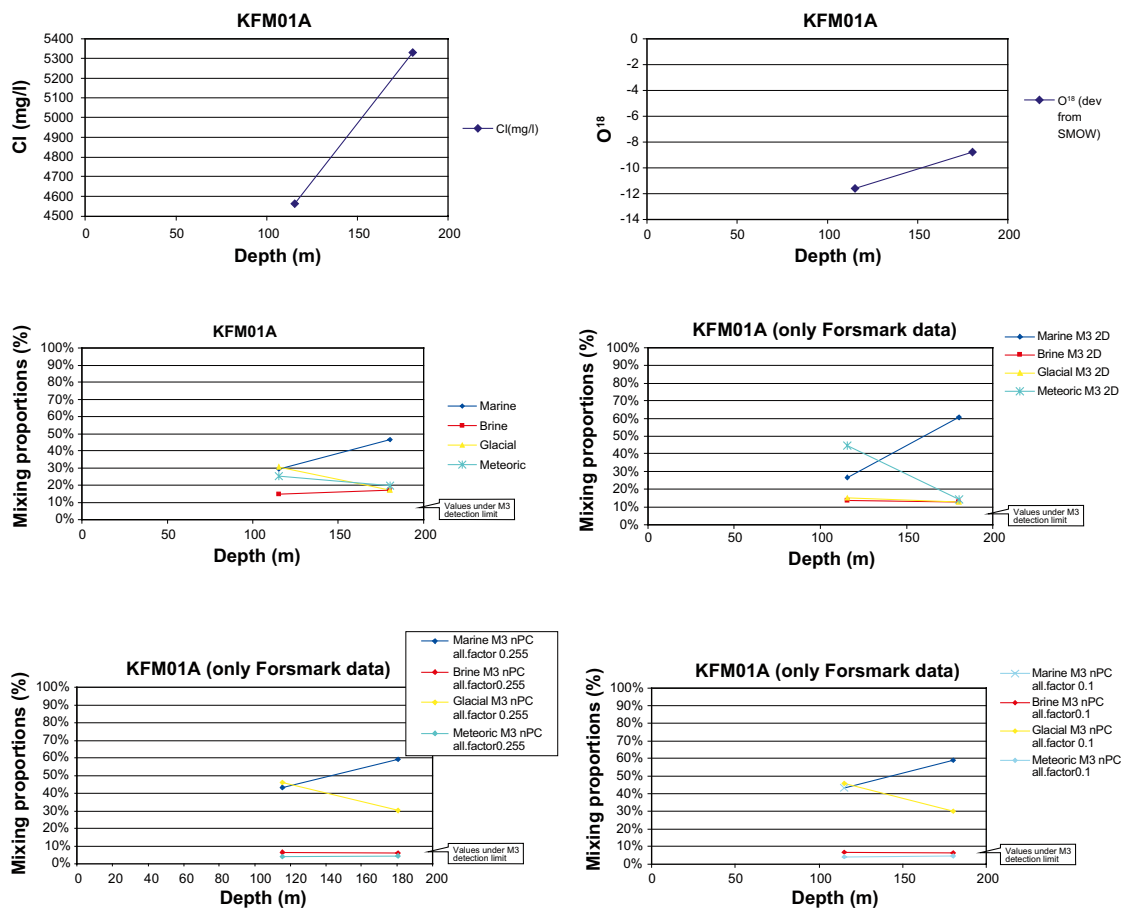


Figure D2-12. Measured Cl, O^{18} and the mixing proportions calculated with the models M3 (Forsmark and Laxemar 2.1 data set) and M3 2D, M3 n-PC (allowance factor 0.255) and M3 n-PC (allowance factor 0.1) applied to only the Forsmark 2.1 data set along KFM01.

Issue 21 conclusions

In general, M3 n-PC predicts less meteoric and more Marine (Littorina + Sea sediment mixing proportions) and less brine mixing proportions at smallest depths than M3 2D. This can help perhaps to better differentiate, at smallest depths (under 500 m depth), the source of Cl (from brine or sea water).

In M3 n-PC fewer samples are included in the polyhedron (as shown in Figure D2-13 and D2-16) when the allowance parameter is 0.1 (the coverage is 80.3% for the Forsmark 2.1 data set and 48.2% for the Forsmark and Laxemar 2.1 data set). In order to include more samples and to have a higher coverage (96.7% as for M3 2D), the allowance factor should be 0.255 for the Forsmark 2.1 dataset. The mixing proportions obtained with a too high allowance factor are erroneous when comparing the consistency of the results with the Cl measurements. In M3 n-PC fewer samples are included in the polyhedron, the results can be more accurate, but important samples are not included in the calculations.

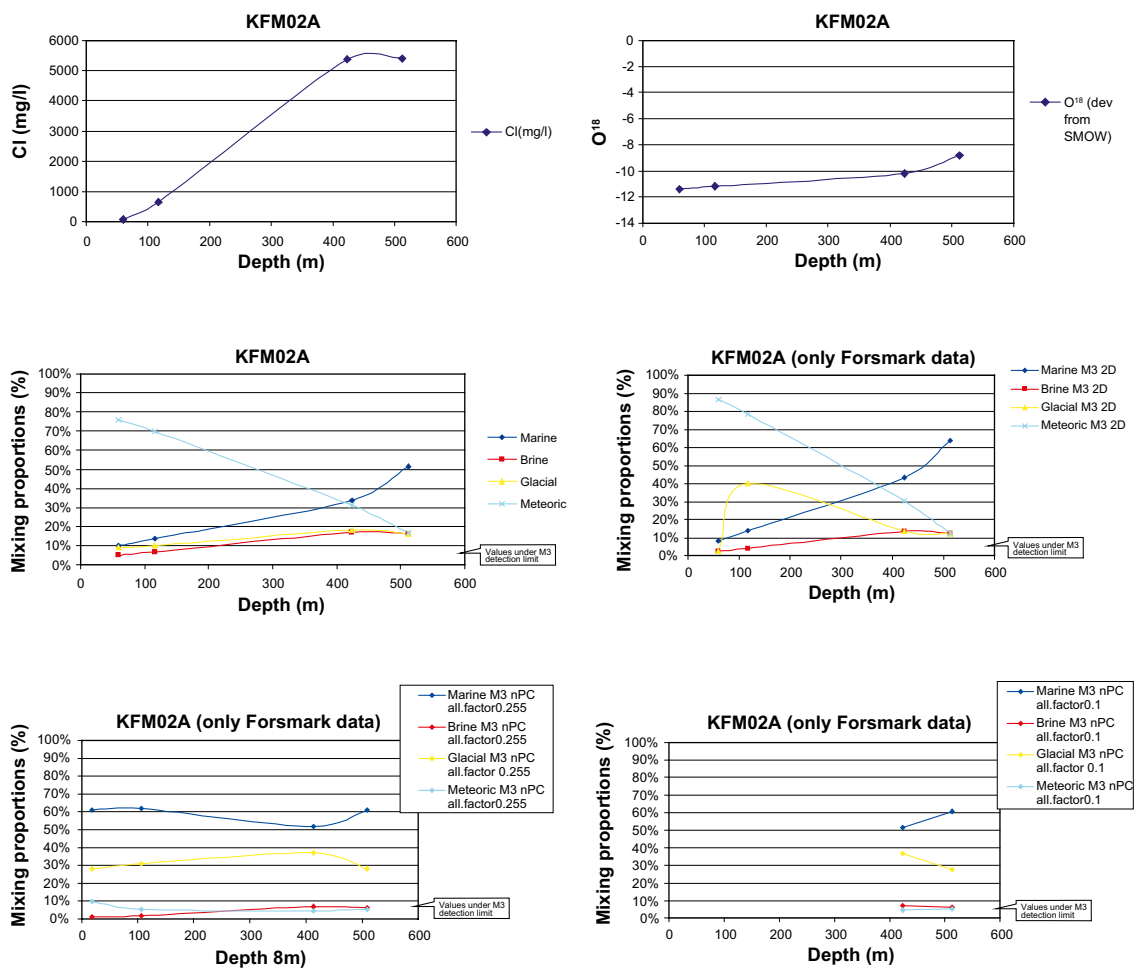


Figure D2-13. Measured Cl, O¹⁸ and the mixing proportions calculated with the models M3 (Forsmark and Laxemar 2.1 data set) and M3 2D, M3 n-PC (allowance factor 0.255) and M3 n-PC (allowance factor 0.1) applied to only the Forsmark 2.1 data set along KFM02.

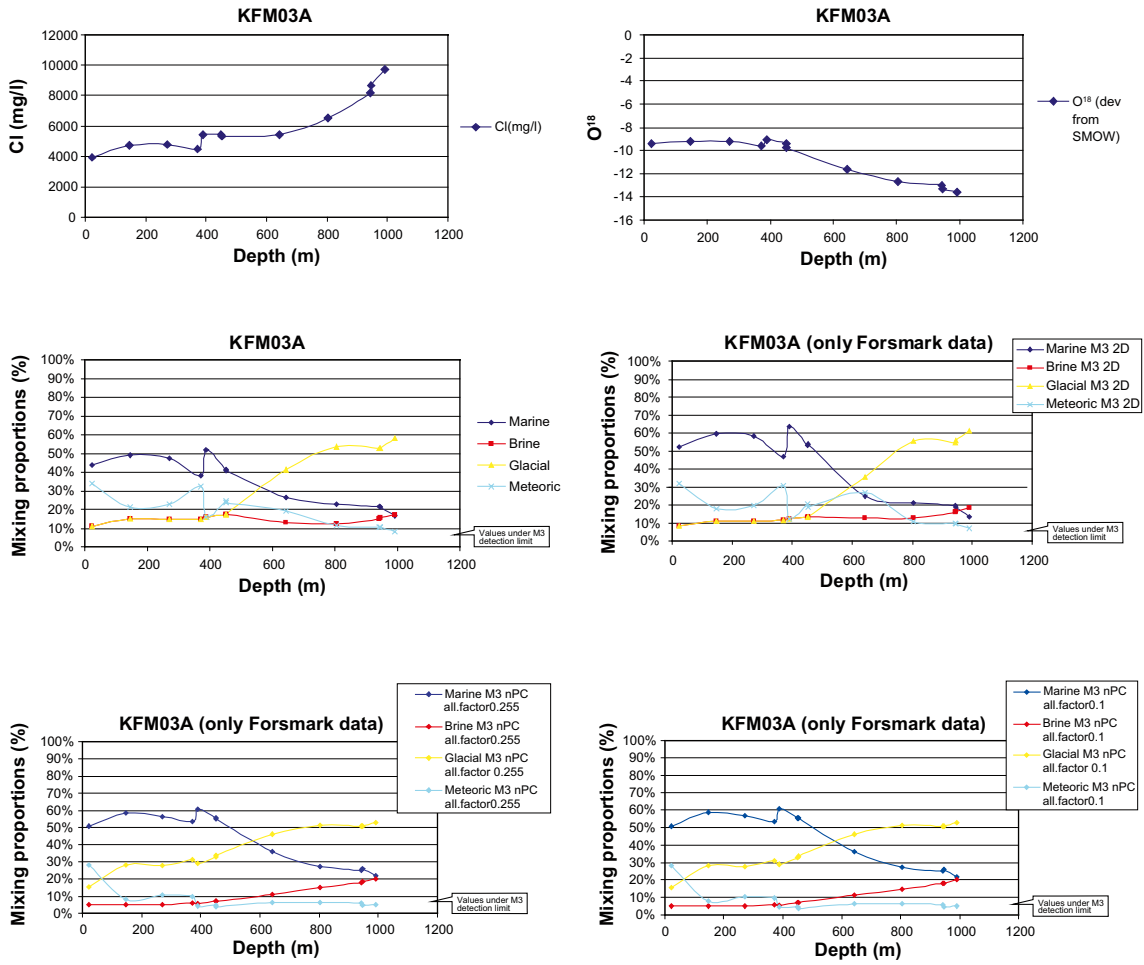


Figure D2-14. Measured Cl, O^{18} and the mixing proportions calculated with the models M3 (Forsmark and Laxemar 2.1 data set) and M3 2D, M3 n-PC (allowance factor 0.255) and M3 n-PC (allowance factor 0.1) applied to only the Forsmark 2.1 data set along KFM03.

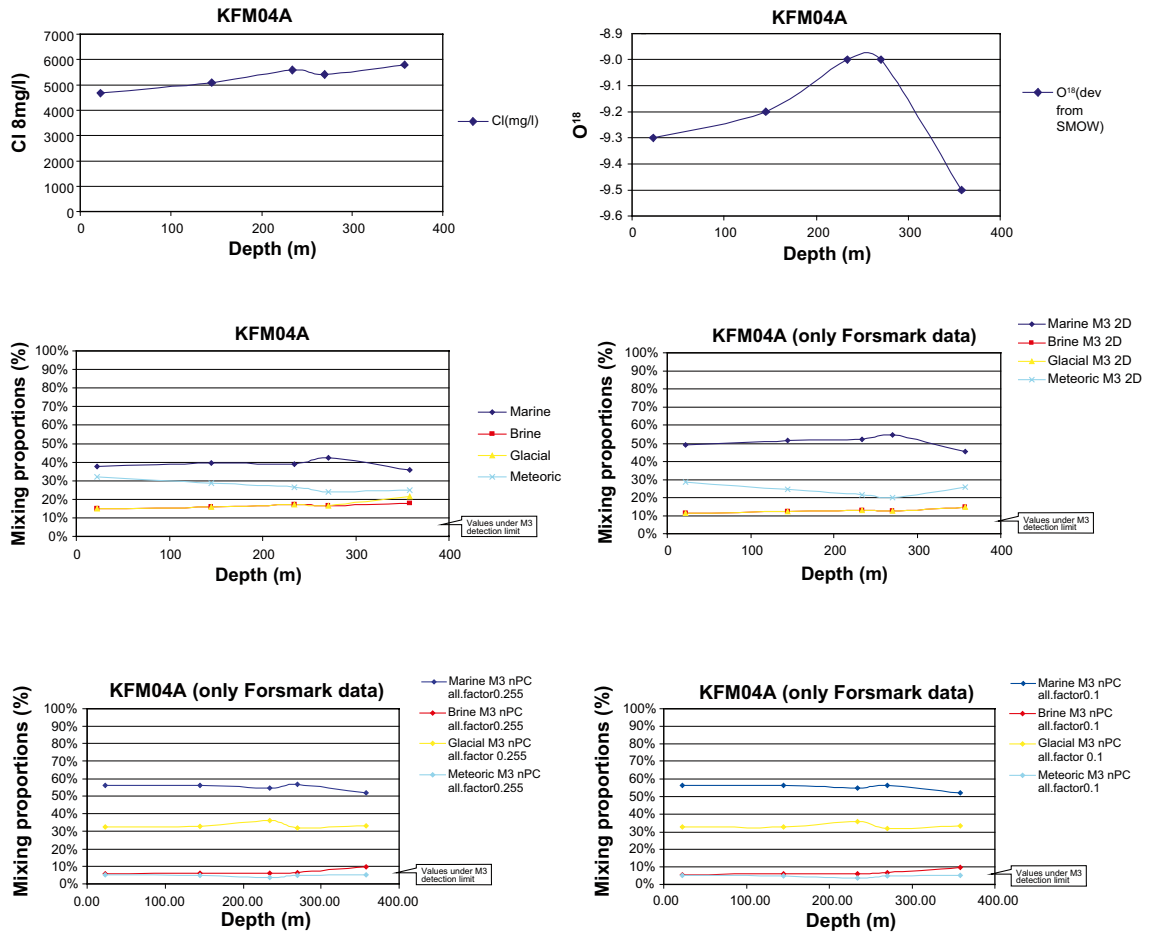


Figure D2-15. Measured Cl, O¹⁸ and the mixing proportions calculated with the models M3 (Forsmark and Laxemar 2.1 data set) and M3 2D, M3 n-PC (allowance factor 0.255) and M3 n-PC (allowance factor 0.1) applied to only the Forsmark 2.1 data set along KFM04.

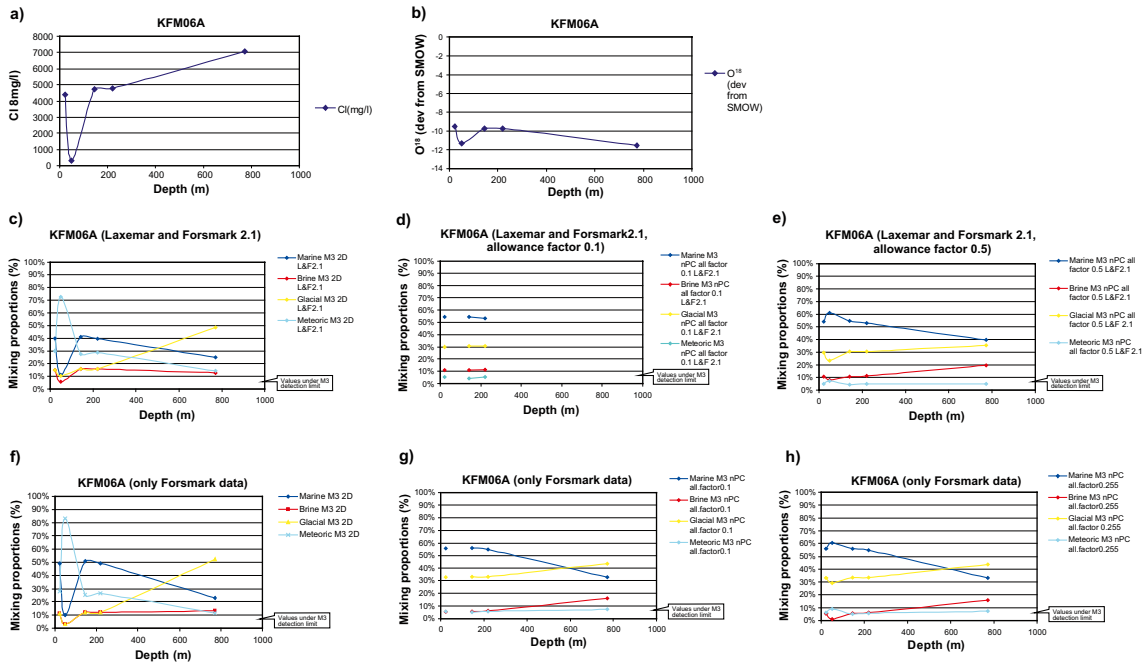


Figure D2-16. Measured Cl , O^{18} and the mixing proportions calculated KFM06: Cl , O^{18} and mixing proportions along the KFM06 borehole depth: a) Cl ; b) O^{18} ; c) M3 2D mixing proportions for Laxemar 2.1 and Forsmark 2.1 data sets together; d) M3 n-PC mixing proportions for Laxemar 2.1 and Forsmark 2.1, allowance factor 0.1 (coverage 48%); e) M3 n-PC mixing proportions for Laxemar 2.1 and Forsmark 2.1, allowance factor 0.5 (coverage 100%); f) M3 2D mixing proportions for only Forsmark 2.1 dataset; g) M3 n-PC mixing proportions for Forsmark data set calculated with the allowance factor 0.1 (coverage 80.3%); h) M3 n-PC mixing proportions for Forsmark data set calculated with the allowance factor 0.255 (coverage 96.7%).

D3 Drilling Impact Study in KFM06

A feasibility of the drilling impact study for the section 353.5–360.62 m in KLX03 was done. The following data were compiled:

- drilling water in and out from the borehole during drilling, Figure D3-1,
- uranine concentration in drilling water in and out from the borehole, Figure D3-2.

The drilling water pumped out is higher than the volume in and this makes the calculations more difficult. More return water is due the air-lift pumping. This creates a complex situation with mixing of formation water and ingoing flushing water (in general tendency to have more return water in poor rock conditions and more of a balance between in and out in tight rock, H. Ask, personal communication, October 2005). However, if the uranine is correctly monitored, the return water can be calculated based on the percentage of uranine, and a water balance and DIS calculations can be done.

The uranine budget in KFM06A /from Wacker and Nilsson 2005a/ gives the following information in Table D3-1.

Based on the average content of 122, the following calculations can be done:

- Drilling water pumped out = 60% of the total volume pumped out from the borehole.
- Water in = 1,087 m³ (Figure D3-1, blue curve).
- Water out = 1,968 m³ (Figure D3-1, magenta curve).
- 60% Water out = 1,180 m³ (Figure D3-1, yellow curve).

The Uranine budget suggests that approximately 400 m³ of the flushing water was lost to the borehole and the adjacent host bedrock. The estimation should be regarded as rather uncertain due to the systematic error and the correction. It became clear later on that the remaining flushing water was going to be a major problem that required extra long pumping periods.

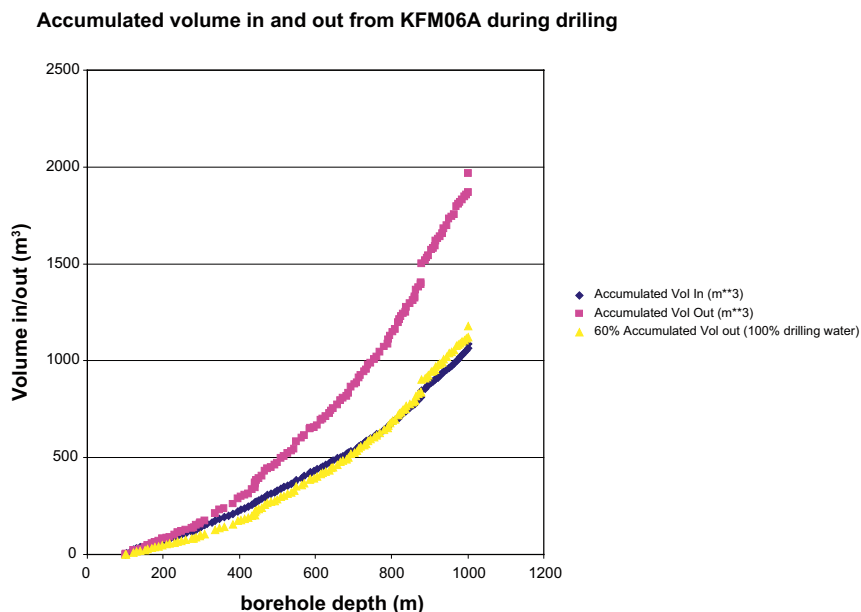


Figure D3-1. Drilling water pumped in (blue) and out (yellow) from the borehole during drilling. The water pumped out (magenta) represents drilling water and formation water as well, based on the measured uranine concentration.

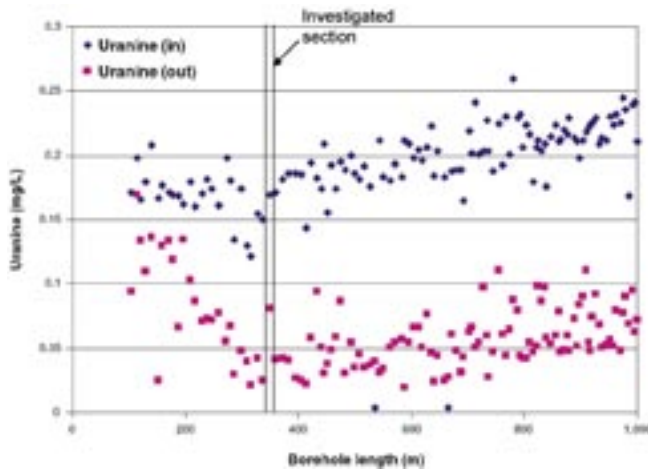


Figure D3-2. Uranine concentration in the drilling water pumped in and out from the KFM06 borehole during drilling.

Issue 23 conclusions

In order to perform a drilling impact study, a water balance of the drilling water flushed in and out from the borehole should be performed. The water pumped out is usually higher than the volume in, being mixed with formation water and making the calculations more difficult. If the uranine is correctly monitored, the return water can be calculated based on the percentage of uranine, and a water balance and DIS calculations can be done for the borehole. Based on the reviewers' comments, the DIS study is proposed to be applied on a simplified systematic way to all the core boreholes.

Table D3-1. Amount of Uranine added to KFM06 via the flushing water during core drilling and the amount recovered from the contemporary mammoth pumping.

Uranine	(g)
1) Added, according to the log book	200.5
2) Added, calculated from the average corrected Uranine concentration and total volume of flushing water	210
3) Recovered, estimated from average corrected Uranine concentration and volume return water	122

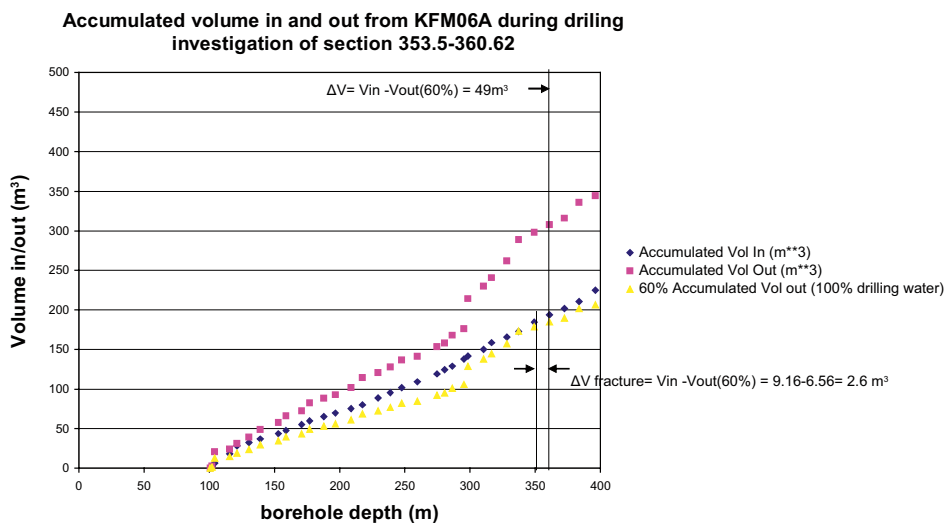


Figure D3-3. Drilling water pumped in and out from the KFM06 borehole during drilling, section 353.5–360.62 m. The drilling water volume lost in the fracture during drilling was 2.6 m³.

D4 The use of DIFF measurements

The electrical conductivity (EC) measurements performed during the DIFF (differential flow measurements) measurements could give valuable information about not only the inflow/outflow from the borehole but also disturbances of and changes in chemistry. These measurements are the first measurements conducted after drilling and it is therefore of special interest to follow these changes in comparison with chemistry such as Cl obtained from the borehole at sampling campaigns. The variability can indicate e.g. disturbances and can hence be used for confidence building.

The EC was measured along KFM06 without and during pumping (Figure D4-1). The EC and the measured Cl during sampling along the borehole are compared in Figure D4-2. The measured EC reflects mixing processes in the open borehole rather than undisturbed bedrock conditions. For modeling and model calibrations with hydrogeology only sample from sealed off bedrock sections should be used. The EC distribution and the comparison with measured Cl should be investigated in all boreholes.

Issue 24 conclusions

The EC can be a good indicator of the representativity of the groundwater samples.

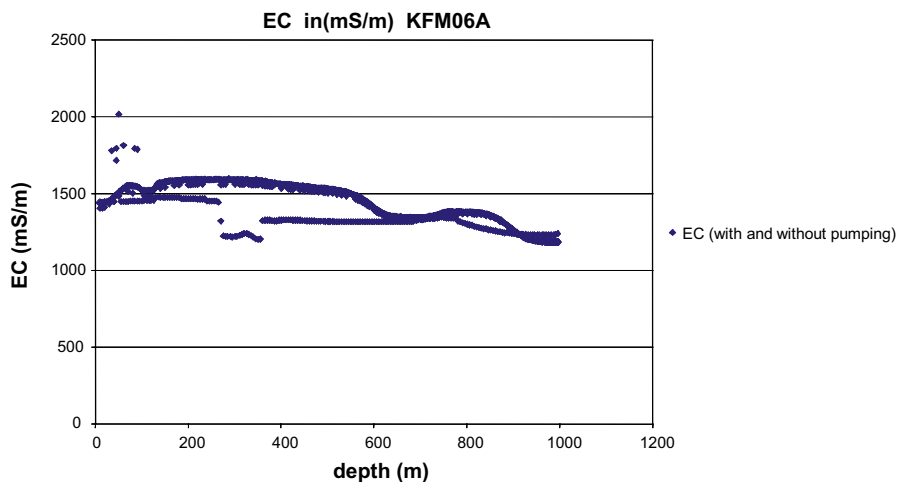


Figure D4-1. Electrical conductivity measured by DIFF(differential flow) measurements along KFM06.

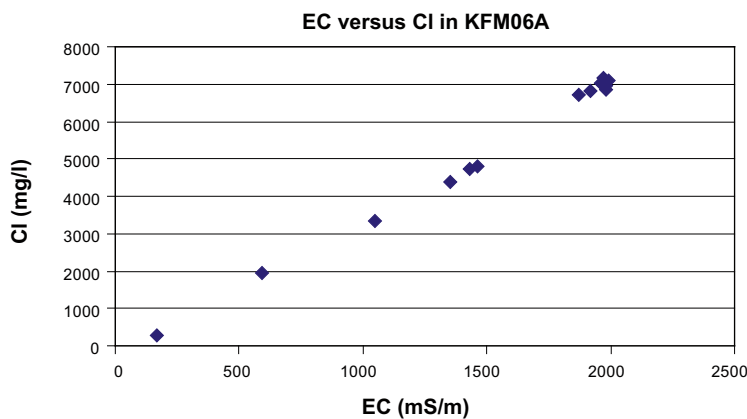


Figure D4-2. Electrical conductivity versus Cl measured along KFM06.

D5 Concluding remarks

This work represents the phase 2.1 of the hydrochemical evaluation and modelling of the Forsmark data. This comprises M3 modelling, tests of the new M3 hyperspace code, recommendations when and how to use the 2D or n-PC versions and 2D visualisation of the data along the boreholes. At the end of each paragraph the different previous unclear issues were discussed. The following conclusions can be drawn:

- M3 modelling helped to summarize and understand the data. The new M3 code has 2 options: 2D and n-PC (hyperspace), which were used, discussed and the results compared. The new M3 2D code was tested versus the old M3, and the results are identical. The 2D version gathers more data. The n-PC version models fewer samples (the ones included in the polyhedron) but return more accurate mixing proportions.
- The alternative models and the experience from Laxemar 2.1 helped to clarify different previously unsolved issues such as: the use of tritium as a variable (without correcting the age), tests with different end members (the use of meteoric as rain60 with 168TU), the use of only groundwater data in order to build a bedrock model.
- The visualisation of the mixing proportions along the boreholes help to understand the distribution of the data in the domain and to check and compare the results of different models; and therefore to chose the model which describes the best the measured data.
- The DIFF and Cl measurements along a borehole can be used to validate the variance in mixing proportions along the borehole. This information can be used for confidence building.
- The different M3 modelling tests resulted in the following conclusions: a) When calculating mixing proportions only samples from the boreholes will be used, b) the meteoric end member which describes the best the more shallow groundwater compositions is defined by the rain60 water composition, with the tritium value age corrected (168TU); the other end-members such as Littorina and Glacial employed the existing modeled compositions. The use of the Marine (Littorina + Sea sediment), Glacial, Brine and Meteoric end members makes possible the comparison of different sites such as Laxemar and Forsmark.

Forsmark model 2.1 – Issue Report

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E1 Introduction

This report constitutes the contribution of the University of Santiago de Compostela (USC) Team to the version 2.1 of the ChemNet model for the Forsmark site. The results reported here correspond to the work performed during the period since November 2005 until June 2006.

The main objective is to perform a combined analysis of available hydrogeologic and hydrochemical information, with especial emphasis on the following issues:

(Issue 25) Better integration with hydrogeology.

(Issue 26) Conceptual model in 3D.

(Issue 27) Interaction surface/deep groundwater systems.

E2 Issue 27 – Interaction surface/deep groundwater systems

In the current hydrogeological conceptual model it is assumed that meteoric water mainly reaches the shallow aquifer by distributed infiltration on the emerged lands, and then flows through both the Quaternary sediments and the granitic bedrock towards discharge zones, located mainly in the lakes and near the Baltic coastline.

Figure E2-1 shows a plot of tritium versus Cl^- in those soil pipe samples (near surface groundwater) located at the discharge zones (selected by topographic and geochemical reasons). It can be seen that the lowest tritium contents are measured in soil pipes under 3 lakes (Bolundsfjärden, a small lake in SFM12 named Gällsboträsket and Eckarfjärden). However, groundwater under these 3 lakes shows very different salinities. Near surface groundwater under Bolundsfjärden show Cl^- concentration values higher than the present Baltic Sea water, indicating a relevant contribution of relict marine water from older stages (i.e. Littorina). By the contrary, shallow groundwater under Eckarfjärden shows Cl^- concentrations much lower (i.e. more diluted groundwater). Finally, shallow groundwater under Gällsboträsket (SFM12) shows an intermediate salinity. It is worth noting that groundwater samples located under the Baltic Sea shows Cl^- contents lower than the sea water, which is consistent with the occurrence of local discharge of fresh groundwater under the sea.

The occurrence of brackish near surface groundwater under Bolundsfjärden points towards the discharge of older groundwater under this lake, and/or the presence of “trapped” relict water not yet flushed out. It is worth noting that a major uncertainty remains on the hydrogeological role of Bolundsfjärden, since measured groundwater heads in soil pipes are lower than the water lake head (Follin 2006 personal communication). This fact is not consistent with a hydrogeologic discharge zone, pointing towards the presence of relict saline water under this lake. Further research should be done in order to confirm this hypothesis.

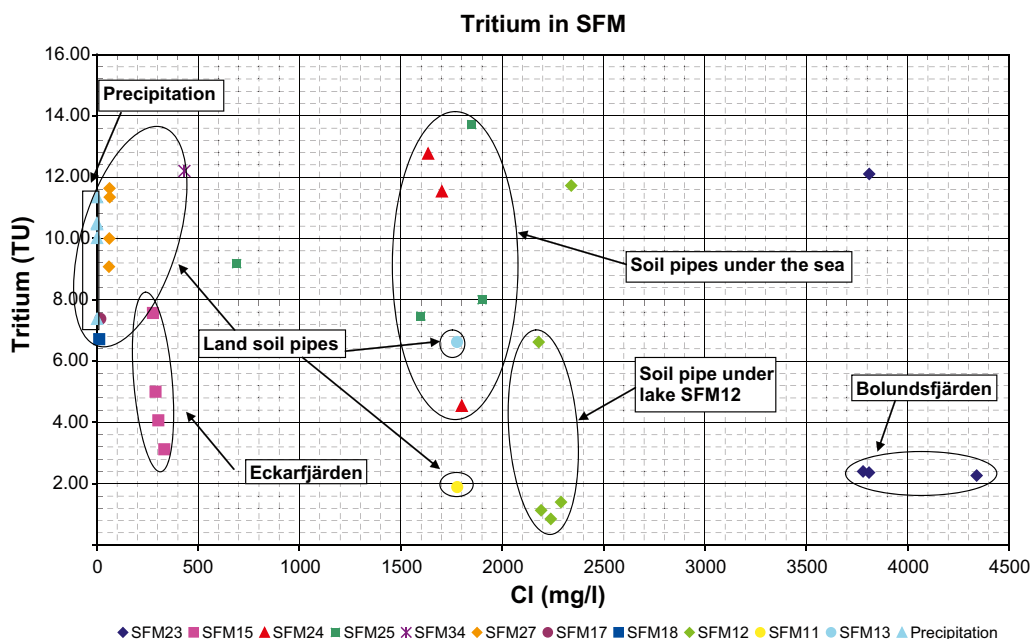


Figure E2-1. Tritium versus Cl^- in soil pipe samples (near surface groundwater) located at local topographic depressions.

It is worth noting the main difference in the near-surface water under Eckarfjärden, with low tritium values which indicate the influence of sub-modern groundwater close to the surface, but with no signature of older marine components.

Figure E2-2 shows a plot of $\delta^{18}\text{O}$ versus Cl^- in soil pipe samples located at the presumably discharge zones. Littorina and average Baltic Sea values has been included in the plot. It can be seen that near surface groundwater at presumably discharge zones plot along a hypothetical mixing line between Littorina water and fresh soil pipes water, with the exception of groundwater samples under Eckarfjärden, which shows clearly the absence of Littorina influence.

The hydrochemical and isotopic patterns of near surface hydrochemistry at the presumably discharge zones in Forsmark show differences between them. Some of the discharge zones may correspond exclusively to very shallow and local groundwater systems, probably involving only flow through the Quaternary deposits. These very local systems show dilute groundwater and ^3H and ^{18}O values close to modern precipitation. On the other hand, there are places where a mixing between meteoric and old marine water seems clear (Bolundsfjärden as the clearest one). Whether this indicates the discharge of deeper groundwater or, may be, the presence of “trapped” relict water, not yet flushed out, should be further investigated, as indicated previously. In this context, it has been hypothesized that effective recharge into the granitic bedrock at Forsmark could be as low as a few millimetres/year, due to both the presence of low permeability Quaternary cover and the low topographic driving forces. This hypothesis could provide the explanation for the signatures of old marine water in the near surface groundwater.

As pointed before, hydrochemical and isotopic signatures in Eckarfjärden show significant differences compared to the rest of the discharge zones. Groundwater under this lake is diluted and has relatively low tritium values (3–5 TU) but, according to $\delta^{18}\text{O} - \text{Cl}$ plot, this shallow groundwater seems to be out of the theoretical mixing line with Littorina water. This lake shows several particularities which are worth to be noted. On one hand, Eckarfjärden is the lake located more distant to the coast and close to a pronounced topographical slope-change. Figure E2-3 shows a location map of the main lakes and swamp areas in Forsmark. On the other hand, as it can be also seen in Figure E2-3, the Eckarfjärden lake is located over the outcrop of a major deformation zone (the Eckarfjärden Deformation Zone -EDZ-, named as ZFMNW003A in the Structural Model of Forsmark).

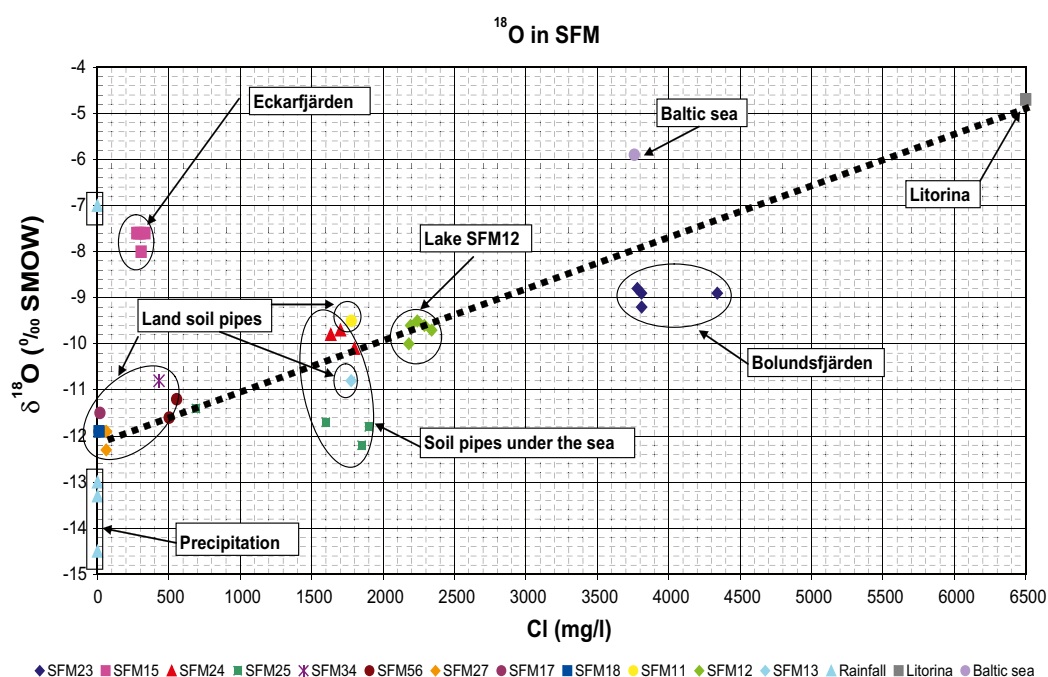


Figure E2-2. ^{18}O versus Cl^- in soil pipe samples (near surface groundwater) located at local topographic depressions.

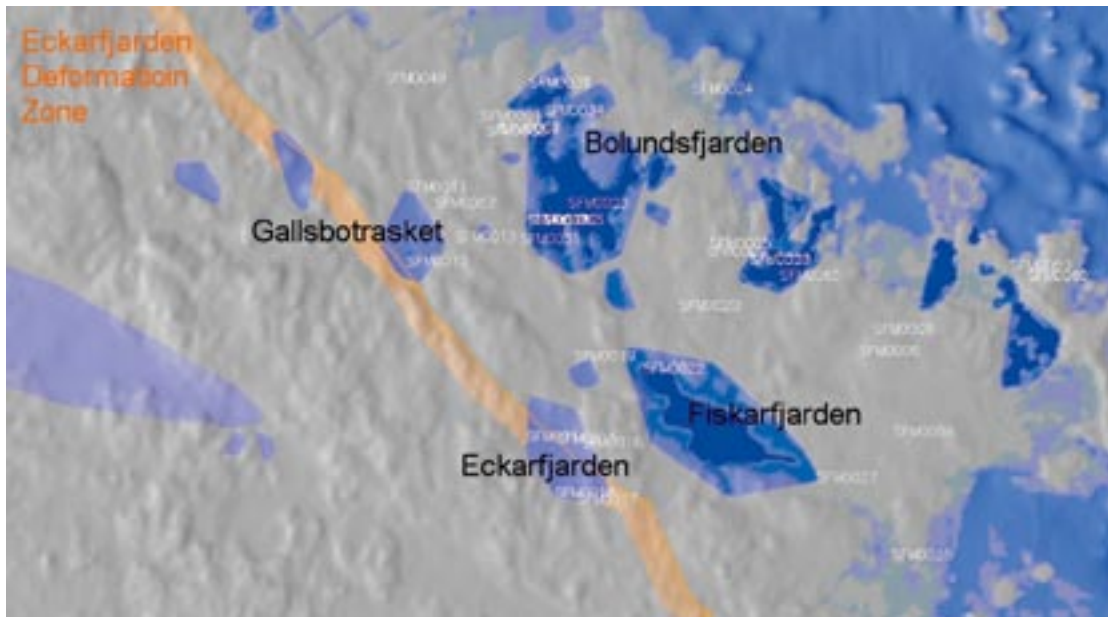


Figure E2-3. Location map showing the main lakes at Forsmark, the spatial distribution of soil pipes and the Eckarfjärden Deformation Zone.

It is worth noting that EDZ is oriented perpendicular to the regional topographic gradient. Then, assuming that EDZ has higher hydraulic conductivity than the surrounding rock mass, it could be expected that this deformation zone would collect the groundwater flow coming from inland positions. This hypothesis is consistent with model results shown in the next section of this report.

The aforementioned model results can be supported hydrochemically, taken into account that near surface groundwater at lakes located over the EDZ (Eckarfjärden and Gällsboträsket) show low salinity, low tritium contents and almost no marine signatures. Figures E2-4 and E2-5 show the spatial distribution of chloride and tritium values of available near surface groundwater samples, respectively. It can be seen that there is other lakes and swamp areas located over

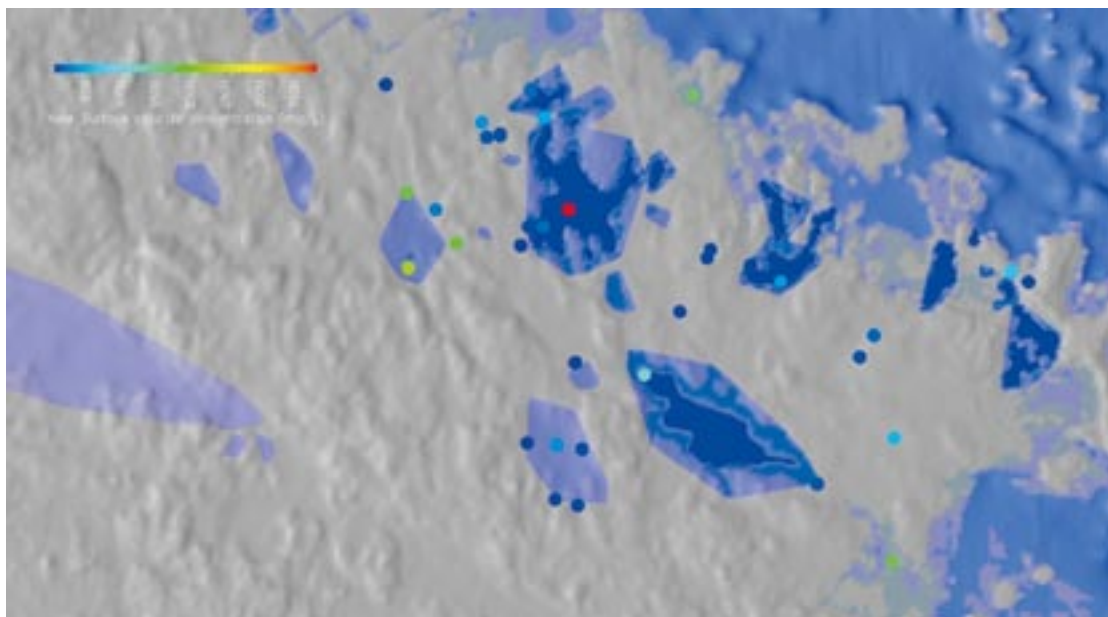


Figure E2-4. Spatial distribution of chloride concentrations measured in soil pipes. Represented values correspond to the mean values when a time series is available.

EDZ without information on near surface hydrochemistry. These areas could be investigated in the future with new soil pipes, in order to provide additional support to the current hypothesis on the role of EDZ in the hydrogeological behaviour of the Forsmark site. This hypothetical discharge of regional groundwater through EDZ could be contributing to the permanence of Littorina water in the bedrock of the Forsmark site, by decreasing the amount of groundwater flow able to flush out of old marine components in Forsmark towards the Baltic Sea.

Interesting additional information can be also obtained by looking at the ^{14}C data of the near surface groundwater. Figure E2-6 show the pmc (percent of modern carbon) measured in soil pipes. It can be noticed that pmc contents in soil pipes under major lakes correspond to low values, which provides additional support to the hypothesis of major lakes as being the main groundwater discharge areas in Forsmark.

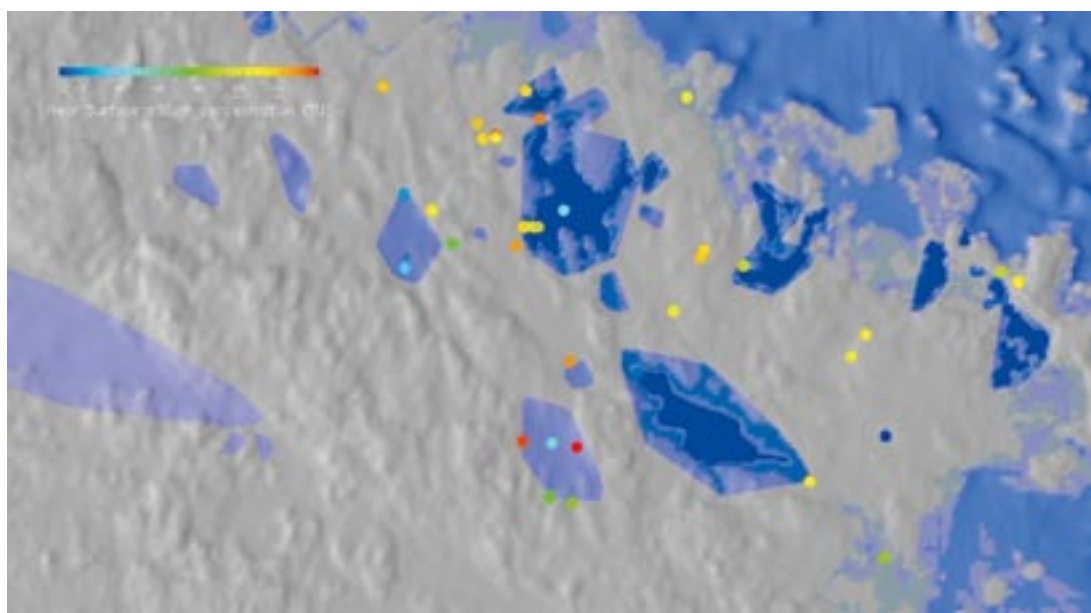


Figure E2-5. Spatial distribution of tritium activities measured in soil pipes. Represented values correspond to the mean values when a time series is available.

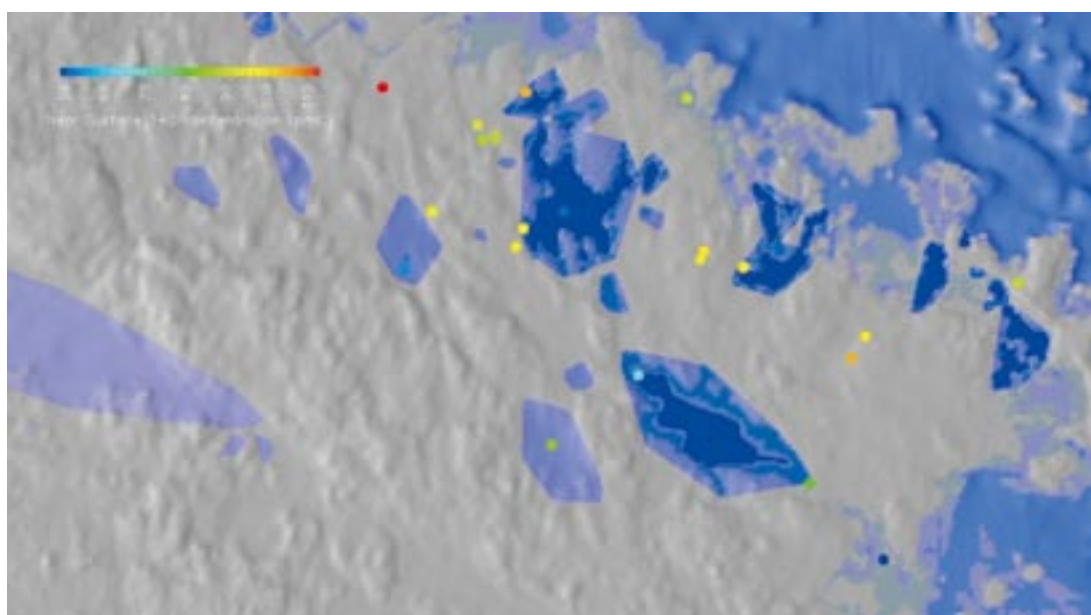


Figure E2-6. Spatial distribution of ^{14}C activities measured in soil pipes. Represented values correspond to the mean values when a time series is available.

E3 Issue 25 – Better integration with hydrogeology, Issue 26 – Conceptual model in 3D

According to hydrogeological site investigation results, deformation zone ZFMN00A2 also plays a significant role on the hydrogeologic behaviour of the Forsmark site. Figure E3-1 shows a NW-SE cross-section through the candidate area.

Hydrogeologic characterization indicates that there is a highly conductive zone in the shallowest 100 m of the bedrock in Forsmark. Down to –100 m, ZFMN002A deformation zone separates two distinct domains. It can be seen in Figure E3-3 that above ZFMN002A there is a number of gently dipping deformation zones which are almost absent below ZFMN002A. This fact makes the rock volume below ZFMN002A less conductive.

Figure E3-2 shows the spatial distribution of chloride concentration values (only representative values) available in bedrock water samples. It can be seen that there is a strong salinity contrast between the waters in the shallowest 100 m of the bedrock and the groundwater below this depth. Figure E3-3 shows the same chloride data but includes the gently dipping ZFMN002A deformation zone. It can be noticed that there are very few representative samples available below ZFMN002A. This fact is related with the lower hydraulic conductivity of the bedrock below this deformation zone which does not allow proper hydrochemical sampling. Then, it should be taken in mind that hydrochemistry provides a biased “picture”, representing information coming from the most conductive part of the bedrock. In this respect, the results of the matrix fluid characterization program is expected to be an extremely useful tool for a proper (“unbiased”) conceptualization of the hydrogeochemical system.

The most conductive part of the first 100 m in the bedrock can be confirmed looking at the tritium contents measured in groundwater samples (Figure E3-4). Water samples above 100 m show high tritium contents typical of modern water. Down to this shallowest 100 m, most of the available samples show tritium contents below 4 T.U. Then, it can be stated that, even in the most conductive zones of the bedrock, groundwater deeper than 100 m is, at least, sub-modern.

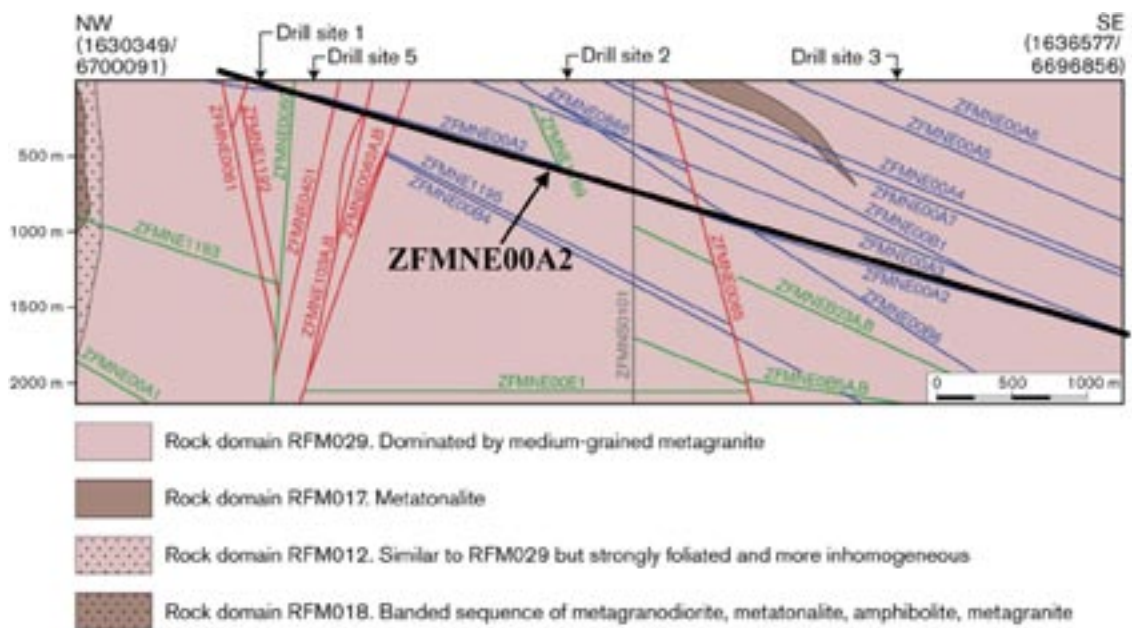


Figure E3-1. NW-SE cross-section through the Forsmark site, as it appears in /Follin et al. 2005/.

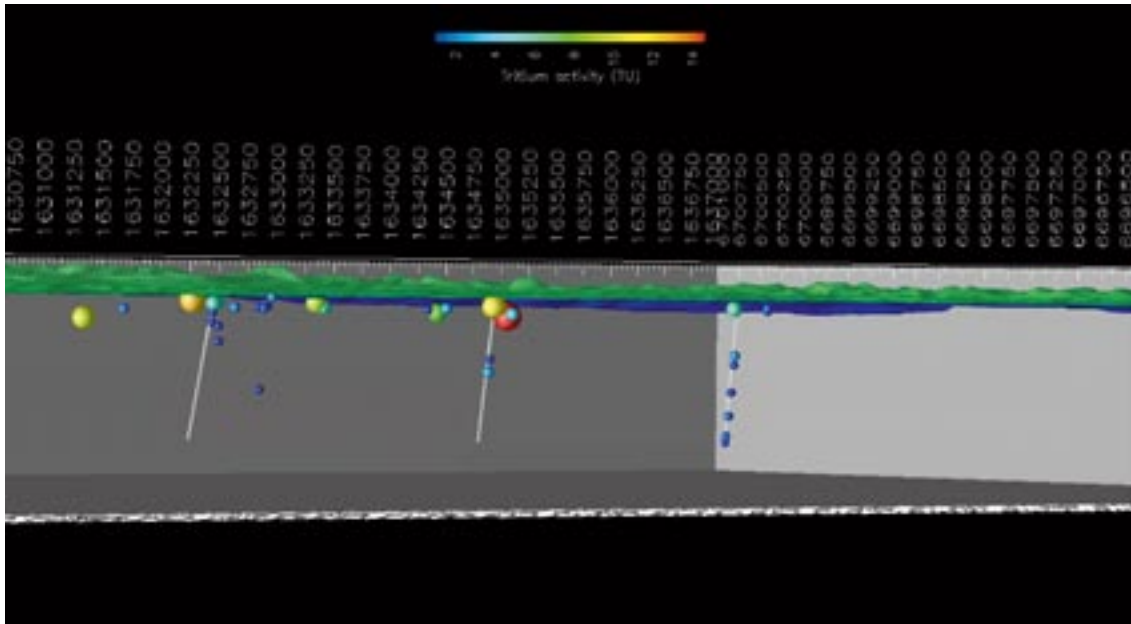


Figure E3-4. Spatial distribution of the tritium activities in the bedrock groundwater samples available in Forsmark. Boreholes KFM01A, KFM02A and KFM03A have been included for location purposes.

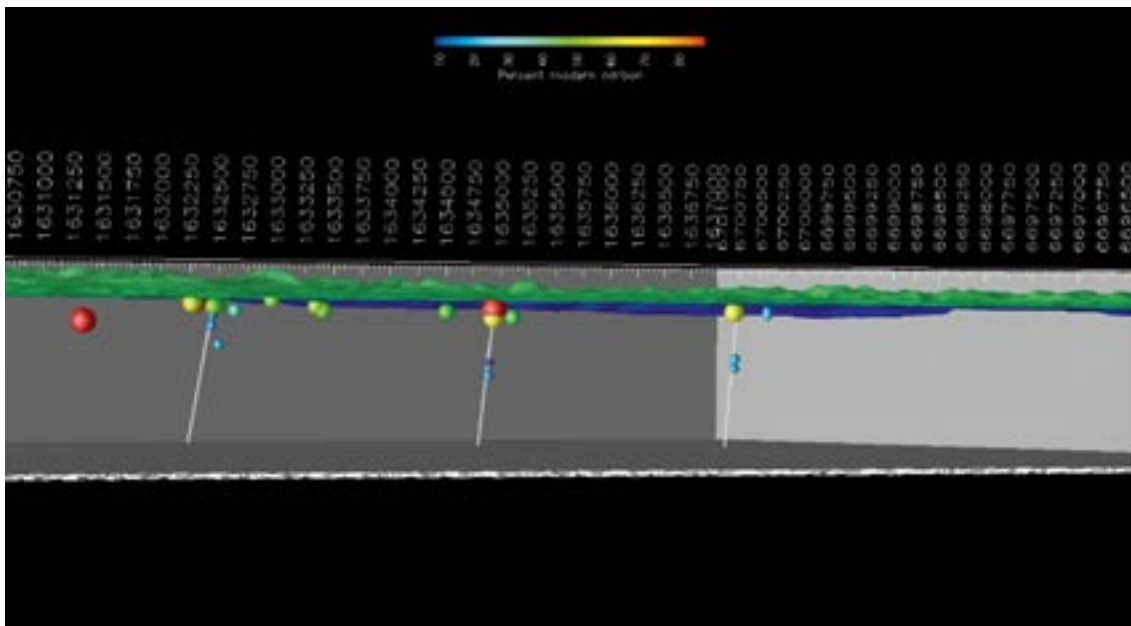


Figure E3-5. Spatial distribution of the ^{14}C activities in the bedrock groundwater samples available in Forsmark. Boreholes KFM01A, KFM02A and KFM03A have been included for location purposes.

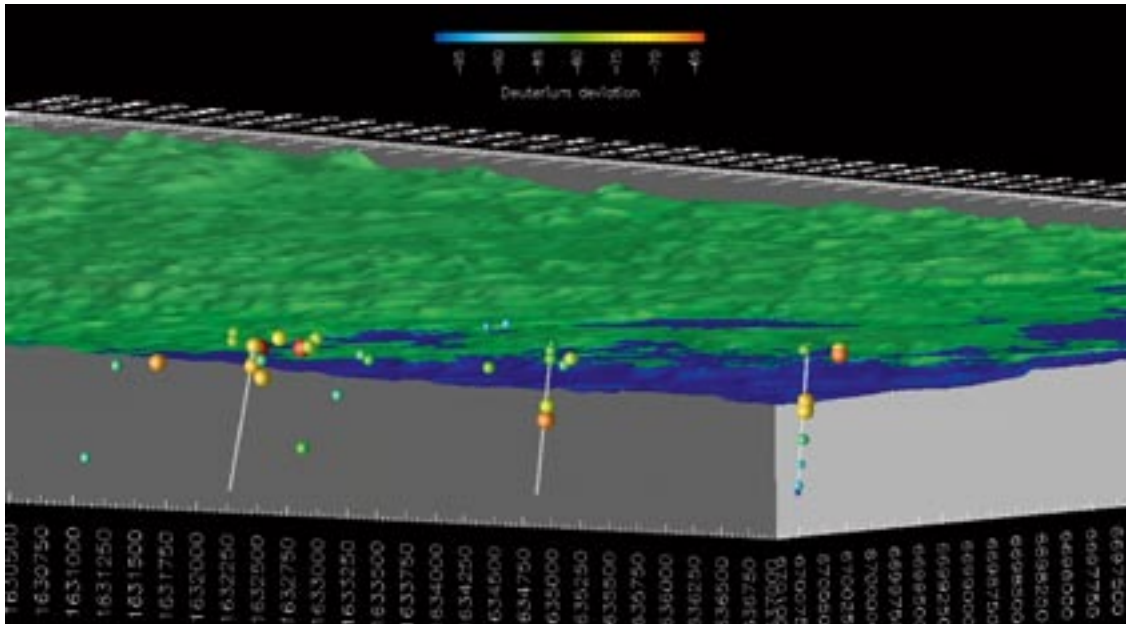


Figure E3-6. Spatial distribution of the ^2H deviations in the bedrock groundwater samples available in Forsmark. Boreholes KFM01A, KFM02A and KFM03A have been included for location purposes.

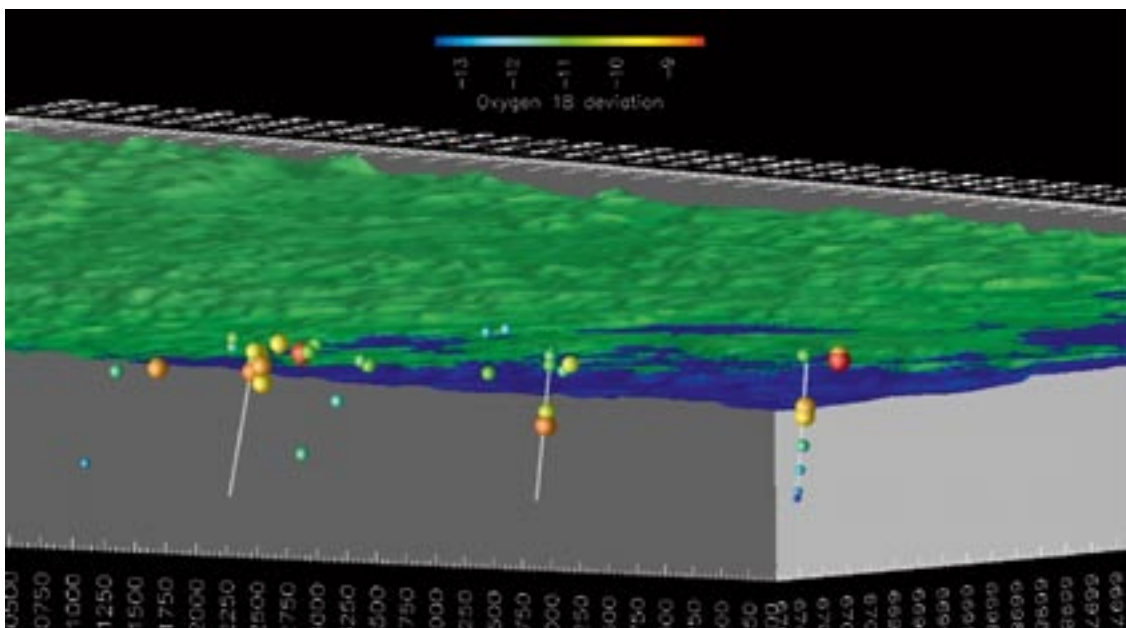


Figure E3-7. Spatial distribution of the ^{18}O deviations in the bedrock groundwater samples available in Forsmark. Boreholes KFM01A, KFM02A and KFM03A have been included for location purposes.

It is worth noting that there are two main exceptions of low stable isotope values (potentially indicative of glacial signatures) in shallow groundwater samples. They correspond to water samples collected in percussion boreholes, located very close to Eckarfjorden Lake and Deformation Zone. Figure E3-8 shows ^{18}O measurements again, but highlighting those values lower than -12 per mil. The aforementioned shallow samples with potential glacial signatures have been remarked in Figure E3-8.

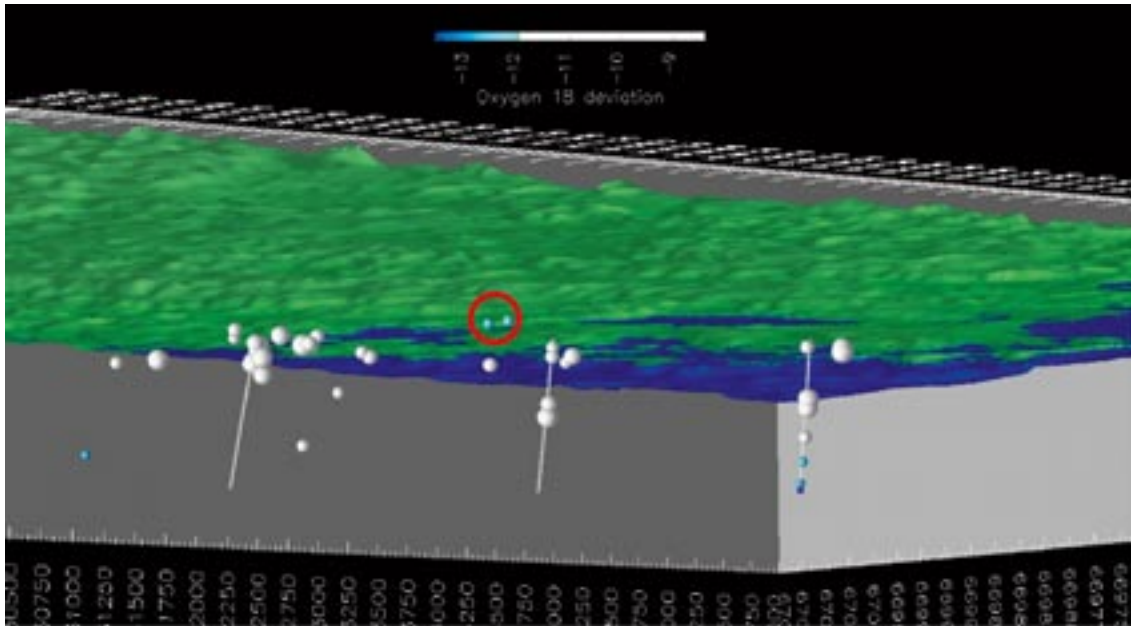


Figure E3-8. Spatial distribution of the ^{18}O deviations in the bedrock groundwater samples available in Forsmark. Values lower than -12 have been highlighted. Two shallow samples with potential glacial signatures have been remarked in a red circle.

An interesting point related with the hydrochemistry of groundwater in Forsmark has been the high uranium content found in some samples. Figure E3-9 shows the spatial distribution of uranium concentrations in representative samples of the Forsmark v2.1 hydrochemical database. It can be noticed that there is a high variation of measured values, ranging from a minimum concentration of $0.337 \mu\text{g/L}$ (borehole KFM07A, at a depth of 925 m), to a maximum concentration of $88.6 \mu\text{g/L}$ (borehole KFM02A at a depth of 512 m).

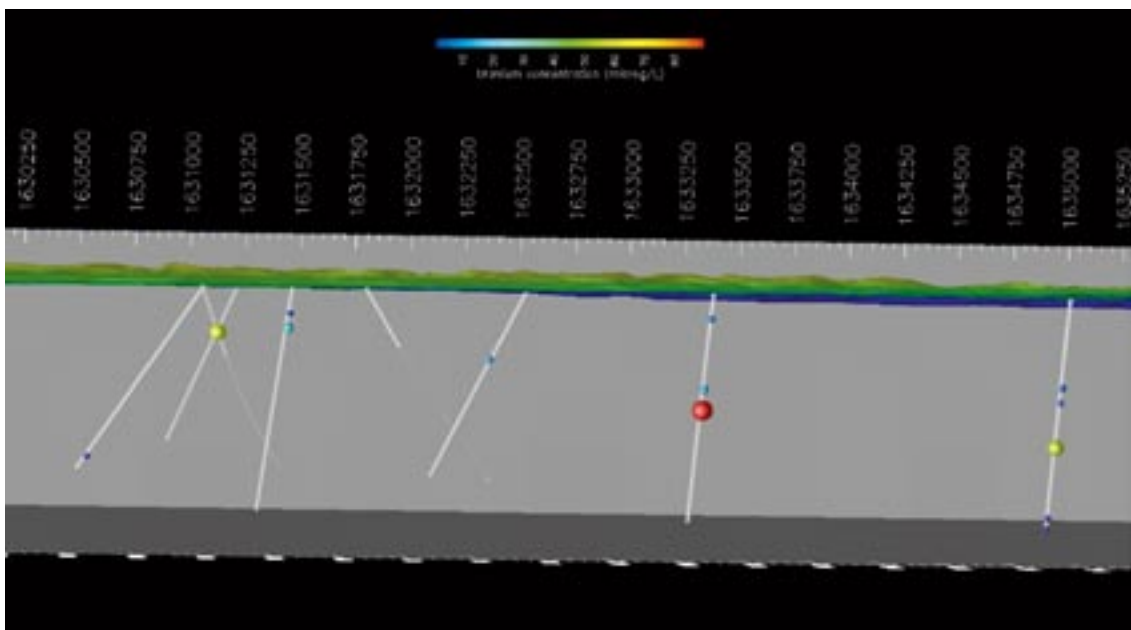


Figure E3-9. Spatial distribution of uranium concentrations in the bedrock groundwater samples available in Forsmark. All cored boreholes are plotted.

As it can be seen in Figure E3-9, there are three samples which show very high uranium concentrations, compared with the rest of measurements available in the database. These three samples have been collected in boreholes KFM02, KFM03 and KFM04, at different depths. A combined analysis of hydrochemical and geologic information allows seeing that these maximum values of uranium correspond to water samples collected at major water-conducting deformation zones. In particular, two of them correspond to water samples collected from ZFMNE00A2, and the other one corresponds to a water sample collected from ZFMNE00B1. Figure E3-10 shows a closer view of uranium concentrations and its relation with the aforementioned deformation zones.

Recently, it has been pointed out that there are galvanic effects from the Fennoscandian HVDC electrical power cable in boreholes KFM04A and KFM09A (SKB Report P-05-265). These two boreholes also contain increased uranium contents in the groundwater. Borehole equipment placed in these boreholes could corrode, and this fact could affect the uranium content. This new observation should be further researched in the future.

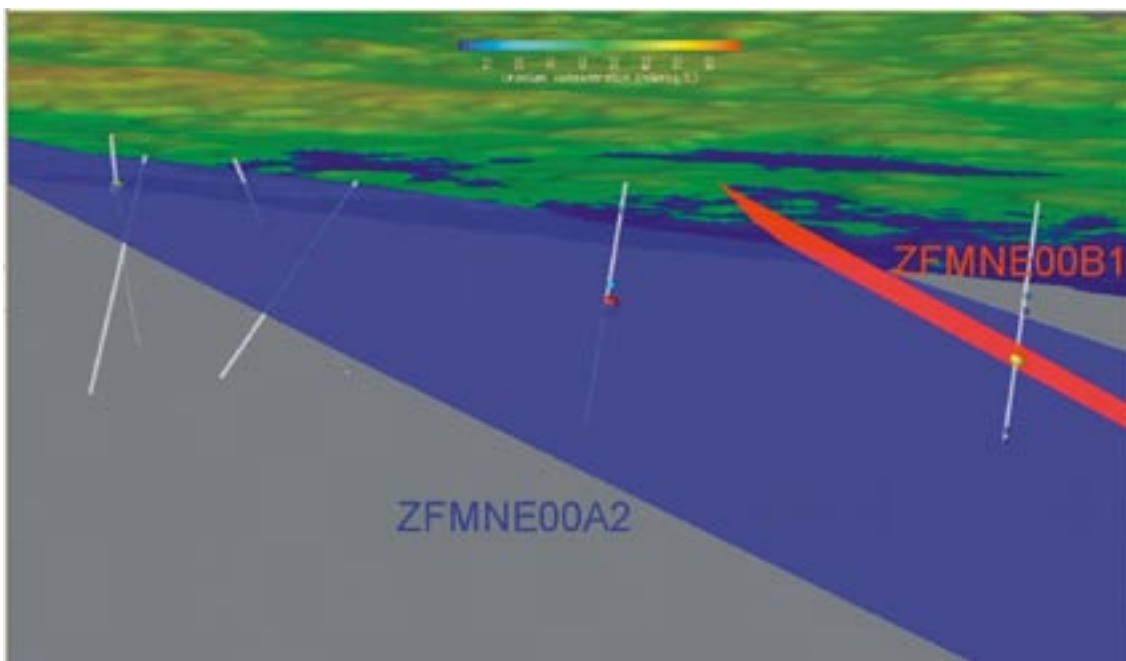


Figure E3-10. Close-up view of the uranium concentrations and its relation with ZFMNE00A2 and ZFMNE00B1.

E4 Conclusions

The hydrochemical and isotopic patterns of near surface hydrochemistry at the discharge (low topography) zones in Forsmark show differences between them. Most of the discharge zones may correspond exclusively to very shallow and local groundwater systems, probably involving only flow through the Quaternary deposits. These very local systems show dilute groundwater and ^3H and ^{18}O values close to modern precipitation. On the other hand, there are places where a mixing between meteoric and old marine water seems clear (Bolundsfjärden as the clearest one). Whether this indicates the discharge of deeper groundwater or the presence of “trapped” relict water, not yet flushed out, should be further investigated. Recent hydrogeological results points towards the second hypothesis since measured groundwater heads in soil pipes are lower than the water lake head, which is not consistent with a hydrogeologic discharge zone (Follin 2006 personal communication).

Down to 100 m depth most of the available samples show tritium contents below 4 T.U. and low ^{14}C values. It can be said that down to this depth water in conductive fractures is at least sub-modern. Stable isotopes indicate that glacial signatures can be recognized in the bedrock, in general at depths higher than 500–600 m.

Hydrochemical and isotopic signatures in Eckarfjärden show significant differences compared to the rest of the discharge zones. Shallow groundwater under this lake is diluted and has relatively low tritium values (3–5 TU) but, according to $\delta^{18}\text{O} - \text{Cl}$ plot, this shallow groundwater seems to be out of the theoretical mixing line with Littorina water. In addition, bedrock water samples collected in percussion boreholes at the Eckarfjorden Deformation Zone show isotopic glacial signatures.

Appendix F

Uranium and radium in groundwater at the Forsmark site, Sweden

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March 2007

F Abstract

This report contributes to the information and understanding obtained of the presence of high uranium and radium concentrations in groundwaters of the Forsmark site, eastern Sweden. Uranium concentrations (up to 122 µg/L) have been found in some groundwaters and these exceed maximum drinking water standards set by both Sweden and the World Health Organisation. Weak correlations of U with HCO₃, SO₄ and Eh have been observed but a more convincing relationship with the residual drill water in the borehole zone is clearer. There appears to be no characteristic relationship between U content and ²³⁴U/²³⁸U activity ratio. In contrast, Ra is clearly related to groundwater salinity and attains concentrations of 23 Bq/L, well above the drinking water maximum of 0.5 Bq/L. Most of the high Ra concentrations, however, occur in brackish groundwater (salinity ~ 5–10 g/L), and are unlikely to be consumed.

A previous test in Canada's Underground Research Laboratory showed that U can be readily mobilised from wall-rock in granitic fracture zones by introduction of O₂. This may be occurring at Forsmark, caused by the presence of residual drill water in the borehole. However, similar characteristics are not seen in groundwaters elsewhere in the Forsmark area (or at Laxemar/Simpevarp) but the presence of induced ground currents from the nearby HVDC transmission station may be an significant cause of U mobilisation.

The characteristics of U distribution and mechanisms of retardation should be well-known for the Forsmark area, as this is likely to be considered when siting a high-level waste repository. As found at the URL in Canada, U is likely to be mobilised by drilling, pumping and excavation activities and this characteristic may require on-site treatment or design changes to meet environmental standards and to conform to requirements of the safety case for a repository.

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F1 Introduction

Anomalously high concentrations of uranium (U) and radium-226 (Ra) have been found in some groundwaters at the Forsmark site, in eastern Sweden, during site characterisation work performed for the Swedish program for geological disposal of nuclear fuel waste (Figure F1-1). High concentrations (up to 122 µg/L U and 23 Bq/L Ra*) have not been previously encountered during studies of other locations in Sweden, including Simpevarp/Laxemar, the companion site further to the south that is also a possible site for nuclear fuel waste disposal.

These findings are of concern to the siting program as they indicate that U is mobile in groundwaters at the Forsmark site and thus U leached from spent fuel in this environment may not be retarded by the processes that cause U to be immobilised at other sites. This report examines the hydrogeochemical data from the Forsmark site and attempts to understand the apparent

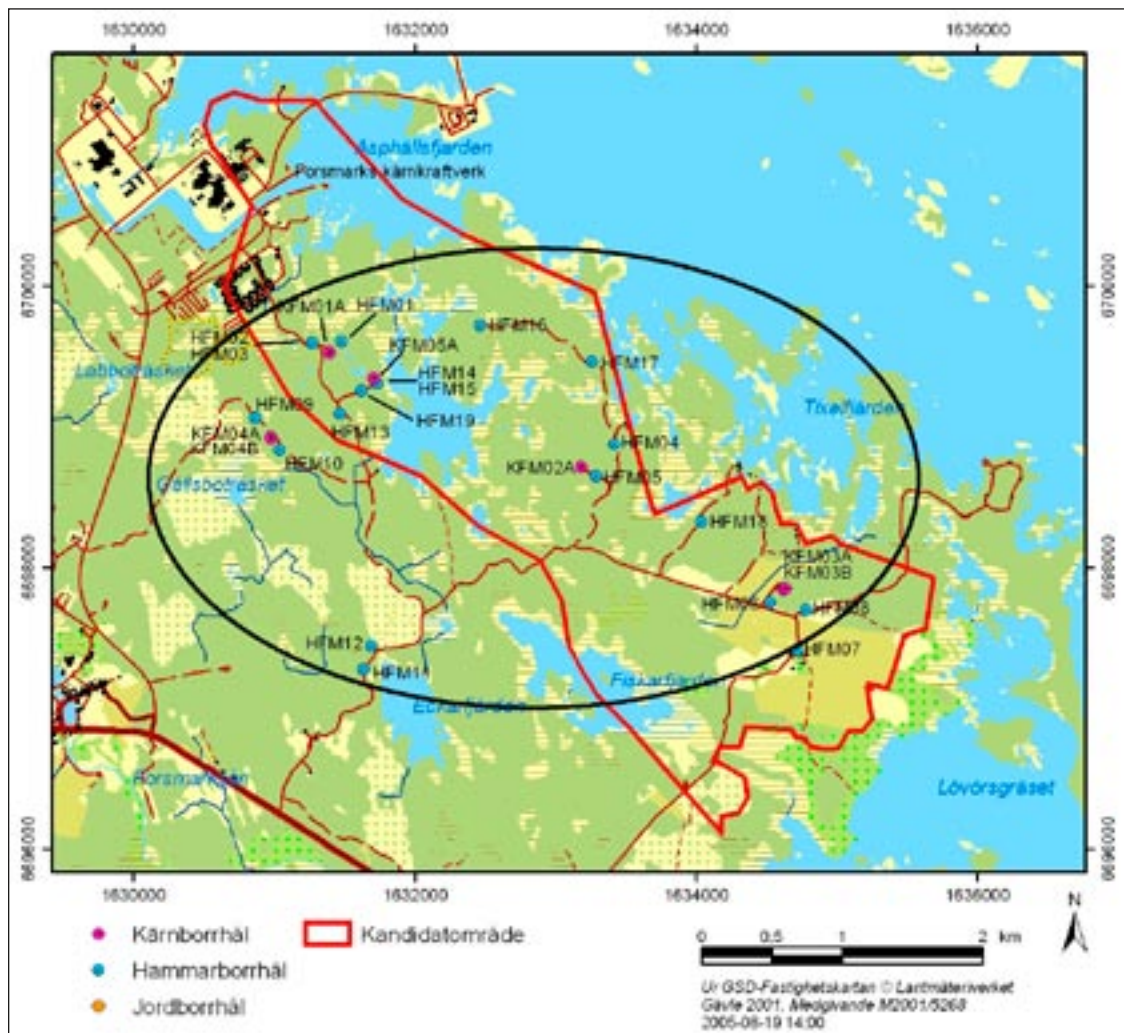


Figure F1-1a. Location of study area (ellipse) and boreholes investigated.

* Concentrations of U are commonly expressed in terms of mass per volume (µg/L) and of radium as radioactivity (Becquerel) per volume (Bq/L). This convention is used here although U may also be given as radioactivity of the most abundant isotope, ²³⁸U. In this case 1µg/L (U) = 12.44 mBq/L. If the radioactivity of U is of concern, then the activity of daughter ²³⁴U must also be considered.

mobility of U and its impact on the site model. The mobility of Ra is of less concern for the site model because it is not present in quantity in spent fuel and only accumulates slowly, by radioactive ingrowth. Comparison is made with high concentrations of U and Ra in groundwater at the Underground Research Laboratory of Atomic Energy of Canada Limited, in southeastern Manitoba.



Figure F1-1b. Detail of KFM-series borehole locations near to the Forsmark power station.

F2 Geochemistry of U and Ra

Uranium is insoluble ($\sim 10^{-10}$ mol/L) in near-neutral, reducing groundwater (pH 6 to 9, Eh < -100 mV). However, U solubility is much greater in mildly reducing and oxidising groundwaters when it complexes with dissolved HCO_3^- to form the soluble anions $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$. Groundwaters that are oxidising and rich in HCO_3^- may contain as much U as 1 g/L /Paquette and Lemire 1981/ but U in most natural waters seldom exceeds 1 mg/L /Gascoyne 1989/.

Uranium occurs in groundwater mainly as the isotopes ^{238}U and ^{234}U in the ^{238}U decay series (Figure F2-1) but, due to solubility enhancement and alpha-particle recoil, the radioactivity level of daughter ^{234}U often exceeds ^{238}U in natural waters by factors of 2 to > 20 . This enhancement of radioactivity is important to consider when making dose calculations and predictions and also when attempting to understand the geochemical conditions of groundwater containing dissolved U.

Radium mainly occurs as the isotope ^{226}Ra and is formed by the decay of ^{230}Th in the ^{238}U decay series. Together with ^{228}Ra , these Ra isotopes are the most important species that contribute to Ra dose and can be used to understand geochemical conditions in groundwater.

In natural waters, Ra exists mainly as the free ion Ra^{2+} , or the uncharged complex RaSO_4^0 /Langmuir and Riese 1985/. Radium is readily removed from solution by absorption on clays and rock silicates and coprecipitation with insoluble sulphates. However, it is stabilized in solution by high concentrations of Ca, Na and Cl /Langmuir and Melchior 1985/.

The standards for maximum levels of U and Ra in drinking water in Sweden are given in Table F2-1. Limits of 100 $\mu\text{g/L}$ and 0.5 Bq/L, respectively, are used, with notification to the user. The World Health Organisation's recommendation for U is 15 $\mu\text{g/L}$. In Sweden there is little information about the content of radioactive elements in drinking water, however, in an investigation of 260 private wells, 20% of the wells contained more than 15 $\mu\text{g/l}$ U (information from the Swedish Geological Survey web site).

Table F2-1. Recommended maximum values of U, Ra and Rn in drinking water according to the regulatory standard /SLVFS 2001:30/.

Radon	< 100 Bq/l	Usable
	100–1,000 Bq/l	Usable but with remark
	> 1,000 Bq/l	Not usable
Total Indicative Dose (TID) (100 $\mu\text{g/l}$ uranium gives 0.1 mSv/year, 0.5 Bq/l radium gives also 0.1 mSv/year)	> 0.1 mSv/year	Usable but with remark

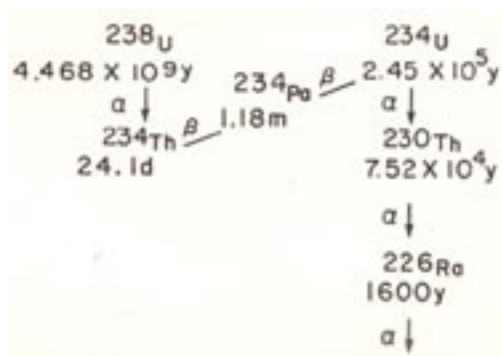


Figure F2-1. The ^{238}U decay series.

F3 U and Ra at Forsmark

Groundwaters from several deep permeable zones in the Forsmark HFM-, KFM- and KFR-series boreholes have recently been found to contain levels of U and Ra that are close to or exceed drinking water standards for Sweden (Table F2-1). The location, chemical composition and radioactive element content of these groundwaters is shown in Appendix A. Analyses of a number of shallow boreholes (mainly soil pipes in the SFM-series) have also been made as these represent local recharging groundwaters.

F3.1 U

Two sets of analysis for U were performed in this study, one by ICP-MS to determine U by mass, and the other by alpha spectrometry to determine U as ^{238}U , the dominant U isotope. For paired results, with one exception, good agreement was found by the proximity of the data points to the 1:1 line in Figure F3-1.

The highest concentrations of U were found in groundwaters from boreholes KFM02A and KFM03A at intermediate depths (~ 500–650 m). The variation of U with depth in the boreholes is shown in Figure F3-2. There is a clear rise in U content (to 120 $\mu\text{g/L}$) as depth increases, to about 550 m, followed by a decrease in U to < 1 $\mu\text{g/L}$ below about 900 m. The increase in U concentrations between 500 and 650 m is most clearly seen in Figure F3-3, where U is plotted against Cl concentration. The sharp increase in U attains concentrations an order of magnitude greater than in the groundwaters bounding it. The cause of this increase is not immediately apparent because examination of the relationships between U and HCO_3^- (for uranyl carbonate complexes) and SO_4 (uranyl for sulphate complexes) shows that neither anion appears to exert significant control over U solubility (Figures F3-4a and b, respectively). The high U concentrations are mainly found in samples containing relatively low amounts of HCO_3^- (100–159 mg/L). There is an indication that higher SO_4 concentrations are needed to get higher U levels because the peaks in Figure F3-4b show a progressively increase in U as SO_4 increases; however, there are many samples that have low U at high SO_4 .

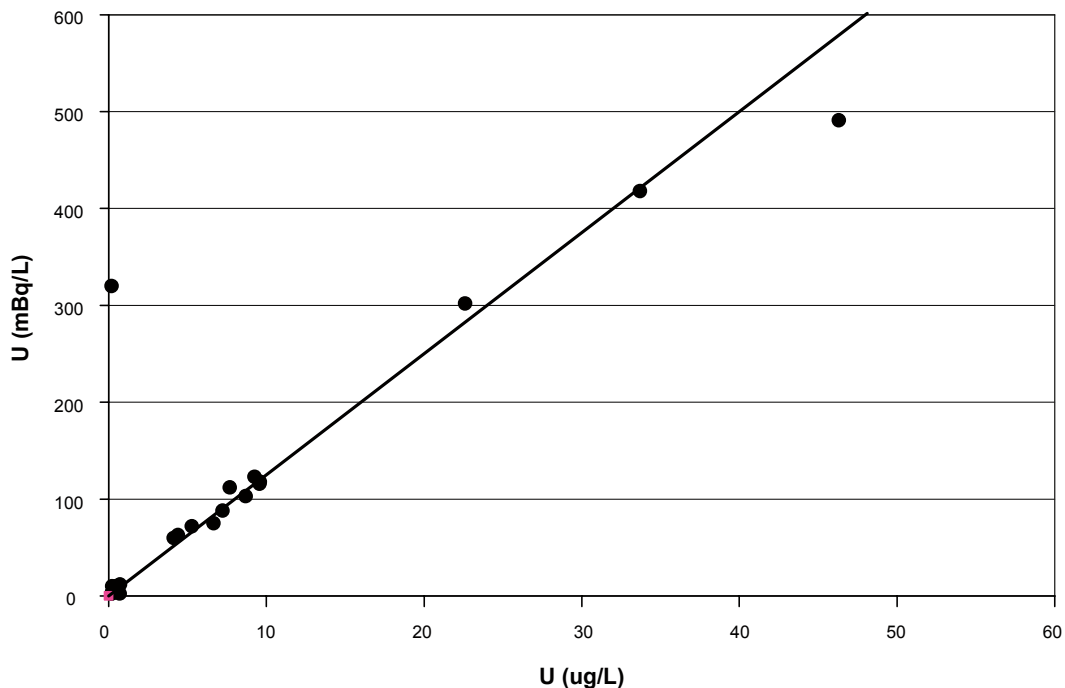


Figure F3-1. Comparison between analytical methods for U determination in this study.

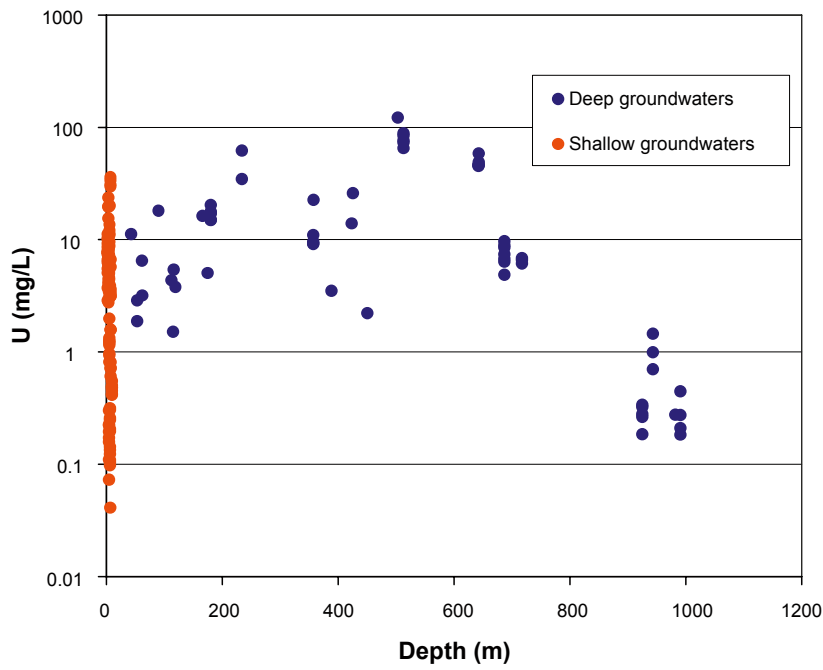


Figure F3-2. Variation of U concentration with depth.

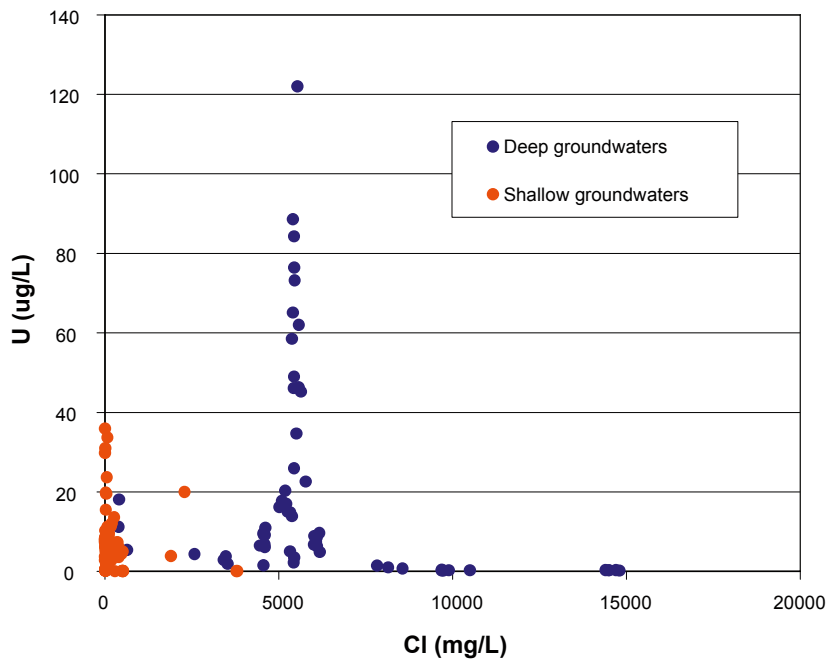


Figure F3-3. Variation of U with Cl concentration.

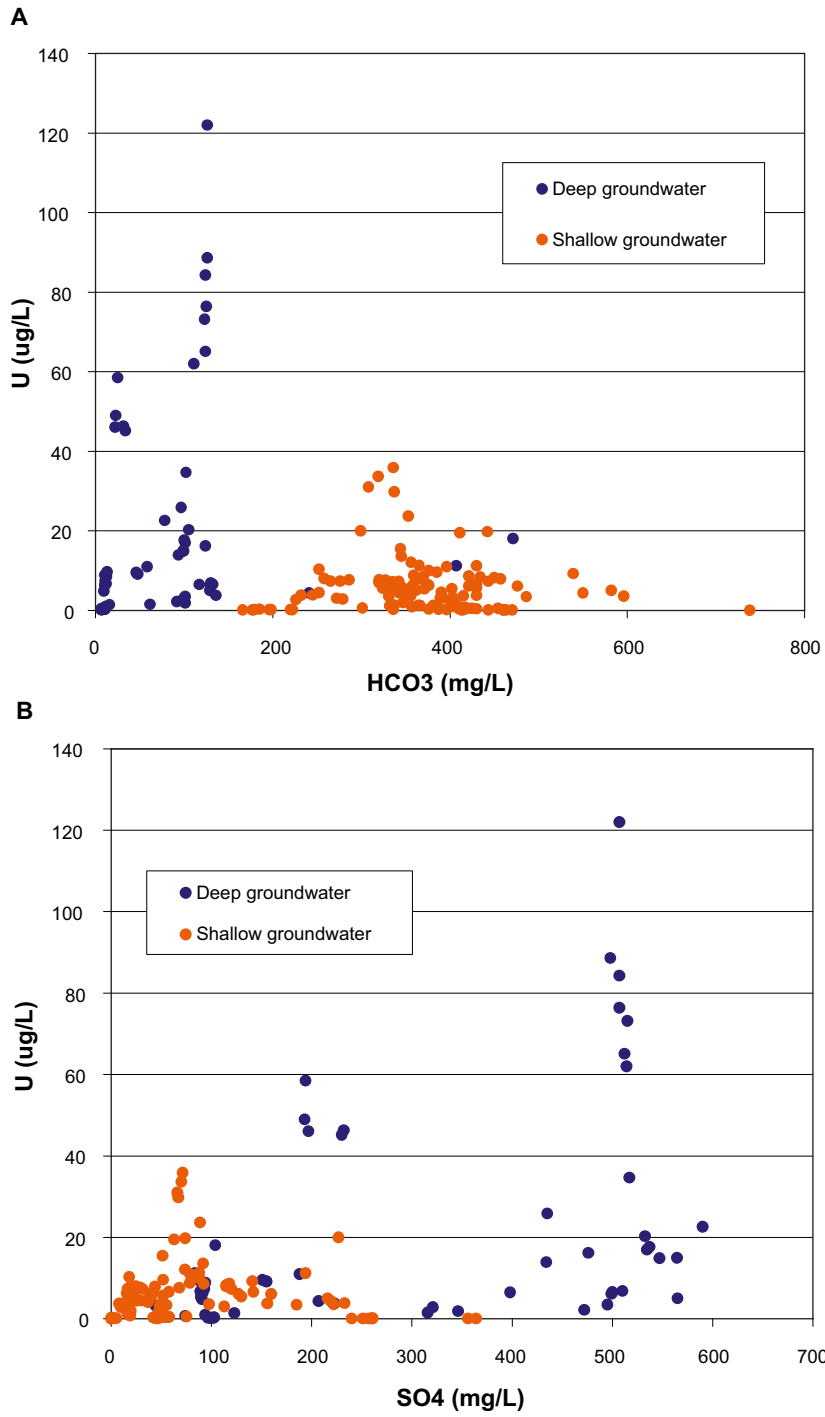


Figure 3F-4. Variation of U with a) HCO₃ and b) SO₄ concentrations.

There are six measurements of Eh potential in the database in Appendix F1, of which five have U concentrations. The relationship between U and Eh is shown in Figure F3-5. While there are insufficient Eh data points to draw any firm conclusions from the graph, there is an indication that U concentrations increase as Eh gets higher. A somewhat clearer correlation can be seen in the relationship between U concentration and content of residual drillwater in the samples (Figure F3-6). Drillwater will contain some O₂ despite the best efforts to remove it before its injection downhole. The high U concentrations with significant drillwater content (between 2 and 8%) would help to mobilise U. The low U contents at 8 to 14% drillwater may be due to consumption of O₂ by the greater availability of reduced species at depth.

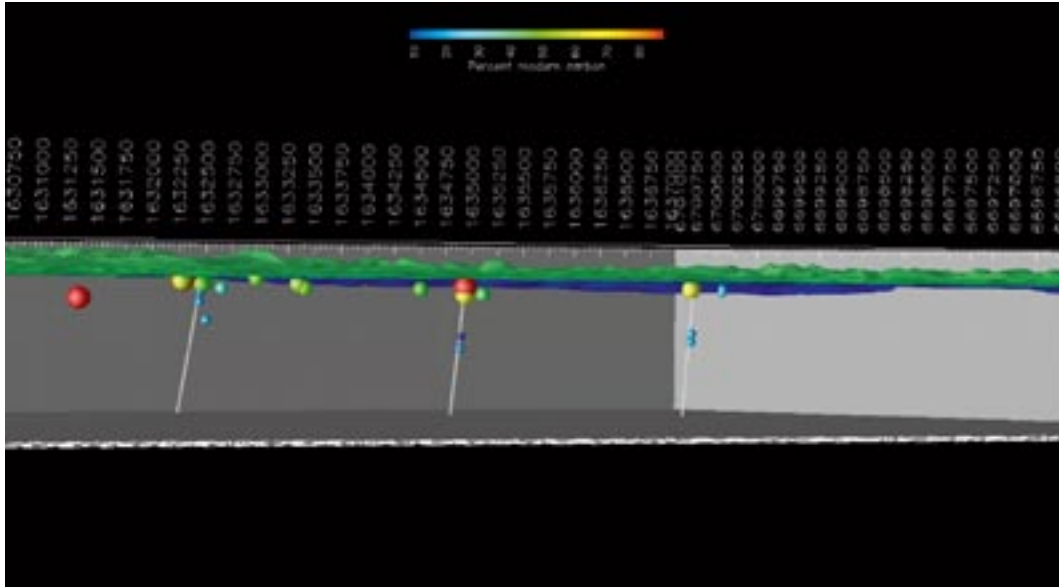


Figure F3-5. Variation of U concentration with Eh.

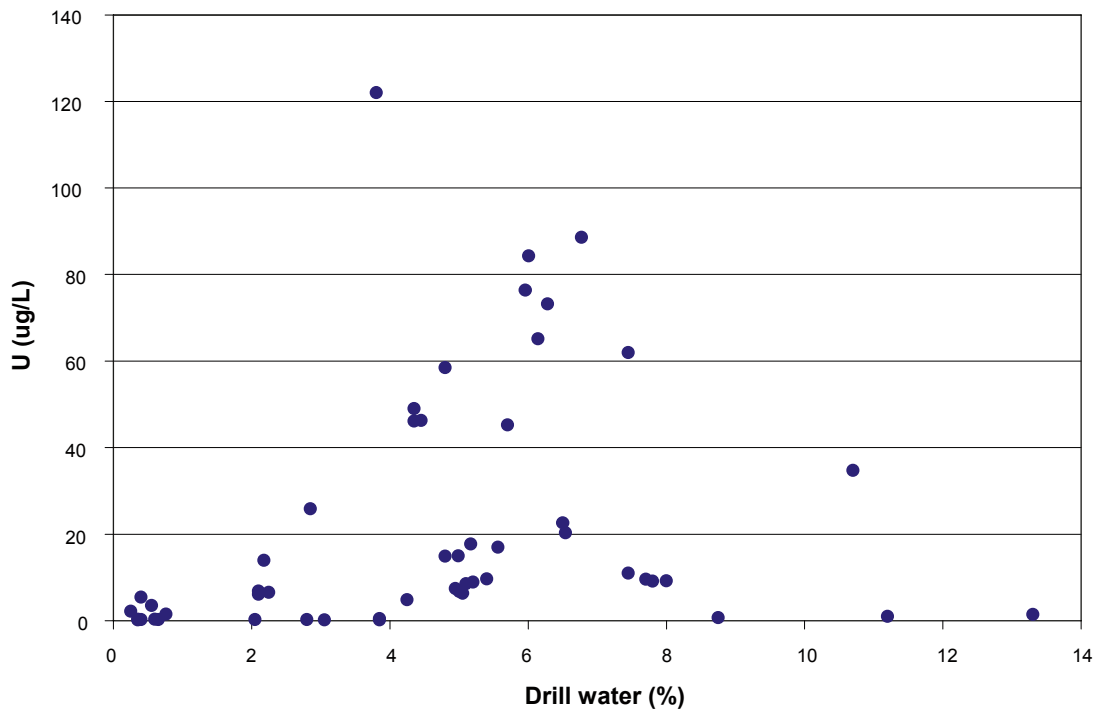


Figure F3-6. Variation of U concentration with fraction of remaining drill water in borehole zone.

F3.2 Ra

Radium concentrations are generally low in the shallow (soil tube) groundwaters (Figure F3-7a) but increase steeply in the deeper groundwaters to 23 Bq/L. As in the case of U, the highest concentrations of Ra were found in groundwaters from boreholes KFM02A and KFM03A at intermediate depths (~ 500–650 m). Some moderately high concentrations were also found in boreholes KFM07A and KFM08A. The increased concentrations of Ra in saline groundwaters can be clearly see in Figure 3-7b although several waters are saline but contain little Ra.

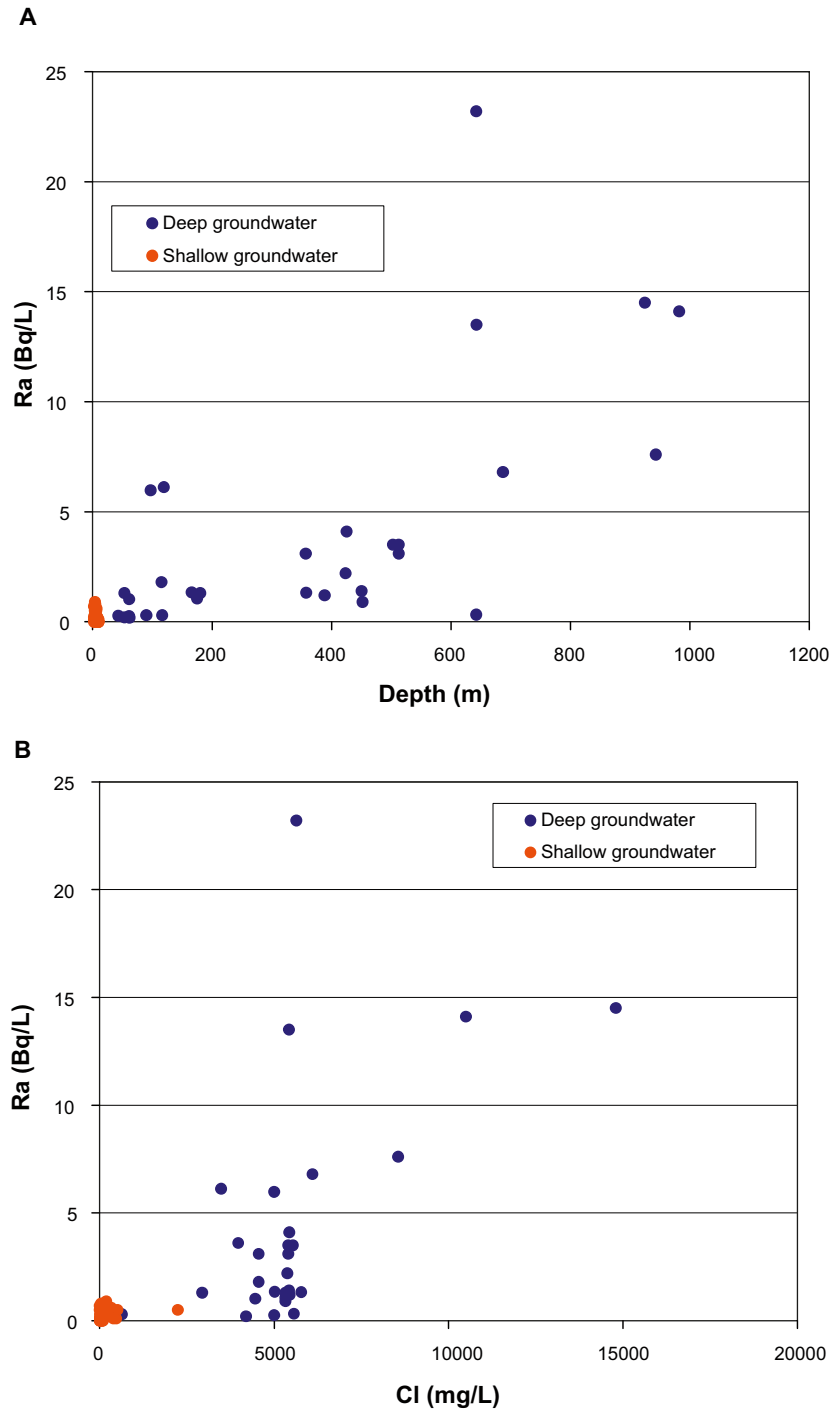


Figure F3-7. Variation of Ra with a) depth and b) Cl concentration.

Figure F3-8 shows the relationship between U and Ra content of all groundwaters. It can be seen that while many waters (particularly the shallower groundwaters) have no apparent correlation, deeper groundwaters if enriched in U are likely to also be higher in Ra content. An inverse correlation between U and Ra might be expected however, because U concentration normally decreases (due to lower redox potential and lack of HCO_3^-) as salinity increases whereas Ra is not affected directly by redox and tends to form soluble complexes as salinity increases.

F3.3 $^{234}\text{U}/^{238}\text{U}$ activity ratios

In all samples, the $^{234}\text{U}/^{238}\text{U}$ activity ratio was greater than unity, indicating recent (< 1 Ma) and preferential dissolution of ^{234}U from the bedrock or surficial sediments. A greater enrichment of ^{234}U was seen in shallow and deep samples (2 to 7) but soil waters and intermediate depth waters varied only from 1 to 3 (Figure F3-9a). Unlike most previous literature, the $^{234}\text{U}/^{238}\text{U}$ ratio does not appear to be correlated with U concentration (Figure F3-9b). This typically occurs because of the combined processes of total U precipitation as Eh decreases and increased influence of alpha-recoil of ^{234}U from adjacent surfaces of solid phases.

F3.4 Regulatory limitations

The variation of U with depth in the boreholes was shown in Figure F3-2. Uranium concentration increases to $122 \mu\text{g/L}$ as depth increases, to about 550 m and then decreases rapidly to $< 1 \mu\text{g/L}$ below about 900 m. Only one sample actually exceeds the Swedish maximum limit for U in drinking water ($100 \mu\text{g/L}$), although many (30) exceed the World Health Organisation limit ($15 \mu\text{g/L}$).

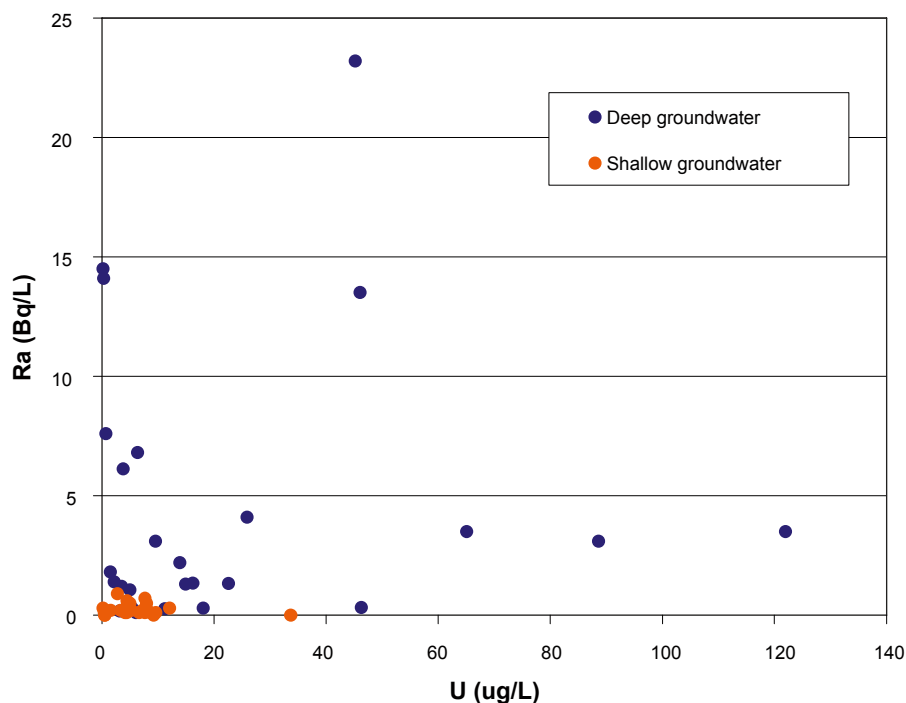


Figure F3-8. Variation of Ra with U.

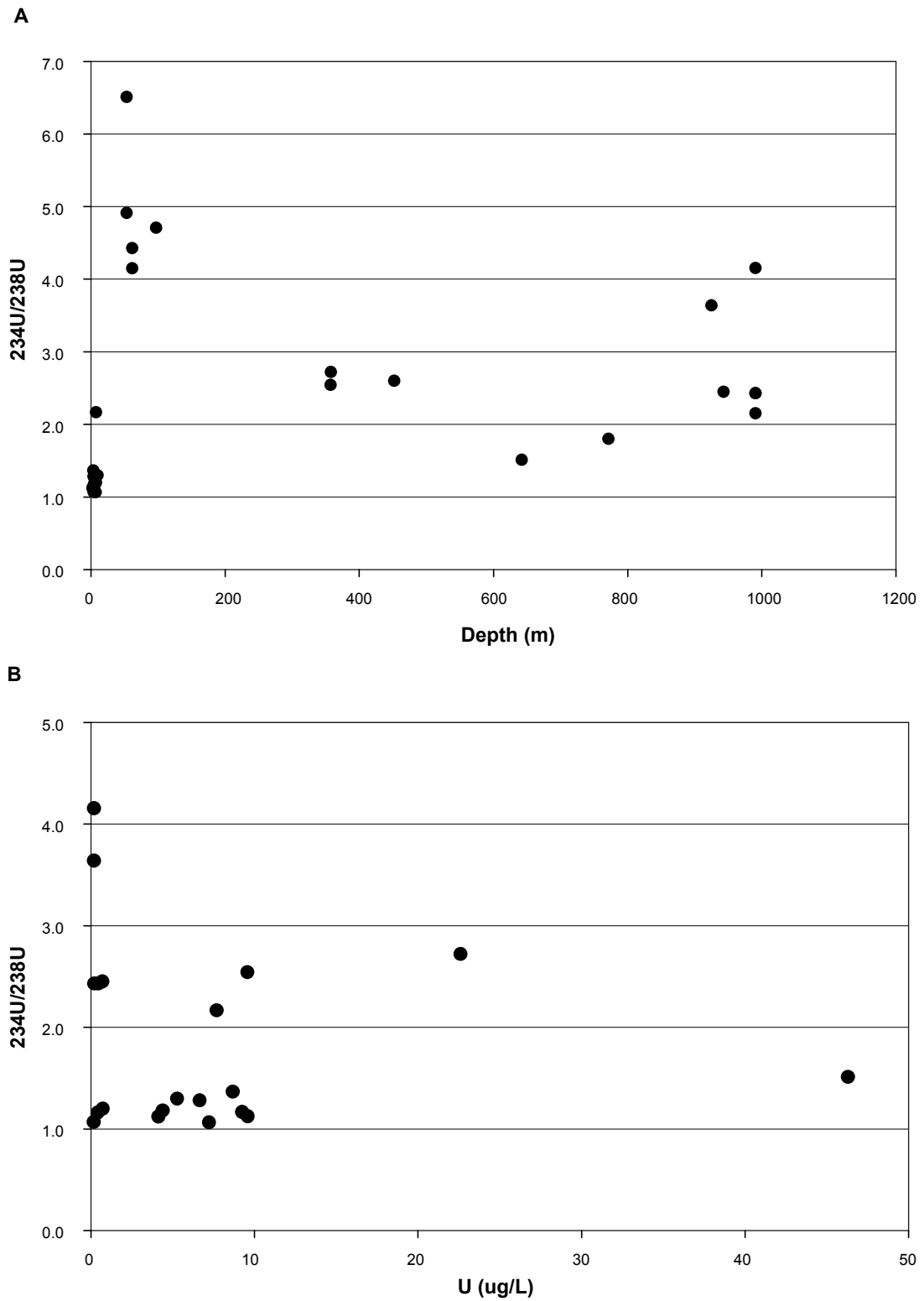


Figure F3-9. Variation of $^{234}\text{U}/^{238}\text{U}$ activity ratio with a) depth and b) U concentration.

Radium concentrations are fairly low in the shallow groundwaters (Figure F3-6a) but increase in the deeper groundwaters to 23 Bq/L, well above drinking water limits (0.5 Bq/L). Indeed, quite a large number of the shallow groundwater values exceed 0.5 Bq/L and, since these waters may be typical of private well waters, these observations should be conveyed to local authorities. In the deeper groundwaters Ra concentrations considerably exceed the drinking water standard. While this may present a problem meeting drinking water limits, most of the Ra-rich waters are quite saline (see the relationship between Ra and Cl, Figure F3-6b) and would not normally be considered as 'drinking water'. However, discharging these waters at the surface (for instance, when pumping and flushing a deep borehole), may constitute a problem because both the salinity and the Ra content are likely to exceed regulatory standards.

F3.5 Corrosion and HVDC

The possibility of enhanced corrosion due to the presence of High Voltage Direct Current (HVDC) around the area of borehole KFM04A has recently been proposed by /Nissen et al. 2005/. Severe corrosion was observed on down-borehole geochemical monitoring equipment and a voltage gradient, causing a ground current, was found in boreholes KFM04A, KFM07A and KFM08A. It may be possible that the corrosive effects cause localised oxidising conditions to develop along a borehole and this could readily mobilise reduced species, such as U, from fracture walls.

While these are not the boreholes with particularly high U contents (KFM02 and KFM03) they all lie in the same general area and the potential for developing oxidising conditions is considerable and should be considered as a possible explanation for the high U in groundwaters in this area.

F3.6 Speciation and solubility modelling

Geochemical modelling of the analytical data in Appendix A has been performed using PHREEQC and the WATEQF4 database for calculation of U speciation and solubility. Only 6 Eh measurements are currently useable and one of these applies to a sample for which U concentration is not determined. Hence, the results of geochemical modelling using potentiometrically measured Eh are limited to 5 samples from the KFM-series boreholes (Table F3-1). The U-species present in the groundwater and their calculated concentrations, plus the likely U-mineral forms that are controlling U solubility and their saturation indices (SI) are given in Table F3-1.

The modelling data show that in all of the groundwaters, the U(IV) redox state prevails and accounts for most of the U in solution. Concentrations of the dominant species, $U(OH)_4$, range from 2×10^{-7} to 6×10^{-9} mol/L, indicating solubility control by the strong reducing conditions (Eh ranges from -245 to -143 mV) in all samples and equilibration mainly with UO_2 (amorphous) whose SI values are closest to 1 in all waters. Only for the most enriched sample (KFM02A, 89 $\mu\text{g/L}$) do the U(VI) anion carbonate complexes collectively exceed the concentrations of the U(IV) species, indicating that the oxidised, more soluble U species are becoming dominant (and these have the highest Eh, -143 mV).

Table F3-1. Geochemical modelling results for the SICADA Forsmark data with U concentration and Eh results.

Borehole #	Zone depth (m)	pH	Eh (mV)	U ($\mu\text{g/L}$)	Speciation	Concentration of species (mol/L)	Mineral phase	SI
KFM01A	115.44	7.47	-195	1.51	U(OH)_4	6.4×10^{-9}	$\text{UO}_2(\text{a})$	1.18
					UO_2^+	2.9×10^{-11}	$\text{U}_3\text{O}_8(\text{c})$	-5.91
					$\text{UO}_2(\text{CO}_3)_3^{-4}$	5.1×10^{-12}	$\text{U}_4\text{O}_9(\text{c})$	12.22
							$\text{UO}_2(\text{c})$	6.35
KFM01A	180.35	7.60	-188	14.9	U(OH)_4	6.2×10^{-8}	$\text{UO}_2(\text{a})$	2.18
					$\text{UO}_2(\text{CO}_3)_3^{-4}$	4.2×10^{-10}	$\text{U}_3\text{O}_8(\text{c})$	-2.47
					UO_2^+	3.8×10^{-10}	$\text{U}_4\text{O}_9(\text{c})$	16.42
					$\text{UO}_2(\text{CO}_3)_2^{-2}$	2.3×10^{-10}	$\text{UO}_2(\text{c})$	6.35
KFM02A	512.54	7.18	-143	88.6	U(OH)_4	2.3×10^{-7}	$\text{UO}_2(\text{a})$	2.75
					$\text{UO}_2(\text{CO}_3)_3^{-4}$	9.4×10^{-8}	$\text{U}_3\text{O}_8(\text{c})$	2.19
					$\text{UO}_2(\text{CO}_3)_2^{-2}$	4.0×10^{-8}	$\text{U}_4\text{O}_9(\text{c})$	20.2
					UO_2^+	7.6×10^{-9}	$\text{UO}_2(\text{c})$	6.93
KFM03A	642.56	7.55	-196	46.1	U(OH)_4	1.9×10^{-7}	$\text{UO}_2(\text{a})$	2.67
					UO_2^+	8.7×10^{-10}	$\text{U}_3\text{O}_8(\text{c})$	-1.50
					U(OH)_3^+	1.2×10^{-10}	$\text{U}_4\text{O}_9(\text{c})$	18.14
					$\text{UO}_2(\text{CO}_3)_2^{-2}$	1.5×10^{-11}	$\text{UO}_2(\text{c})$	6.85
					$\text{UO}_2(\text{CO}_3)_3^{-4}$	5.3×10^{-12}		
KFM03A	943.06	7.78	-245	0.7	U(OH)_4	3.0×10^{-9}	$\text{UO}_2(\text{a})$	0.87
					U(OH)_3^+	6.0×10^{-12}	$\text{U}_3\text{O}_8(\text{c})$	-12.06
					UO_2^+	2.2×10^{-12}	$\text{U}_4\text{O}_9(\text{c})$	8.37
						$\text{UO}_2(\text{c})$	5.05	

c = crystalline.

a = amorphous.

F4 Comparison with URL data, Canada

F4.1 Concentrations in wells and boreholes

In the 1980's, anomalously high levels of U and, occasionally Ra, were found during a Province of Manitoba sampling of private well waters near the site of the Underground Research Laboratory (URL), Lac du Bonnet, in Manitoba, Canada. Concern was expressed at the time by local citizens that the high U was being emitted by the excavation of the URL. Several studies were undertaken at that time to determine the source(s) and cause(s) of the U (and Ra) and, if possible, minimise the effects. This work was presented in two papers and a report describing the anomalies /Betcher et al. 1988, Gascoyne 1989, Gascoyne and Barber 1992/. A filter system was developed to selectively remove U and Ra from drinking water /Gascoyne 1986/.

In summary, U concentrations varied between < 1 and $900 \mu\text{g/L}$ and Ra concentrations between < 0.02 and 38 Bq/L in 74 individual groundwaters. High U concentrations were found in groundwaters in overburden (glacial) clays and in the upper $\sim 200 \text{ m}$ of bedrock where HCO_3 concentrations were high. A seasonal variation in U, from 100 to $800 \mu\text{g/L}$, was found in groundwater from a fracture zone between 70 and 90 m depth in the granite and which outcropped at the surface close to the URL. This cyclicity was observed over a full two-year period and was ascribed to the influx of oxidising groundwater during spring snow-melt and summer rains (a clear pattern in variations in HCO_3 content of the waters was not apparent).

Radium concentrations were low ($< 1 \text{ Bq/L}$) in most URL groundwaters except for two wells (up to 3.5 Bq/L) and some boreholes (up to 38 Bq/L for a saline groundwater with $\text{Cl} = 19 \text{ g/L}$, Figure F4-1). This relationship is commonly found in brines in oil-bearing formations /Langmuir and Melchior 1985/. In the URL area, Ra was frequently low or absent when U was high. Radium might be expected to correlate with U concentrations in groundwaters that have

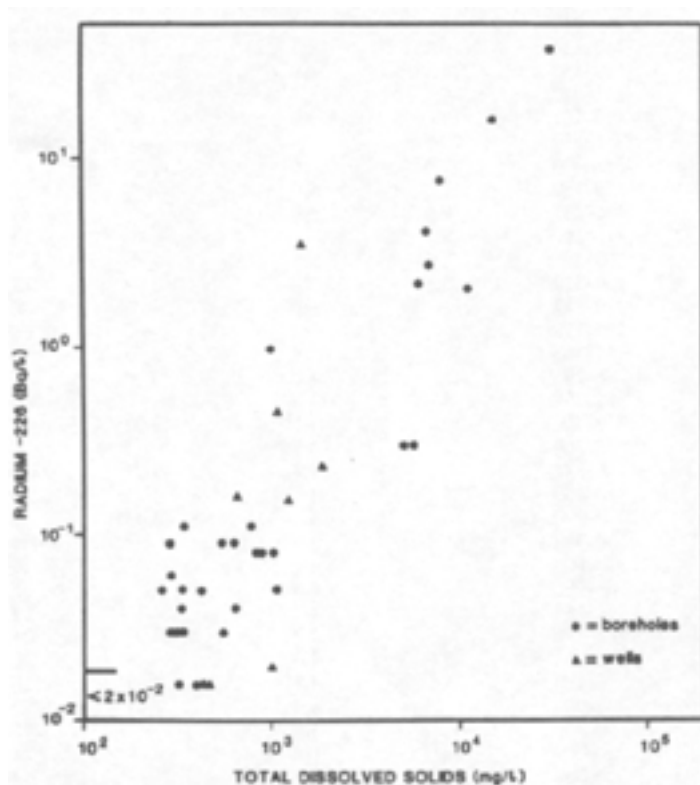


Figure F4-1. Variation of Ra with TDS for URL area groundwaters.

had a chance to equilibrate with the rock because the isotopes ^{238}U , ^{234}U and ^{226}Ra are in the same decay series. This is not usually seen however, because of the different geochemical properties of the two elements, U and Ra, and due to the fact that they are separated in the decay series by a long-lived relatively insoluble isotope of Th, ^{230}Th .

F4.2 Inflow to the URL

Groundwaters discharging from fractures intersecting the URL (Figure F4-2) contained little U ($\sim 10 \mu\text{g/L}$) for the first six years following excavation. Concentrations then began to rise and attained over $100 \mu\text{g/L}$ and have remained high ever since. A larger scale filter was installed underground to remove the U so that the inflowing groundwaters could be discharged to the surface and thus meet Provincial requirements. The cause of the increase in U in these inflows was believed to be due to exhaustion of the reducing capacity of minerals in the flow path over the ~ 6 years that flow was occurring. This phenomenon is shown schematically in Figure F4-3 and is proposed to proceed as follows:

1. Prior to excavation of the URL, oxidising and organic-rich infiltration at the surface flows down through fractures in the bedrock dissolving rock minerals and liberating bound U which is transported in solution as a carbonate anion complex (see section).
2. At about 100–200 m depth, oxygen and most of the dissolved C is consumed and the groundwater becomes reducing and precipitates U on fracture minerals forming a redox front. The zone of precipitation (Figure F4-3a) slowly moves to greater depth as weathering proceeds.
3. Upon excavation of the URL (Figure F4-3b), this process is accelerated and the water table is rapidly depressed around the shaft due to drainage into the URL.
4. The redox front begins to move downwards also, but at a slower pace because reduced minerals (Fe (II) and S (II) mainly) buffer the front migration, moving only when the minerals are fully oxidised.
5. Hence, there is a delay in breakthrough of U in the inflow waters (~ 6 years, in the case of the URL).

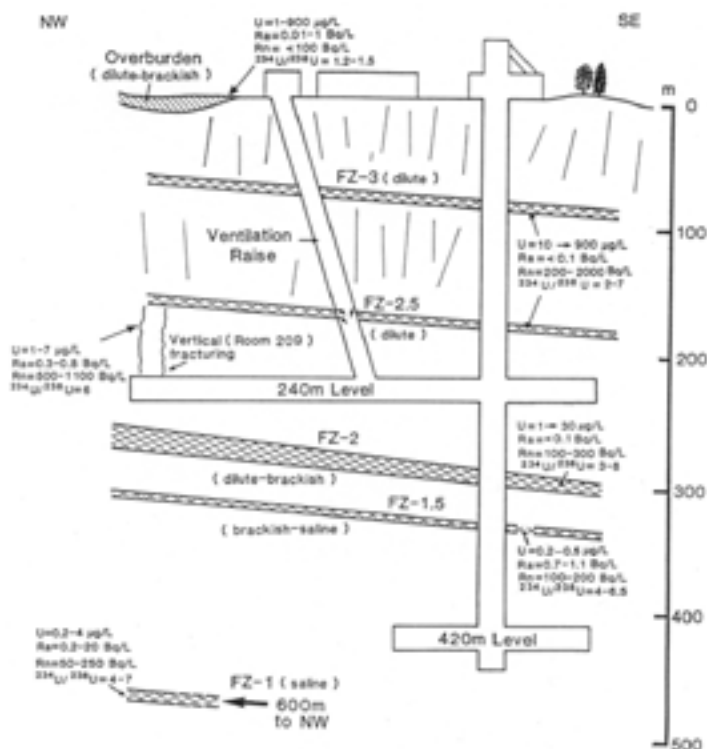


Figure F4-2. Schematic section through the URL showing concentrations of radioelements in the various groundwater types.

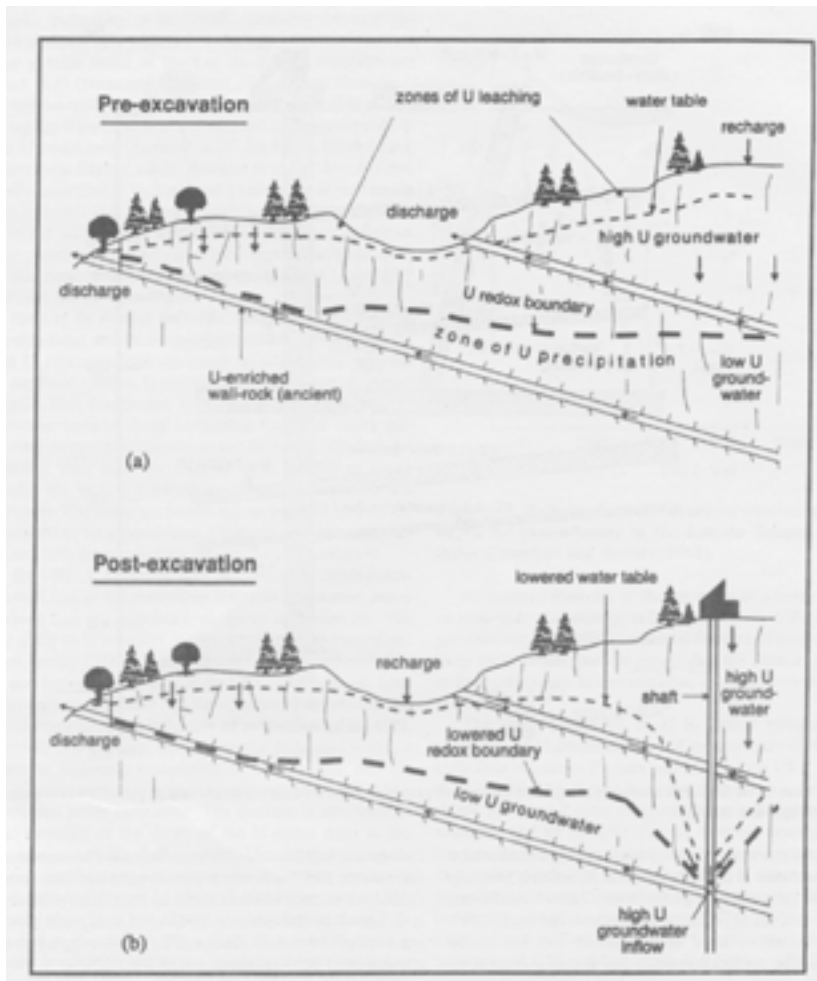


Figure F4-3. Schematic diagram showing a) natural (pre-excitation) and b) post-excitation distribution of U and redox conditions.

Although excavations have not yet begun at Forsmark, it is possible that a similar redox boundary may exist there, at ~ 500 m. The elevated U concentrations have been caused by the introduction of oxidising waters during drilling which have mobilised U existing in U-rich coatings on fracture walls.

F4.3 Redox effects on U mobility in TT13

To test the mechanism proposed in section F4.2 above, a tracer test was designed in two parts: 1) oxygenated, HCO_3 -rich groundwater with its natural U content removed (by filter) was injected into a permeable fracture zone (FZ2) and, to induce flow, water was withdrawn at the same rate from an adjacent borehole (horizontal path distance was ~ 17 m); and 2) the same test as above was performed but without prior removal of U. This test, known as Tracer Test 13 (TT13) was performed over a 3-week period in April 1994. It included several other tracer tests including injection of iodide and colloids, and measurement of variations in $^{234}\text{U}/^{238}\text{U}$ activity ratio and microorganism content. A full report has been published by /Gascoyne et al. 1996/.

The configuration for the injection and withdrawal system for TT13 is shown in Figure F4-4 and the results of the test are given in Figure F4-5. Breakthrough of injected water began 5 hours after injection began and, in sequence, Eh, dissolved O_2 and U (above background) showed breakthrough at 6.5, 7 to 10.5 and 14 hours, respectively, at the withdrawal well. Uranium content peaked after about 150 hours and levelled out at ~ 60 $\mu\text{g}/\text{L}$ for the remainder of this part of the test.

In the second part of TT13, the same water was used but without filtration of its $\sim 80 \mu\text{g/L}$ U content and this resulted in a rapid rise to $120 \mu\text{g/L}$ indicating simple addition, without sorption, of U sources. Loss of the $20 \mu\text{g/L}$ of U is probably due to dispersion or diversion of injected water from the flow path to other parts of FZ2, as shown by conservative tracer testing.

These results indicate the ease of removal of U from minerals in FZ2 under oxidising conditions and support the hypothesis proposed in section F4.2 to account for the observation of U enrichment in natural groundwater inflows to the URL.

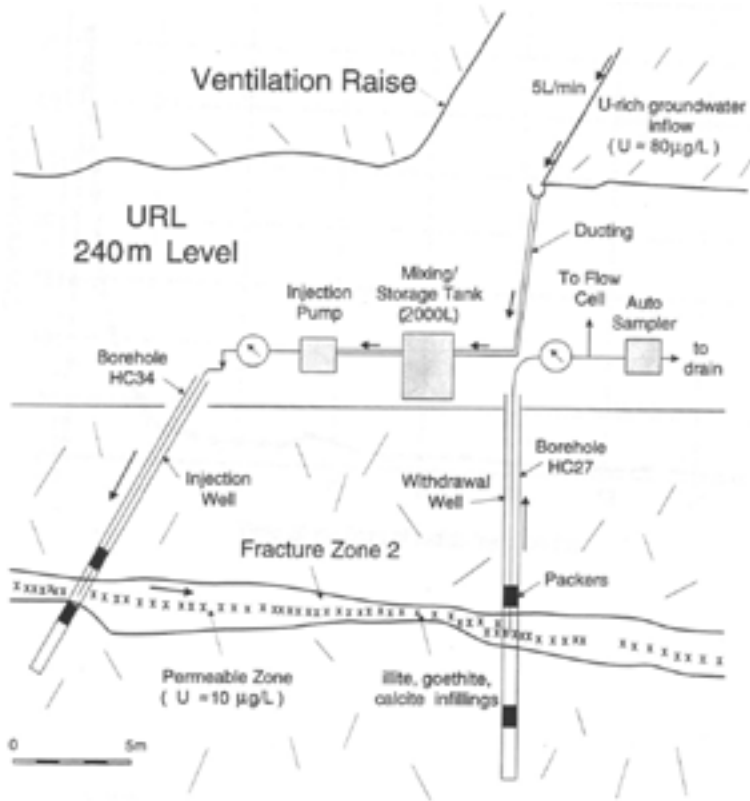


Figure F4-4. Section showing the setup for the tracer test TT13.

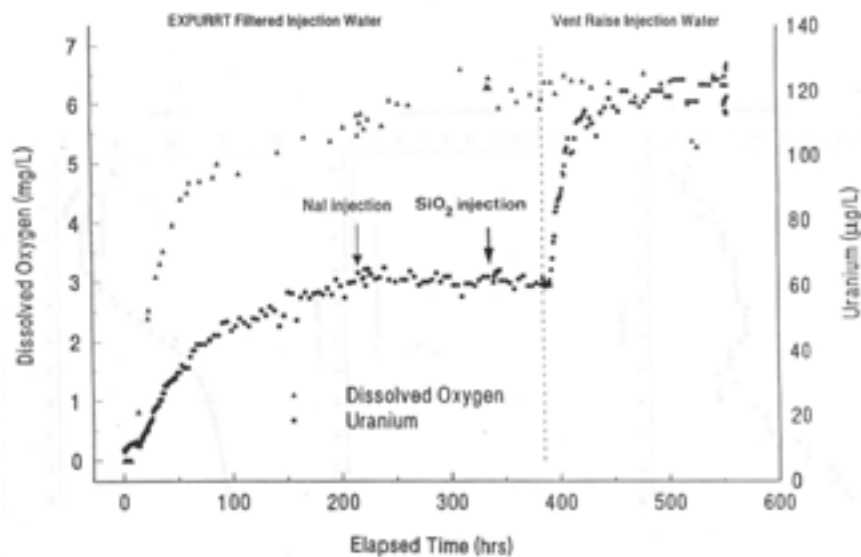


Figure F4-5. Diagram showing the change in dissolved oxygen and U concentrations during tracer test TT13.

F5 Summary and Conclusions

High U concentrations have been found in brackish groundwaters from intermediate depth (~ 400–600 m) in some boreholes in the Forsmark area, eastern Sweden. The concentrations (up to 122 µg/L) exceed maximum drinking water standards set by both Sweden and the World Health Organisation. Weak correlations of U with HCO₃, SO₄ and Eh have been observed but a more convincing relationship with the fraction of drill water still in the borehole zone is clearer. Unlike many other studies, there appears to be no characteristic relationship between U content and ²³⁴U/²³⁸U activity ratio.

In contrast to U, however, Ra is clearly related to groundwater salinity and attains concentrations of 23 Bq/L, well above the drinking water maximum of 0.5 Bq/L. Most of the high Ra concentrations, however, occur in brackish groundwater (salinity ~ 5–10 g/L), and is unlikely to be consumed.

Results from a previous leaching test in Canada's Underground Research Laboratory showed that U can be readily mobilised from wall-rock in granitic fracture zones at intermediate depths by introduction of O₂. A similar process is believed to be occurring at Forsmark due to the introduction of drill water. It might be expected, therefore, that groundwaters elsewhere in the Forsmark area (and at Laxemar/Simpevarp) might show the same characteristics but this does not appear to be the case. It is possible that U may be enriched in these areas of Forsmark, due to early hydrothermal or alteration activity on the major fault line that goes through the area but the presence of induced ground currents from the nearby HVDC transmission station may be an additional; (and, largely, unique) cause of U mobilisation.

It is important that the distribution and concentration range of U is well known for the Forsmark area, as this may be considered when siting a high-level waste repository. As found at the URL in Canada, U is likely to be mobilised by drilling, pumping and excavation activities and this characteristic may require on-site treatment or design changes to meet environmental standards and to conform to requirements of the safety case for a repository.

Appendix F1

Summary of Forsmark hydrogeochemical data showing U and Ra concentrations.

Borehole	Date	(m) Depth	(mg/l) Na	(mg/l) K	(mg/l) Ca	(mg/l) Mg	(mg/l) HCO3	(mg/l) Cl	(mg/l) SO4	(pH unit) pH	(mV) Eh	(mg/l) DOC	(%) BALANCE	(ug/l) U	(mBq/kg) U238	(mBq/kg) U234	U234/U238	(Bq/l) RA226	(Bq/l) RN222
HFM02	2005/11/09 07:35:00	43.00	339.0	14.00	68.0	20.9	407.00	396.0	83.70	7.82		9.8	1.46	11.20				0.27	12.50
HFM04	2005/11/07 13:30:00	62.00	153.0	6.04	31.0	7.6	390.00	56.3	44.80	7.71		8.3	0.36	3.18				0.18	120.00
HFM13	2005/11/09 10:25:00	166.00	1,710.0	25.20	1,180.0	198.0	124.00	5,020.0	476.00	7.34		2.2	-1.05	16.20				1.34	381.00
HFM15	2005/11/09 10:25:00	90.00	358.0	9.37	97.2	15.2	471.00	406.0	104.00	7.44		13.0	1.18	18.10				0.30	52.40
HFM19	2005/11/09 15:37:00	175.00	2,050.0	57.20	960.0	259.0	129.00	5,330.0	565.00	7.21		35.7	-1.45	5.03				1.06	31.30
KFM01A	2003/01/17 15:30:00	115.44	1,740.0	25.60	874.0	142.0	61.50	4,562.8	315.65	7.47	-195.000	1.5	-1.76	1.51				1.80	180.70
KFM01A	2003/02/27 12:00:00	180.35	2,000.0	29.20	934.0	204.0	99.50	5,329.5	546.97	7.60	-188.000	2.3	-3.73	14.90				1.30	290.80
KFM01A	2005/11/09 11:15:00	119.50	1,430.0	20.70	658.0	95.3	136.00	3,480.0	223.00	7.71		34.0	-0.80	3.78				6.12	146.00
KFM02A	2003/06/13 09:00:00	512.54	2,040.0	34.20	934.0	226.0	126.00	5,410.0	498.00	7.18	-143.000	2.1	-2.99	88.60				3.10	563.10
KFM02A	2003/06/13 09:00:00	512.54	2,060.0	33.30	921.0	231.0	124.00	5,410.0	512.00	7.10			-2.77	65.10				3.50	1,202.00
KFM02A	2003/11/07 09:00:00	116.50	366.0	9.74	139.0	31.0	354.00	642.0	89.60	7.52		11.0	-0.31	5.40				0.30	167.50
KFM02A	2004/02/05 09:30:00	423.50	1,820.0	21.40	1,140.0	198.0	93.40	5,380.0	434.00	7.37		-1.0	-2.81	13.90				2.20	363.30
KFM02A	2005/11/07 14:07:00	425.50	1,930.0	26.30	1,240.0	201.0	96.50	5,440.0	435.00	7.36		1.2	-0.11	25.90				4.10	400.00
KFM02A	2005/11/07 14:35:00	503.00	2,160.0	36.40	890.0	244.0	126.00	5,540.0	507.00	7.19		1.5	-2.65	122.00				3.50	1,350.00
KFM03A	2003/09/16 08:35:00	388.50	2,110.0	47.60	925.0	223.0	101.00	5,450.0	495.00	7.30		1.3	-2.29	3.49				1.20	138.50
KFM03A	2003/10/17 08:47:00	450.50	2,070.0	26.80	985.0	202.0	91.80	5,430.0	472.00	7.49		1.2	-2.31	2.21				1.40	168.70

Borehole	Date	(m) Depth	(mg/l) Na	(mg/l) K	(mg/l) Ca	(mg/l) Mg	(mg/l) HCO3	(mg/l) Cl	(mg/l) SO4	(pH unit) pH	(mV) Eh	(mg/l) DOC	(%) BALANCE	(ug/l) U	(mBq/kg) U238	(mBq/kg) U234	U234/U238	(Bq/l) RA226	(Bq/l) RN222
KFM03A	2004/02/04 13:30:00	642.56	1,660.0	14.30	1,440.0	52.7	22.00	5,430.0	197.00	7.55	-196.000	1.6	-2.84	46.10				13.50	1,572.00
KFM03A	2004/02/26 09:00:00	943.06	1,890.0	10.40	3,100.0	17.6	9.90	8,560.0	73.90	7.78	-245.000	1.5	-1.00	0.70	2.40	5.88	2.45	7.60	417.80
KFM03A	2004/04/15 10:05:00	452.06	2,180.0	27.50	1,070.0	216.0	93.70	5,330.0	511.00	7.42	-176.000		1.49	40.40	105.00	2.60		0.90	123.00
KFM03A	2005/06/23 13:05:00	642.25	1,820.0	22.10	1,530.0	80.4	31.50	5,570.0	232.00	7.46		1.2	-0.24	46.30	491.00	742.00	1.51	0.32	2,900.00
KFM03A	2005/11/07 10:45:00	642.25	1,850.0	21.60	1,550.0	80.2	33.70	5,640.0	230.00	7.49		1.4	0.11	45.20				23.20	3,529.00
KFM03A	2005/11/07 12:40:00	982.00	2,120.0	12.80	4,110.0	9.6	10.70	10,500.0	47.00	6.27		13.0	0.05	0.28				14.10	13.00
KFM04A	2004/04/20 00:00:00	357.56	1,980.0	13.80	1,540.0	165.0	78.10	5,780.0	590.00	7.27		1.7	0.41	22.60	302.00	822.00	2.72	1.32	110.00
KFM06A	2005/02/15 10:30:00	357.06	1,450.0	13.00	1,300.0	71.2	45.70	4,560.0	151.00	7.33		-1.0	0.58	9.57	116.00	295.00	2.54	3.10	146.00
KFM07A	2005/03/22 09:25:00	924.77	2,850.0	13.70	5,840.0	19.9	6.19	14,800.0	99.30	8.00		-1.0	-0.39	0.18	2.50	9.10	3.64	14.50	138.00
KFM08A	2005/09/13 00:00:00	687.07	1,560.0	10.60	2,090.0	14.1	10.40	6,100.0	91.50	7.79		-1.0	-0.21	6.35				6.80	224.00
KFR01	1987/02/16 00:00:00	53.40	1,500.0	7.10	970.0	160.0	83.00	4,200.0		7.50		1.2		22.00	108.10	4.91		0.21	74.40
KFR01	2000/07/05 12:03:00	53.40	1,400.0	10.10	486.0	115.0	125.00	2,940.0	360.00	7.50		2.0	1.26	79.10	515.00	6.51		1.30	669.00
KFR10	1987/01/07 00:00:00	97.14	1,500.0	16.00	1,100.0	270.0		5,000.0		7.30		1.6		197.30	928.80	4.71		5.97	725.00
KFR10	2000/05/26 12:03:00		1,550.0	16.00	740.0	175.0	134.00	3,970.0	409.00	7.40			-1.92	206.00	957.00	4.65		3.61	671.00
KFR7A	1987/03/10 00:00:00	61.35	1,800.0	15.00	970.0	250.0	110.00	5,000.0		7.30		3.0		104.40	433.20	4.15		0.26	713.00
KFR7A	2000/05/10 12:03:00	61.35	1,780.0	14.70	852.0	227.0	115.00	4,460.0	386.00	7.60		1.3	1.18	89.20	395.00	4.43		1.02	646.00
SFM0001	2002/09/20 10:30:00	4.45	321.0	18.90	91.7	40.6	476.00	392.4	159.79	7.30			0.40	6.09				0.10	28.00
SFM0001	2003/06/05 07:41:00	4.45	255.0	15.10	80.5	32.0	422.00	259.4	126.07	7.47			2.89					0.50	25.80
SFM0001	2003/10/28 08:30:00	4.45	408.0	23.70	98.0	51.9	582.00	509.0	216.00	7.24			-1.19	5.02				0.50	33.00

Borehole	Date	(m) Depth	(mg/l) Na	(mg/l) K	(mg/l) Ca	(mg/l) Mg	(mg/l) HCO3	(mg/l) Cl	(mg/l) SO4	(pH unit) pH	(mV) Eh	(mg/l) DOC	(%) BALANCE	(ug/l) U	(mBq/kg) U238	(mBq/kg) U234	U234/U238	(Bq/l) RA226	(Bq/l) RN222
SFM0001	2004/10/12 11:00:00	4.45	380.0	22.20	91.1	46.8	550.00	473.0	219.00	7.30			-2.42	4.39	63.00	81.00	1.29	0.10	24.40
SFM0002	2002/09/20 14:15:00	4.71	43.1	5.40	129.0	9.5	390.00	113.1	18.00	7.20			-3.97	4.59				0.50	47.00
SFM0002	2003/06/04 19:30:00	4.71	21.8	4.09	108.0	8.0	341.00	40.6	18.10	7.36			-0.64					0.80	58.70
SFM0002	2003/10/28 08:30:00	4.71	36.9	5.23	129.0	9.2	342.00	99.8	29.90	7.05			-0.30	4.47				0.60	78.30
SFM0002	2004/10/12 09:20:00	4.71	21.7	4.79	115.0	7.8	346.00	51.4	22.50	7.08			-0.66	5.27	72.00	85.00	1.18	0.20	25.00
SFM0003	2002/09/20 12:40:00	9.98	33.5	13.70	97.3	27.0	454.00	17.9	75.30	7.40		12.0	-2.78	0.55				-0.10	26.00
SFM0003	2003/06/04 15:45:00	9.98	27.6	13.40	92.4	26.8	429.00	8.8	49.25	7.52			0.01					-0.10	16.00
SFM0003	2003/10/28 08:30:00	9.98	25.2	13.50	94.5	27.3	425.00	12.9	57.90	7.30			-0.31	0.48				-0.10	21.50
SFM0003	2004/10/12 07:35:00	9.98	24.3	13.70	93.3	26.4	418.00	11.3	56.20	7.28			-0.14	0.42	5.70	7.40	1.30	0.10	9.80
SFM0005	2003/06/03 11:42:00	2.71	8.3	1.87	104.0	4.8	319.00	8.9	16.76	7.19			1.30					0.10	74.90
SFM0006	2003/06/03 10:45:00	3.71	29.6	24.60	170.0	14.1	435.00	68.1	105.63	7.69			0.32					-0.10	7.70
SFM0008	2003/06/02 18:44:00	5.64	9.2	7.05	140.0	17.6	441.00	18.3	74.91	7.20			-1.08					0.10	20.10
SFM0008	2003/10/29 10:00:00	5.64	63.6	7.50	186.0	18.2	356.00	198.0	73.80	6.99			2.90	12.10				0.30	40.40
SFM0008	2004/10/15 10:11:00	5.64	39.4	5.92	138.0	12.2	385.00	113.0	51.90	7.06			-3.51	9.59	118.00	137.00	1.16	0.10	29.70
SFM0009	2003/10/29 10:00:00	2.50	7.2	3.15	117.0	7.8	327.00	4.2	68.00	7.11			0.12	7.65				0.70	46.20
SFM0009	2004/10/13 14:10:00	2.50	6.4	2.67	103.0	6.5	320.00	8.4	29.00	7.07			-0.75	7.69	112.00	126.00	1.13	0.10	33.70
SFM0012	2003/06/04 22:00:00	5.85	1,160.0	34.00	287.0	92.8	344.00	2,239.9	202.70	7.23			-0.09					0.50	64.60
SFM0015	2003/06/04 12:20:00	6.84	320.0	28.40	34.5	60.8	709.00	332.7	1.00	7.50			0.65					0.60	74.70
SFM0027	2003/10/30 08:30:00	7.50	140.0	8.15	36.2	12.2	402.00	62.3	47.50	7.64			-1.21	1.58				0.20	177.30

Borehole	Date	(m) Depth	(mg/l) Na	(mg/l) K	(mg/l) Ca	(mg/l) Mg	(mg/l) HCO3	(mg/l) Cl	(mg/l) SO4	(pH unit) pH	(mV) Eh	(mg/l) DOC	(%) BALANCE	(ug/l) U	(mBq/kg) U238	(mBq/kg) U234	U234/U238	(Bq/l) RA226	(Bq/l) RN222
SFM0027	2004/10/18 11:25:00	7.50	128.0	8.20	42.4	13.5	416.00	65.4	49.90	7.65			-3.40	0.73	12.00	26.00	2.17	0.20	148.60
SFM0029	2003/10/28 08:30:00	7.50	33.4	5.42	121.0	12.9	403.00	42.5	55.30	7.09			-1.34	3.37				0.20	14.60
SFM0029	2004/10/13 16:04:00	7.50	28.3	5.29	127.0	12.9	430.00	35.7	57.70	7.05			-2.11	6.65	75.00	90.00	1.20	0.10	9.60
SFM0031	2003/10/30 08:30:00	4.00	18.6	10.50	150.0	17.6	457.00	7.4	115.00	6.98			-0.73	7.95				0.50	28.50
SFM0031	2004/10/14 12:45:00	4.00	23.7	10.60	130.0	20.2	421.00	8.4	118.00	7.35			-0.83	8.68	103.00	132.00	1.28	0.10	148.60
SFM0032	2003/10/30 08:30:00	3.50	48.1	6.13	98.9	9.1	364.00	32.5	43.80	7.03			0.64	7.91				0.30	48.40
SFM0032	2004/10/14 10:50:00	3.50	32.0	5.80	101.0	8.8	350.00	32.0	36.70	7.05			0.00	4.13	60.00	82.00	1.37	0.10	18.60
SFM0037	2003/10/31 07:15:00	2.50	89.9	9.08	102.0	23.9	451.00	68.3	122.00	7.02			-3.24					0.20	29.30
SFM0037	2004/10/14 16:41:00	2.50	111.0	12.10	119.0	32.0	539.00	95.2	141.00	6.98			-1.85	9.25	123.00	138.00	1.12	-0.10	32.60
SFM0049	2004/10/12 14:45:00	4.50	12.1	1.83	63.4	4.4	198.00	17.6	5.39	6.71			3.09	0.17	2.40	2.80	1.17	0.30	18.70
SFM0057	2003/11/04 09:45:00	3.95	70.8	4.61	116.0	7.4	226.00	187.0	17.10	7.11			1.02	2.75				0.90	35.40
SFM0057	2004/10/13 08:30:00	3.95	92.0	5.92	182.0	11.4	335.00	311.0	25.70	6.85			-2.15	7.22	88.00	94.00	1.07	0.20	22.70
SFM0060	2004/10/14 17:17:00	7.10	26.3	6.13	124.0	9.1	319.00	71.3	70.10	7.10			-2.52	33.70	418.00	445.00	1.06	-0.10	36.30

**Time dependent perturbations in Forsmark KFM
groundwater sampling: Possible implications for
pristine U content**

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G Abstract

Data of Forsmark KFM groundwater samples are analyzed. Numerous of these groundwater samples show uranium concentrations that are higher than were originally expected from thermodynamic calculations. The data analysis is made especially with the objective of identifying the reason for these unexpected uranium concentrations. As other studies proceeded, it was shown that the U concentrations found at the Forsmark site are similar to those found at other comparable sites. The present study, nevertheless, shows that the U concentrations are associated with sampling perturbations and thus may benefit from being discussed in some detail. There are eight KFM boreholes with sampling at different depths. In some cases sampling campaigns consist of pumping for several days, weeks or even several months. During such campaigns, several samples are collected. A key problem is the presence of high drill water contents, originating from bringing down the drill holes. Even extended pumping or waiting for several years, the drill water is not removed quantitatively. Somewhat higher uranium concentrations are found especially at intermediated depths. They are associated with the presence of drill water and show a correlation with the iron content. It is thus suggested that the uranium is associated with iron bearing minerals in the accessible pore space. It is furthermore suggested, that at low depths these have not been deposited in the available pore space or have been washed out by relatively oxidizing water. At depths below approximately 700 m, it is suggested that the uranium minerals are stable in the presence of drill water, and probably have not been deposited in the accessible pore space. In summary, in many cases, high uranium concentrations appear to be drilling and sampling artifacts.

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G1 Introduction

Sampling of groundwater in a series of Forsmark groundwater (KFM) show U concentrations that are higher than expected from original thermodynamic considerations. In this paper, Forsmark groundwater samples are analyzed with respect to the possible explanation for these U concentrations. Data originate from the SIDADA database, version 06_063. The samples are from the drill holes KFM 01A to 08A. The individual samples originate from different depths in these drill holes and are taken in different sampling campaigns. In some cases singular samples are taken for a specific bore hole and depth. In other cases, a sequence of samples is taking along with pumping for a specific bore hole and depth. Finally, some sample points are revisited after considerable time, up to more than 3.5 years after the first sampling campaign. The origin and analytical results of individual samples is shown in Table 1.

The different sampling campaigns are analyzed. Where this is the case, revisiting the horizons in a specific bore hole after considerable time is included in the analysis. Emphasis is on the development of different indicators with pumping and the drill water content. The different indicators include physico-chemical conditions, and concentrations of chemical components and isotopes. Thereafter an overall analysis is made with respect to the U concentrations, especially in view of sampling depth and drill water content. Finally the relation between the U and Fe concentrations is discussed. In addition, the possible relation between Fe and Mn is briefly discussed.

G2 Objective

The objective is to identify the reasons and processes responsible for U concentrations found in numerous of the KFM groundwater samples, where, based on thermodynamic calculations under specific assumptions, these U concentrations were originally considered surprisingly high.

G3 Individual sampling campaigns

The individual sampling campaigns are discussed for different depths in the different KFM bore holes. The positions of the upper and lower packers are not given, but only the mean depth between the packers (Secmid).

KFM01A (115 and 120 m)

There are two different sampling campaigns at:

- 115 m, starting 2003.01.17, with sampling after 24, 31 and 38 days, and
- 120 m, starting and taking place almost 34 months afterwards.

The two campaigns sample water that is similar with respect to, for example pH, ^{18}O and D.

There are, however, grave differences in basically all other indicators. The sampling in 2005 (34 months later) contains more freshwater, as seen by the appearance of tritium, lower Na and Cl concentrations and a much lower value for ^{34}S . Simultaneously, the uranium, iron and carbonate concentrations are higher by a factor between 2.2 and 2.5 at this later sampling. Even more dramatic is the increase in DOC from around 2 to 34 mgC/L. This shows that the groundwater sampled in the 2003 campaign is a very different one than that sampled late 2005, although the groundwaters originate from similar depth.

Within the first sampling campaign, there is no systematic decrease in the drill water content. The values for Na, Fe(tot), DOC, ^{34}S and possibly pH seem to change systematically with increasing pumping (Figure G3-1a). There is only one value for the U concentration, and thus a trend with pumping of drill water content cannot be identified.

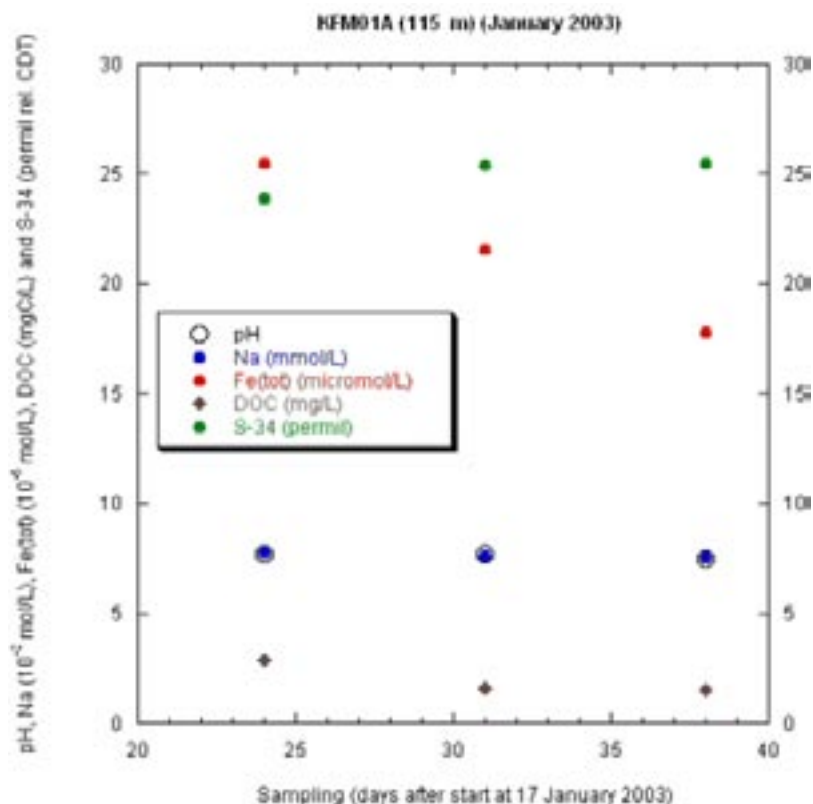


Figure G3-1a. Values for pH, ^{34}S and concentrations of Na, Fe(tot) and DOC at different pumping/sampling times for campaign starting 17 January 2003 in KFM01A at 115 m depth.

Table G3-1. Selected SICADA data for KFM groundwaters. Blocks of samples from similar depths in a bore hole are marked by light grey or light blue blocks. The time of sampling in such cases is given as the time at the later sampling campaign and the time since the previous sampling campaign (in months “m.”). Stable isotopes are given as shift in ‰ rel. the respective standards given.

IDCODE	Start date	Secmid (m)	Time of sampling (days)	Drill water pH content (%)	Drill water pH	El. Cond (mS/m)	U (nmol/L)	Na (mmol/L)	Cl (mmol/L)	Cl/Na	HCO3 (mmol/L)	Fe (tot) (µmol/L)	DOC (mg/L)	O-18 (SMOW)	D (SMOW)	T (TU)	C-13 (PDB)	C-14 (pmc)	S-34 (CDT)
KFM01A	2003.01.17	115	24	0.9	7.7			77.4	127.9	1.7	1.03	25.5	2.9	-11.5	-87.3	-0.8			23.9
	“	“	31	0.7	7.7			76.5	114.9	1.5	1.02	21.6	1.6	-11.5	-89.2	-0.8			25.4
	“	“	38	0.8	7.5		6.3	75.7	128.5	1.7	1.01	17.8	1.5	-11.6	-88.2	-0.8	-9.0	13.4	25.5
	2005.11.09	120	0/33.7 m.		7.7	1,050	15.9	62.2	98.0	1.6	2.23	43.9	34.0	-11.6	-87.4	1.3			15.6
	2003.02.27	180	8	6.5	7.7	1,534	85.3	86.5	146.1	1.7	1.72	33.6	3.3	-8.8	-70.2	-0.8	-7.7	18.5	25.0
	“	“	15	5.6	7.7	1,487	71.4	87.0	147.1	1.7	1.66	20.3	1.1	-8.8	-69.6	-0.8	-7.5	18.0	25.1
	“	“	21	5.2	7.5	1,493	74.4	86.1	143.4	1.7	1.64	14.1	4.1	-8.8	-73.0	-0.8	-7.5	17.9	25.4
	“	“	29	5.0	7.6	1,564	63.0	86.5	148.1	1.7	1.62	9.4	3.2	-8.8	-69.1	1.3			
	“	“	32	4.8	7.6	1,481	62.6	87.0	150.1	1.7	1.63	9.6	2.3	-8.8	-69.3	-0.8	-6.5	16.7	25.6
KFM02A	2003.06.13	513	87	6.1	7.1	1,590	273.5	89.6	152.4	1.7	2.03	22.3							
	“	“	94	6.3	7.3	1,610	307.6	91.3	153.8	1.7	2.02	21.1	2.0						
	“	“	101	6.0	7.2	1,600	321.0	91.7	153.5	1.7	2.05	21.6	2.4						
	“	“	108	6.0	7.2	1,600	354.2	89.6	153.2	1.7	2.03	24.3							
	“	“	129	6.8	7.2	1,600	372.3	88.7	152.4	1.7	2.07	33.0	2.1	-8.8	-67.0	2.4	-7.0	16.9	24.9
	2005.11.07	503	0/29 m.	3.8	7.2	1,610	512.6	93.9	156.1	1.7	2.07	40.4	1.5	-8.7	-66.2	0.9			21.9
	2003.11.07	117	11	0.4	7.5	274	22.7	15.9	18.1	1.1	5.80	24.1	11.0	-11.2	-80.9	-0.8	-12.4	65.1	20.8
	2004.02.05	424	18	2.2	7.4	1,640	58.4	79.1	151.5	1.9	1.53	13.3	-1.0	-10.2	-75.6	-0.8	-5.9	7.7	26.0
	2005.11.07	426	? /23 m.	2.9	7.4	1,570	108.8	83.9	153.2	1.8	1.58	24.8	1.2	-10.0	-76.4	0.9			22.5
KFM03A	2003.09.16	389	20	0.6	7.3	1,670	14.7	91.7	153.5	1.7	1.66	14.0	1.3	-9.1	-69.4	2.0	-5.9	20.2	25.0
	2003.10.17	451	7	0.3	7.5	1,600	9.3	90.0	153.0	1.7	1.50	16.4	1.2	-9.4	-70.8	-0.8	-5.3	19.2	25.4
	2004.04.15	452	0 /6 m.	0.4	7.4	1,580		94.8	150.1	1.6	1.54	19.6		-9.7	-72.4	-0.8	-4.4		25.7
	2003.11.06	991	18	2.1	8.2	2,630	1.1	87.8	278.6	3.2	0.15	0.4	1.2	-13.6	-99.9	-0.8			28.9
	“	“	20	2.4	8.3	2,670		86.1	278.6	3.2	0.12	0.5	1.1	-13.6	-99.1	-0.8			
	“	“	25	3.1	8.3	2,650	0.8	86.5	274.4	3.2	0.11	0.5	1.3	-13.5	-98.6	-0.8			28.9
	“	“	32	3.9	8.3	2,560	0.9	86.1	273.0	3.2	0.11	0.6	1.4	-13.6	-98.5	-0.8			29.6
	“	“	32	3.9	8.3	2,560	1.9	86.1	273.0	3.2	0.11	0.6	1.4	-13.6	-98.5	-0.8			29.6
	2005.11.07	982	0 /24 m.	2.8	6.3	2,760	1.2	92.2	295.8	3.2	0.18	24.6	13.0	-13.8	-97.8	-0.8			29.1

IDCODE	Start date	Secmid (m)	Time of sampling (days)	Drill water pH content (%)		El. Cond (mS/m)	U (nmol/L)	Na (mmol/L)	Cl (mmol/L)	Cl/Na	HCO3 (mmol/L)	Fe (tot) (µmol/L)	DOC (mg/L)	O-18 (SMOW)	D (SMOW)	T (TU)	C-13 (PDB)	C-14 (pmc)	S-34 (CDT)
	2004.02.04	643	6	4.8	7.4	1,530	245.8	73.5	151.5	2.1	0.41	8.2	2.3	-11.6	-84.4	-0.8			26.4
	"	643	16	4.4	7.5	1,690	205.9	72.2	153.2	2.1	0.37	4.9	1.3	-11.7	-85.5	-0.8			27.6
	"	643	19	4.4	7.6	1,620	193.7	72.2	153.0	2.1	0.36	4.2	1.6	-11.6	-84.3	-0.8			27.8
	2005.06.23	642	0 /16.5 m.	4.5	7.5	1,590	194.5	79.1	156.9	2.0	0.52	10.9	1.2	-11.4	-80.7	1.5			23.6
	2005.11.07	642	0 /21 m.	5.7	7.5	1,580	189.9	80.4	158.9	2.0	0.55	19.1	1.4	-11.4	-83.5	0.8			25.1
	2004.02.26	943	5	13.3	7.3	2,110	6.1	79.6	220.6	2.8	0.26	7.7	2.6	-12.4	-88.6	1.1			25.4
	"	943	13	11.2	7.4	2,040	4.2	80.4	229.6	2.9	0.20	5.2	2.5	-13.0	-90.8	1.3			25.8
	"	943	31	8.8	7.8	1,990	2.9	82.2	241.1	2.9	0.16	3.9	1.5	-12.6	-92.8	0.8			27.3
KFM04A	2004.01.16	234	6	10.7	7.3	1,610	145.8	78.3	155.2	2.0	1.67	61.8	1.9	-9.0	-70.7	-0.8			23.1
	"	"	25	7.5	7.2	1,620	260.5	79.1	157.2	2.0	1.82	38.0	1.5	-9.0	-84.4	-0.8			24.5
	2004.04.20	358	29	6.5	7.3	1,660	95.0	86.1	162.8	1.9	1.28	37.5	1.7	-9.5	-69.9	-0.8	-6.6	19.9	25.5
KFM05A	2004.09.24	717	11	2.3	7.4	1,330	27.6	77.8	128.2	1.6	2.16	67.9							
	"	"	17	2.1	7.3	1,380	25.8	77.0	129.6	1.7	2.13	66.8	4.5						
	"	"	24	2.1	7.2	1,390	28.8	78.3	129.3	1.7	2.13		5.2						
KFM06A	2004.12.14	772	48	1.6	8.3	1,990		73.5	199.4	2.7	0.09	1.4	1.6	-11.5	-81.7	-0.8	-20.4	36.9	38.4
	2005.02.15	357	2	7.5	7.3	1,370	46.2	66.5	130.1	2.0	0.95	28.4	1.3	-11.3	-86.3	-0.8			27.6
	"	"	9	7.8	7.4	1,360	38.4	62.6	129.6	2.1	0.78	21.3	1.1	-11.8	-89.1				27.3
	"	"	16	8.0	7.4	1,360	38.7	63.0	128.7	2.0	0.77	20.5	1.1	-11.6	-85.6	-0.8			27.0
	"	"	20	7.7	7.3	1,350	40.2	63.0	128.5	2.0	0.75	20.0	-1.0	-11.9	-86.0	-0.8	-8.0	29.2	27.5
KFM07A	2005.03.22	925	2	0.6	7.6	3,640	1.4	120.9	405.6	3.4	0.12	5.1	2.0	-12.9	-87.1	-0.8			22.8
	"	"	16	0.4	8.0	3,650	1.4	123.0	414.1	3.4	0.12	4.4	-1.0	-13.0	-87.0	-0.8			24.7
	"	"	23	0.4	8.0	3,680	1.2	123.0	408.5	3.3	0.11	4.1	-1.0	-13.0	-86.6	-0.8			25.0
	"	"	30	0.7	8.0	3,680	1.1	122.2	408.5	3.3	0.11	3.2	-1.0	-13.1	-86.3				25.2
	"	"	34	0.4	8.0	3,670	0.8	123.9	416.9	3.4	0.10	3.4	-1.0	-13.1	-86.7				30.2
KFM08A	2005.09.13	687	7	4.3	7.2	1,710	20.4	65.7	174.1	2.7	0.16	0.4	1.0	-13.3	-95.8	-0.8			30.9
	"	"	13	5.0	7.7	1,700	28.4	65.2	169.3	2.6	0.19	2.3	-1.0	-13.2	-96.2	-0.8			30.8
	"	"	20	5.0	7.8	1,690	31.2	65.2	171.0	2.6	0.18	3.9	-1.0	-13.2	-96.0	0.9			31.2
	"	"	27	5.1	7.8	1,690	35.7	66.1	171.5	2.6	0.20	4.7	-1.0	-13.2	-96.0	-0.8			31.1
	"	"	45	5.4	7.2	1,700	40.6	67.8	173.8	2.6	0.21	9.2	2.6	-13.3	-93.0	-0.8			27.8
	"	"	48	5.1	7.8	1,690	26.7	67.8	171.8	2.5	0.17	12.9	-1.0	-13.2	-92.9	-0.8			29.1
	2005.10.17	"	???	5.2	7.5	1,690	37.4	63.9	169.9	2.7	0.17	9.0	-1.0	-13.2	-93.9	-0.8			31.5

In Figure G3-1b, the relative changes in pH, Na, Fe(tot), DOC and ³⁴S is shown for the sampling campaign starting 17 January 2003. There are significant decreases in Fe(tot) and DOC and an increase in ³⁴S, whereas the possible changes in pH and Na are minor.

In summary, the sampling at 115 and 120 m depth in KFM01A does not have sufficient data to draw firm conclusions about the behavior of uranium. During 38 days of pumping, the groundwater composition shows some changes. The drill water content remains low and stable, and tritium is not found. The ¹⁸O and Deuterium data show comparably strong depletion. Revisiting the same horizon after 34 months (at 120 m Secmid), a different groundwater is found. Now the sample contains tritium, very high organic content and a different sulfur origin. In this context, also the uranium concentration is increased from 6.3 to 15.9 nmol/L. The increase in uranium concentration when tritium containing water is entering could reflect the uranium concentration of such groundwater entering, or oxidation of uranium containing minerals.

The reason for the lack in significant decrease in drill water content with pumping between 24 and 38 days is difficult to understand. It may be related to significant amounts of drill water in the accessible pore space, leading to a slow removal of the drill water. This could also be a first approach to why the uranium possibly released by oxidation from the entering drill water is not effectively removed by pumping. The tritium containing water sample after 34 months may indicate cross-contamination in the borehole. Another possibility could be the sinking of surface near groundwater, possibly as a consequence of excessive groundwater pumping in the intermediate period.

KFM01A (180 m)

There is one sampling campaign at this depth of 180 m, starting 27 February 2003 with sampling at between 8 and 32 days. There are small but systematic trends in drill water content, U, Fe(tot), HCO₃⁻ and DOC concentrations, and in the values for ¹³C, ¹⁴C and ³⁴S contents (Table G3-1 and Figure G3-2a). In Figure G3-2b, the numbers are shown, normalized to the respective number at 8 days pumping, highlighting that the DOC concentrations do not show a clear systematic.

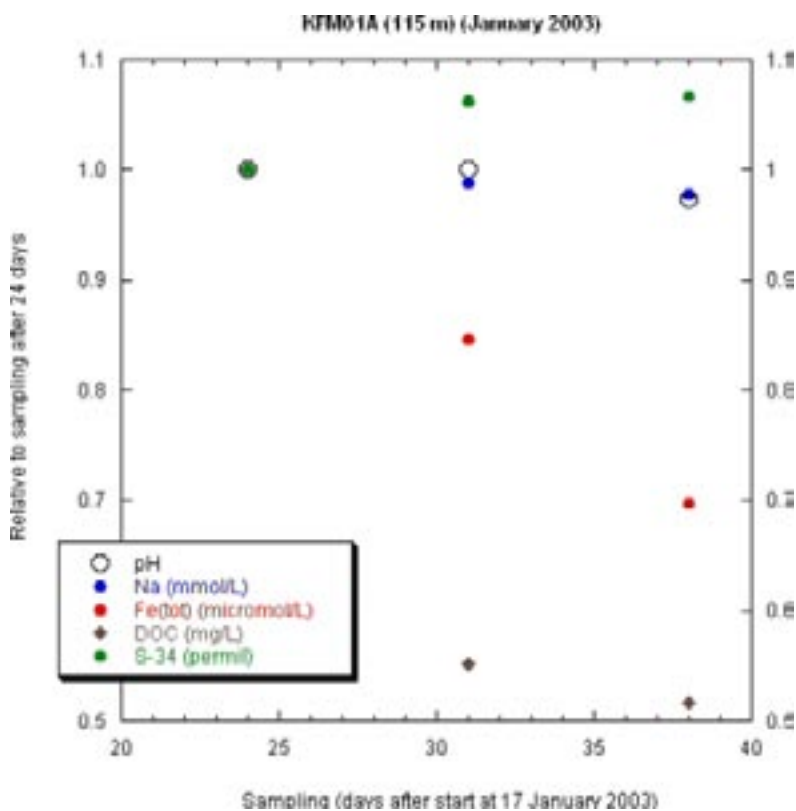


Figure G3-1b. Values for pH, ³⁴S and concentrations of Na, Fe(tot) and DOC at different pumping/sampling times, relative to values after 24 days, at campaign starting 17 January 2003 in KFM01A at 115 m depth.

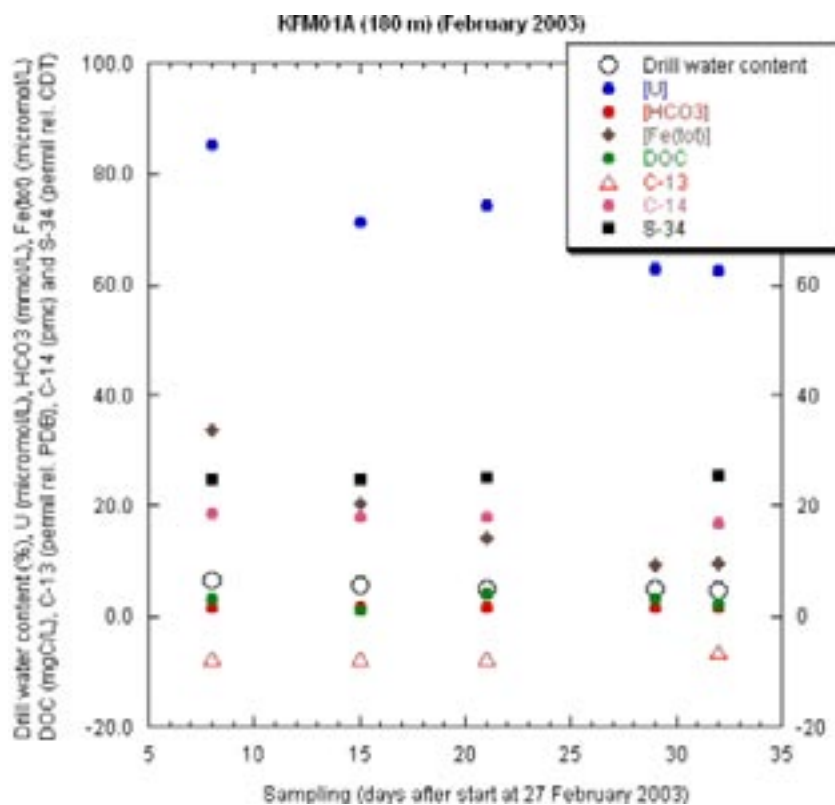


Figure G3-2a. Values for drill water content, U, HCO_3^- , $\text{Fe}(\text{tot})$ and DOC concentrations, and values for ^{13}C , ^{14}C and ^{34}S contents at different pumping/sampling times at campaign starting 27 February 2003 in KFM01A at 180 m depth.

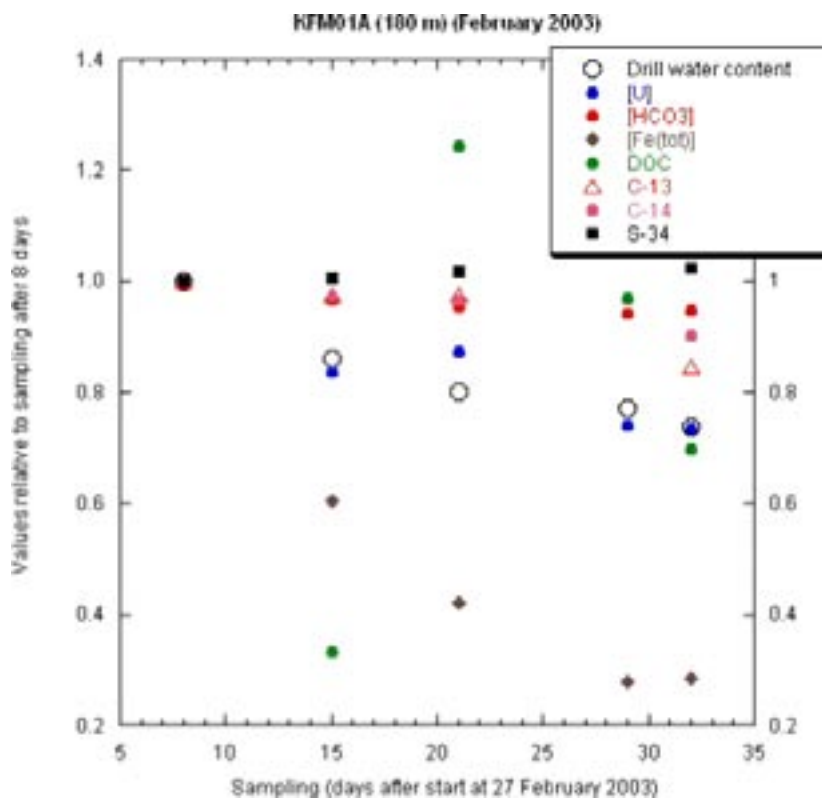


Figure G3-2b. Values for drill water content, U, HCO_3^- , $\text{Fe}(\text{tot})$ and DOC concentrations, and values for ^{13}C , ^{14}C and ^{34}S contents at different pumping/sampling times, relative to values 8 days after start of campaign, at campaign starting 27 February 2003 in KFM01A at 180 m depth.

In the course of pumping, a decrease in drill water content should finally result in the original unperturbed groundwater. As seen in Table G3-1, however, after 32 days of pumping the drill water content is still 4.8%, down from 6.5% after 8 days of pumping. In Figure G3-2c the concentrations and values for different species are shown against the drill water content. The outcome of linear regression with the drill water content is shown in Table G3-2. For extrapolation to zero drill water content, the outcome is that the uranium concentration approaches zero, however with a large uncertainty. Bicarbonate is hardly affected by a dependency with the drill water content with a reasonable extrapolated value of 1.3 mmol/l. DOC shows a large uncertainty in the dependency with drill water content and thus the reasonable extrapolated value of 2.5 mgC/L is not trustworthy. The isotope values also show relatively large uncertainties in the dependency with the drill water content. The extrapolated values, however, are reasonable. Contrary to this, the extrapolated Fe(tot) concentration is highly negative and thus is meaningless. This shows that the iron content cannot be described by a simple mixing between original groundwater and drill water. Contrary to this, the redox sensitive iron appears to be subject to chemical reactions.

Extrapolation of the values to 100% drill water gives mainly meaningless values, simply demonstrating that the uncertainties are too large for extrapolation so far beyond the measured range. The extrapolated values for the U and Fe concentrations are absolutely unrealistic, and the value for ^{13}C can only be expected for highly depleted methane resulting from microbial decomposition of carbon dioxide. Correspondingly, the ^{14}C value has no meaning and is out of range and the ^{34}S value is lower than can be expected for a surface near drill water origin.

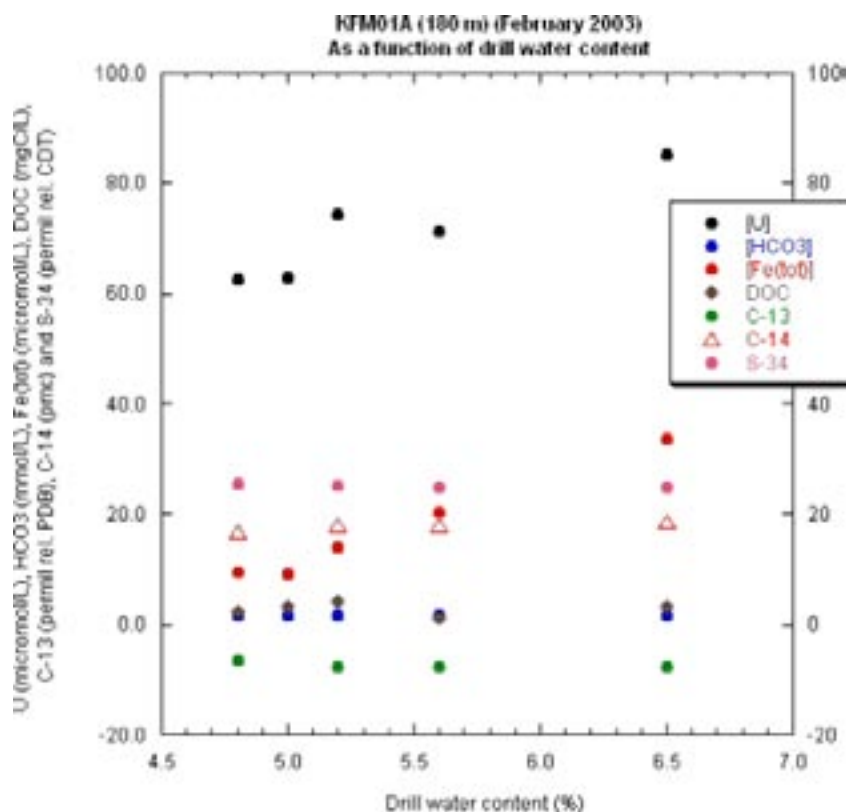


Figure G3-2c. U, HCO_3^- , Fe(tot) and DOC concentrations, and values for ^{13}C , ^{14}C and ^{34}S contents as a function of drill water content at campaign starting 27 February 2003 in KFM01A at 180 m depth.

Table G3-2. Linear regression of different data against drill water content for KFM01A at 180 m depth, the sampling campaign starting 27 February 2003 (cf. Figure G3-2c). Groundwater denotes the extrapolated value for zero drill water content, whereas “Drill water” denotes extrapolation to 100% drill water content.

Linear regression:	“Groundwater”		Slope	±	“Drill water”
	Intercept	±			
pH	8.748	0.384	-0.1124	0.0342	-2.492
El Cond. (S/m)	1.752	0.040	0.0265	0.0036	4.402
Na (10^{-2} mol/L)	8.719	0.1192	-0.0582	0.0106	2.899
Cl (10^{-2} mol/L)	28.106	0.1634	-0.456	0.0145	-17.494
HCO ₃ ⁻ (mmol/L)	-0.0385	0.0384	0.0221	0.0034	2.1715
DOC (mgC/L)	-0.559	1.192	0.2485	0.1059	24.291
O-18 (‰ rel. SMOW)	-13.105	1.461	0.0394	0.1298	-9.165
D (‰ rel. SMOW)	-101.07	0.692	0.931	0.0615	-7.97
T (TU)	0.2895	0.9802	0.070	0.087	7.2895
S-34 (‰ rel. CDT)	30.907	1.403	-0.427	0.1247	-11.793
U (nmol/L)	-3.449	1.172	0.7071	0.1042	67.261
Fe (µmol/L)	-3.694	2.095	0.8373	0.1862	80.036

In summary, the uranium concentration for extrapolation to zero drill water content approaches zero (with a considerable uncertainty). With increasing pumping time, the uranium concentration also decreases. The Fe(tot) concentration also decreases with increasing pumping time and may stabilize around 9.5 µmol/L. Extrapolation to zero drill water content, however, leads to a highly negative Fe concentration. The behavior of these two redox sensitive elements suggests that redox reactions are involved and not simply mixing of drill water and the “true” groundwater. Extrapolation to zero drill water content leads to realistic values for the other variables and systematic trends are also seen with increasing pumping time. Extrapolation of these variables to 100% drill water is subject to high uncertainties and the results are not reasonable.

KFM02A (513 and 503 m)

There is one sampling campaign at the depth of 513 m, starting 13 June 2003 with sampling at between 87 and 129 days pumping. Another sampling took place at 503 m depth around 29 months later (7 November 2005). Along with the sampling time there are general increases in the U and Fe(tot) concentrations, accompanied by a variation in the drill water content with a possible increase at 129 days (Figure G3-3a). Other indicators show no specific trends or there is a considerable lack in data (especially isotopes). The last sampling of the first campaign, 129 days after start, shows 6.8% drill water, 2.4 TU and 16.9 pmc. These tritium and ¹⁴C concentrations are considerable for groundwater at this depth. The tritium concentration may be the result of 6.8% drill water. The same may be true for the high ¹⁴C concentration, it may however, also reflect ¹⁴C originating from the actual groundwater.

Figure G3-3b shows the correlation between U, Fe(tot) and tritium with the drill water content for both sampling campaigns. The separate sampling campaign in 2005 shows a reduction in the drill water content to less than half of that found in the 2003 samples. One may recognize a decrease in the tritium content to zero with zero drill water content. Recognizing a trend in U and Fe(tot) with the drill water content in the 2003 sampling campaign requires considerable goodwill. Contrary to this, 29 months later, the Fe(tot) and U concentrations have increased considerably. This indicates transformations of these redox sensitive elements and possibly slow back-diffusion into the easily accessible flow system.

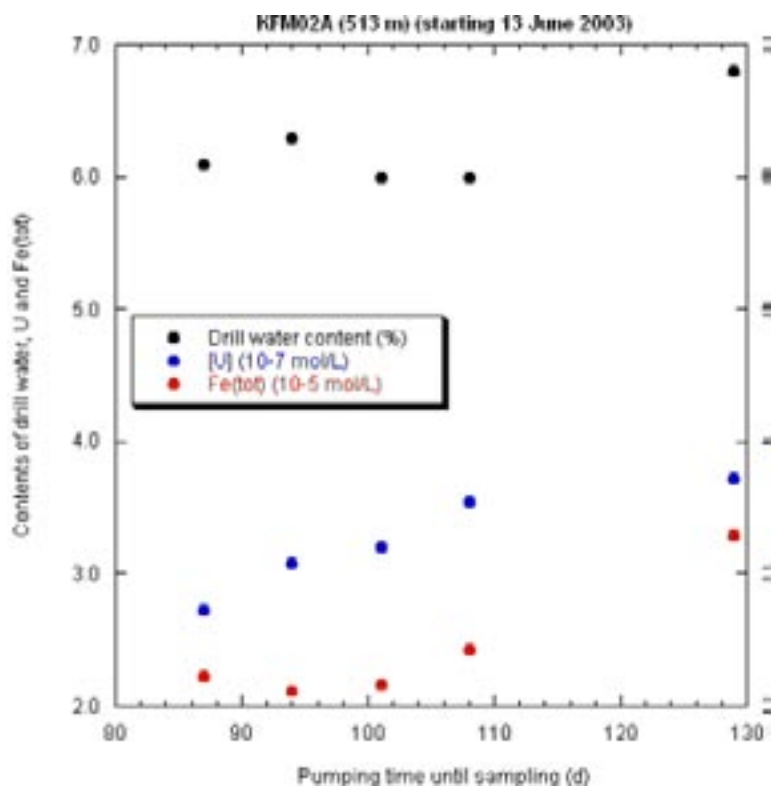


Figure G3-3a. Concentrations of drill water, U and Fe(tot) as a function of pumping/sampling time at campaign starting 13 June 2003 in KFM02A at 513 m depth.

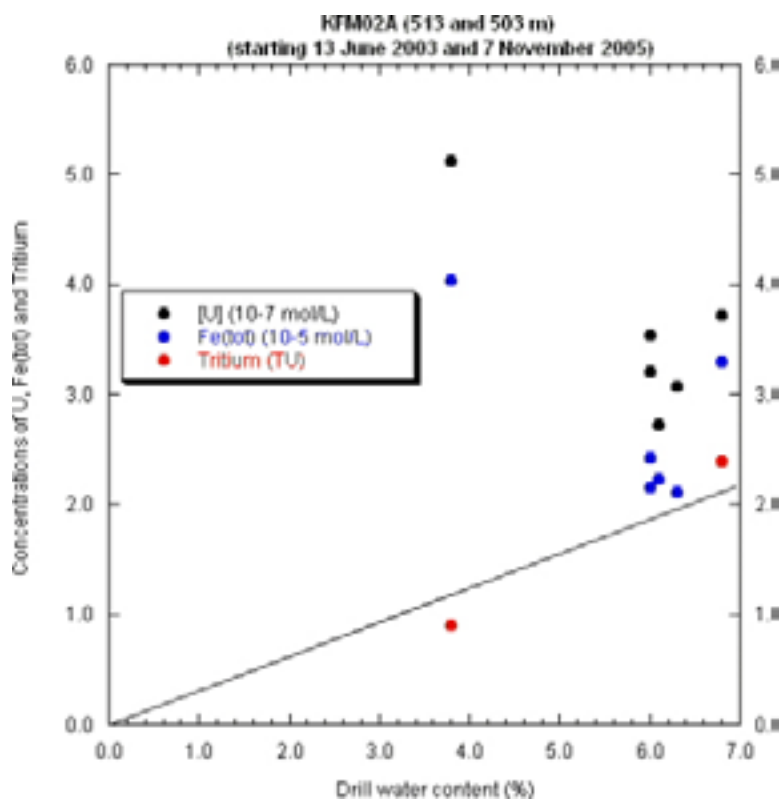


Figure G3-3b. Concentrations of U, Fe(tot) and tritium as a function of drill water content at campaign starting 13 June 2003 in KFM02A at 513 m depth and taking place 7 November 2005 at 503 m depth.

KFM02A (117 m)

There is only one sampling point at 117 m depth, where sampling is done 11 days after the campaign started, 7 November 2003. The water shows similarities with samples from similar depth in KFM01A with respect to the low drill water content, stable water isotopes and tritium below the detection limit. Accompanying the low drill water content is a fairly low U concentration. The high bicarbonate and DOC concentrations indicate fairly recent microbial decomposition of young organic (soil/plant) matter, also supported by the ^{13}C and high ^{14}C values. The low salinity could also support recharge water origin. This, however, is in some contrast to the relatively high depletion in stable water isotopes and the lack in tritium. The low U concentration could also be an indicator for the minerals having lost a great part of the uranium inventory due to long-term flushing with relatively oxidizing water, also applicable to the samples in KFM01A from similar depth.

KFM02A (424 and 426 m)

The sample at 426 m depth is taken 23 months later than the sample at 424 m depth. In this later sample, there are marginal changes in the electric conductivity, and the Na and bicarbonate concentrations. The stable water isotope composition does not change. Contrary to this, DOC is found, tritium appears and the ^{34}S content changes significantly. This would indicate that fresh water has entered the fracture system during the 23 months between the first and the second sampling. In this context, the uranium and Fe(tot) concentrations increase almost by a factor of two. Together with the above findings on the coherent changes in the Fe and U concentrations, this raises the question to which extent oxidative uranium release is associated with dissolution of iron containing minerals.

KFM03A (991 and 982 m)

Sampling at 991 m depths was made at between 18 and 32 days after start, 6 November 2003. The bicarbonate concentration shows a slight decrease with increasing pumping time. The uranium concentrations scatter around low values around 1 nmol/L. Contrary to this, the Fe(tot) concentration increases with increasing pumping time. More surprising, the drill water content is systematically increasing by a factor of about two between the first and the last sampling (Figure G3-4a). In Figure G3-4b it is also shown that the bicarbonate concentration decreases and the Fe(tot) increases with increasing drill water concentration.

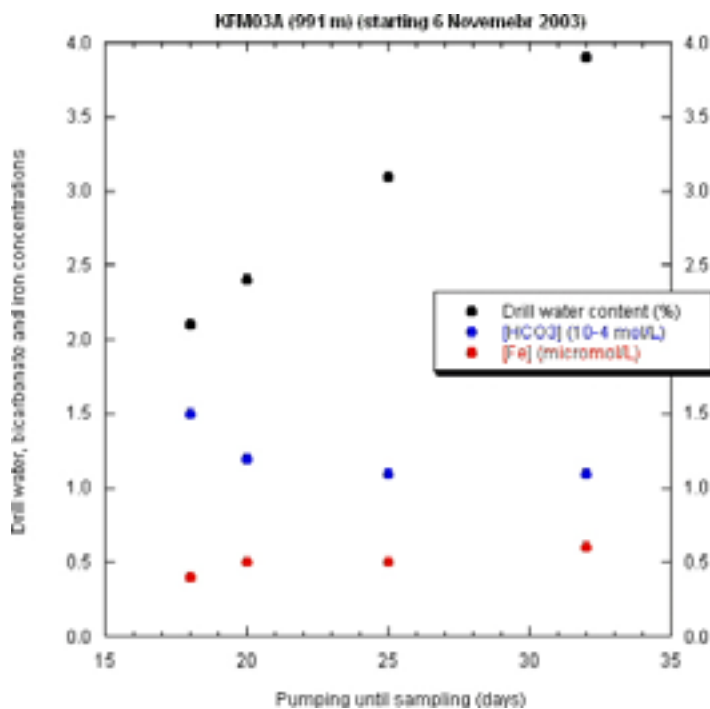


Figure G3-4a. Concentrations of drill water, bicarbonate and Fe(tot) as a function of pumping/sampling time at campaign starting 6 November 2003 in KFM03A at 991 m depth.

increasing pumping time, the values 24 months later (at 982 m) are somewhat surprising. There are slight changes in the concentrations of various elements and isotopes, but a drop in pH by two units, an increase in Fe(tot) from about 0.5 to 24.6 $\mu\text{mol/L}$, and an increase in DOC from about 1.3 to 13 mgC/L . Tritium is not found and thus a surface near groundwater in-flow is not the reason for the drop in pH. The persistent presence of drill water even after 24 months leads to the question of how the fracture is affected by the handling in the drill hole for the time period of two years. The combination of the drop in pH and increase in DOC (and Fe) may indicate microbial activity.

KFM03A (943 m)

Sampling at 943 m depths was made at between 5 and 31 days after start, 26 February 2004. The sampling campaign shows low uranium concentrations and systematic behavior of a large number of groundwater sample indicators with both the pumping time until the different samplings (Figure G3-5a) and the drill water content (Figure G3-5b). The drill water content is decreasing steadily with pumping, however, not coming close to negligible drill water amounts at the end of the campaign (after 32 days).

Because of the systematic dependencies with decreasing drill water content, one may test if the outcome is simple mixing, not severely affected by geochemical reactions (cf. above, KFM01A, 180 m). The outcome of linear regression of the different indicators with the drill water content is shown in Table G3-3. Extrapolation to pure groundwater is achieved by the “intercept” (i.e. zero drill water). Extrapolation to pure drill water is also shown (extrapolation to 100% drill water). As expected, the extrapolation to 100% drill water results in numerous invalid numbers, reflecting the high sensitivity against extrapolation well beyond the measured range. Concerning the extrapolated “groundwater” composition, the numbers for pH, electric conductivity, and Na and Cl concentrations are realistic (but not necessarily correct). Bicarbonate and DOC show slightly negative numbers, however, also zero falls within the uncertainty ranges. ^{18}O is very much independent of the drill water content, the D value, however, does not appear to be realistic. The tritium concentration is slightly positive, with zero within the uncertainty range. The ^{34}S content appears unrealistically high.

The redox sensitive elements U and Fe show negative concentrations below their uncertainty ranges. This shows that their behavior cannot be described solely by mixing with drill water.

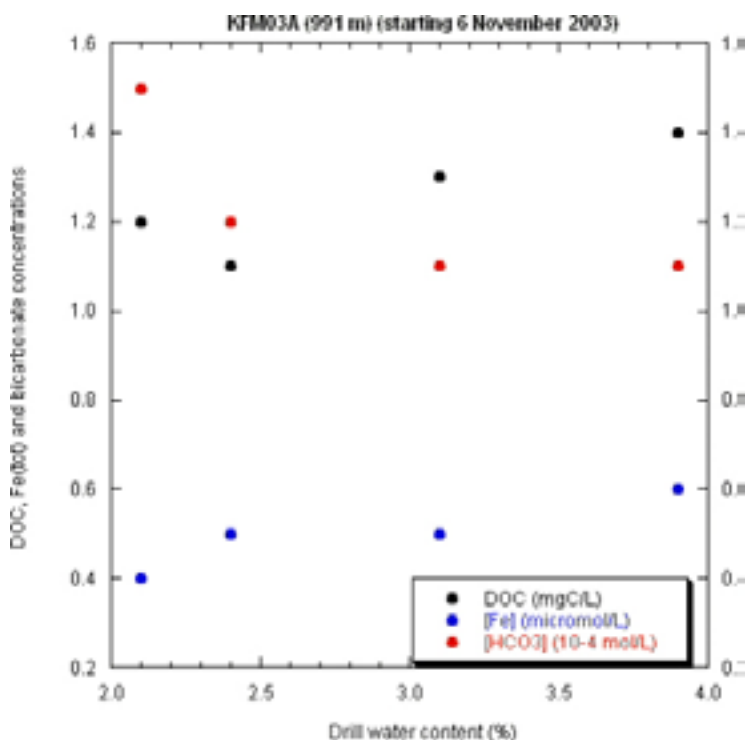


Figure G3-4b. Concentrations DOC, bicarbonate and Fe(tot) as a function of drill water content at campaign starting 6 November 2003 in KFM03A at 991 m depth.

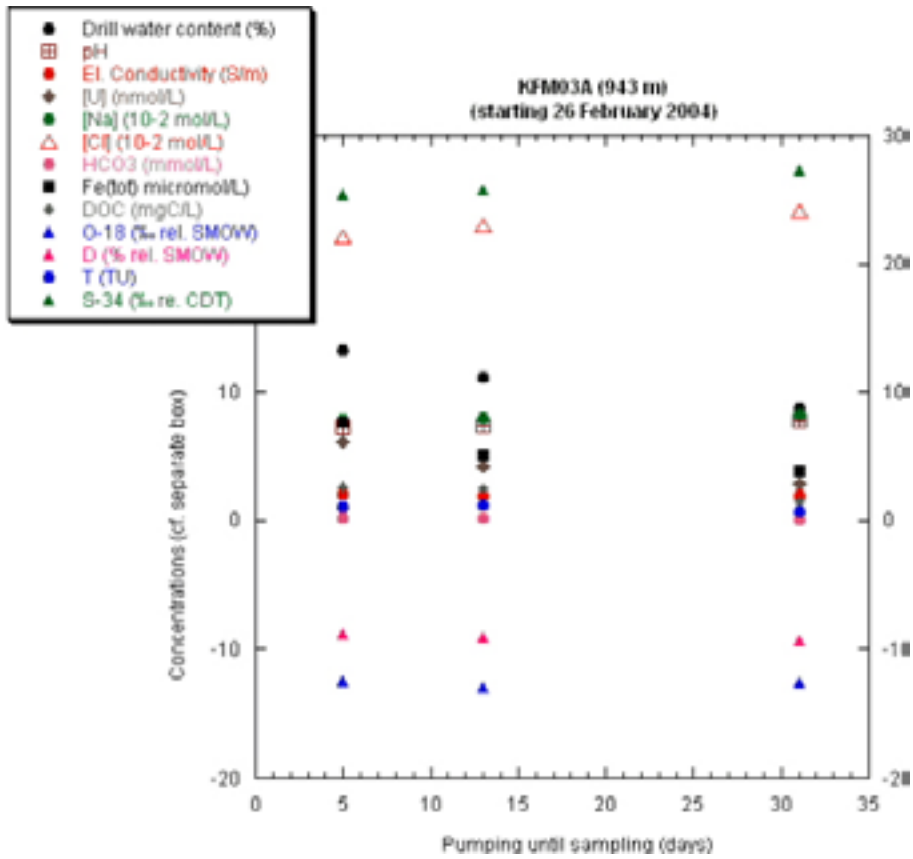


Figure G3-5a. Concentrations of different indicators as a function of pumping/sampling time at campaign starting 23 February 2004 in KFM03A at 943 m depth (note that D is given in % rel. SMOW).

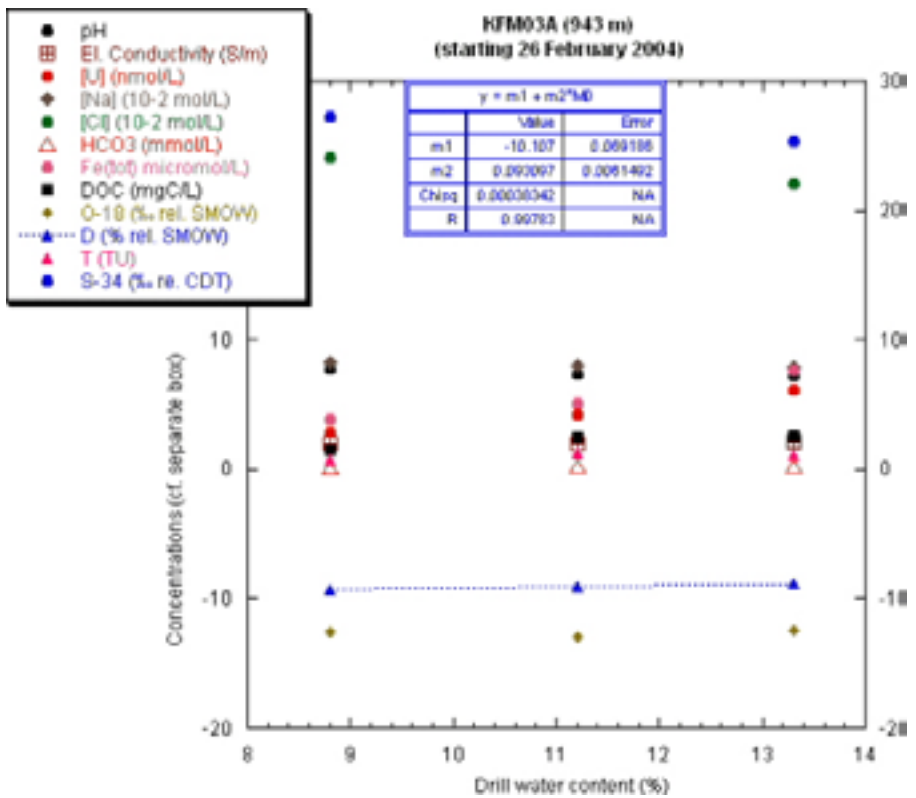


Figure G3-5b. Concentrations of different indicators as a function of drill water content at campaign starting 23 February 2004 in KFM03A at 943 m depth (note that D is given in % rel. SMOW).

Table G3-3. Linear regression of different data against drill water content for KFM03A at 943 m depth, the sampling campaign starting 23 February 2004. “Groundwater” denotes the extrapolated value for zero drill water content, whereas “Drill water” denotes extrapolation to 100% drill water content.

“Groundwater” Lin. regression:	Intercept	±	Slope	±	“Drill water”
pH	8.748	0.384	-0.1124	0.0342	-2.492
El Cond. (S/m)	1.752	0.040	0.0265	0.0036	4.402
Na (10 ⁻² mol/L)	8.719	0.1192	-0.0582	0.0106	2.899
Cl (10 ⁻² mol/L)	28.106	0.1634	-0.456	0.0145	-17.494
HCO ₃ ⁻ (mmol/L)	-0.0385	0.0384	0.0221	0.0034	2.1715
DOC (mgC/L)	-0.559	1.192	0.2485	0.1059	24.291
¹⁸ O (‰ rel. SMOW)	-13.105	1.461	0.0394	0.1298	-9.165
D (‰ rel. SMOW)	-101.07	0.692	0.931	0.0615	-7.97
T (TU)	0.2895	0.9802	0.070	0.087	7.2895
³⁴ S (‰ rel. CDT)	30.907	1.403	-0.427	0.1247	-11.793
U (nmol/L)	-3.449	1.172	0.7071	0.1042	67.261
Fe (µmol/L)	-3.694	2.095	0.8373	0.1862	80.036

KFM03A (451 and 452 m)

Samplings at 451 and 452 m depths refers to on sample taken 7 days after a start date of 17 October 2003, followed by a new sampling about 6 months later. The data are very similar between the two samplings. As also found above, the contribution by drill water is not decreasing significantly despite the long time between the two different samplings.

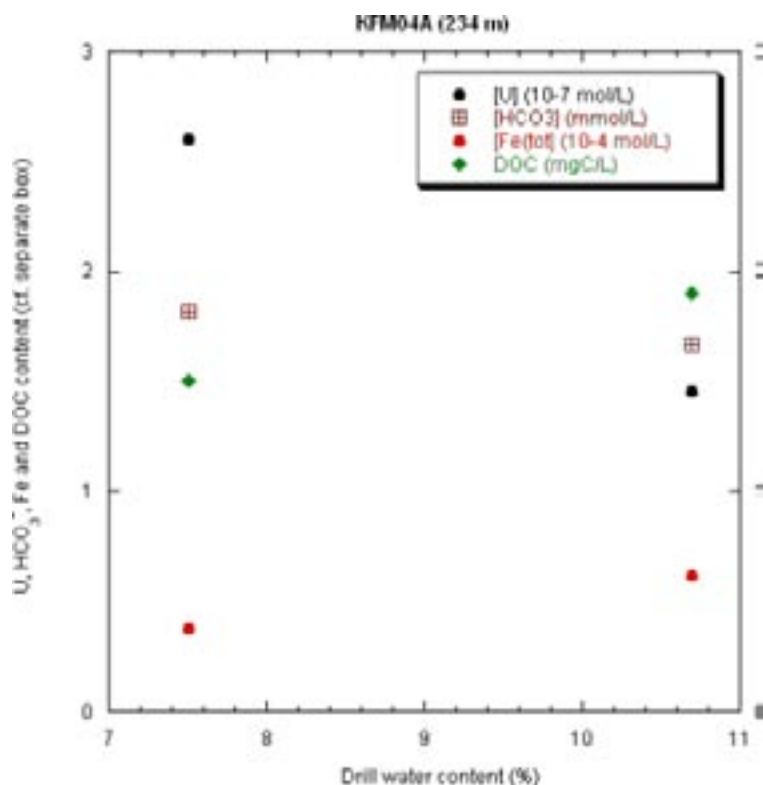


Figure G3-6. Concentrations of different indicators as a function of drill water content at campaign starting 16 January 2004 in KFM04A at 234 m depth (note that D is given in % rel. SMOW).

KFM03A (389 m)

There is only one sample taken at 398 m depth. Consequently, trends with pumping time or drill water content cannot be analyzed. One may compare the sample with those from 451/452 m depth. At 398 m depth the drill water content is about twice as high as at 451/452 m depth, and the uranium concentration is almost twice as high. All other numbers are comparable, with possible exception for tritium that is found at 389 m depth but below detection limit at 451/452 m depth. To which extent the tritium reflects younger groundwater or higher intermixing with drill water is not clear, especially as the carbon isotopes show basically identical numbers.

KFM04A (234 m)

There are two samples taken at this depth where the drill water content is decreasing with increasing pumping time. The drill water content, however, is still 7.5% after 25 days of pumping. In Figure G3-6, the U, HCO_3^- , Fe and DOC concentrations are shown against the drill water content. The Fe and DOC concentrations decrease with decreasing drill water content. The concentrations of HCO_3^- and especially of U, however, increase. Other indicators do not change significantly with pumping or drill water content. The reason for the behavior of U cannot be given, but the high drill water content suggests that U could be affected through its redox sensitivity.

KFM04A (358 m)

There is only one sample from this sample depth in this borehole. The drill water concentration is 6.5%. No specific statement can be made with respect to the U concentration of 95 nmol/L.

KFM05A (717 m)

There are three samples from this depth and this bore hole, namely 11, 17 and 24 days after start of sampling campaign, 24 September 2004. The concentration of drill water does not decrease with increasing pumping time, but remains around 2.1%. The other groundwater components also show no significant change with pumping, including U with about 27 nmol/L, Fe with about 67 $\mu\text{mol/L}$ and HCO_3^- with about 2.14 mmol/L. Consequently, no statements can be made concerning the behavior of U. The low but persistent drill water content, however, again leads to the question how far into the fracture and in which flow accessible regions the drill water has penetrated.

KFM06A (357 (and 772 m))

There is one campaign at 357 m depth, with sampling between 2 and 20 days after start, 15 February 2005. The drill water content does not decrease with pumping time and remains at about 7.8%. With respect to the other indicators, some of them show a slightly different number at the first sampling (after two days). Thereafter, there is basically no change in the composition of the samples, with U concentrations around 39 nmol/L. The Fe concentrations are also relatively high with numbers around 20 to 21 $\mu\text{mol/L}$. All samples are strongly affected by high drill water concentrations. The high U and Fe concentrations may be associated with each other in the form of co-dissolution of U and Fe containing minerals. For U this could be understood as oxidation in view of the high drill water content. For Fe, however, this does not appear to be a feasible explanation.

For the single sample at 772 m depths, the U concentration is not known.

KFM07A (925 m)

There is one campaign at 925 m depth, with sampling between 2 and 34 days after start, 22 March 2005. At this sampling, the drill water content, and U and Fe concentrations remain low. At the first sampling (after 2 days) the water may be slightly different as seen by a pH of 7.6, contrary to 8.0 in the thereafter following samples, and correspondingly 2 mg DOC/L, followed by values below the detection limit. In Figure G3-7, the drill water content, and U, HCO_3^- , and Fe(tot) concentrations are shown against the pumping time. The data for the drill water content shows some scattering, expected for these low concentrations. The figure shows that even at such low disturbance due to drill water well below 1%, pumping may lead to changes in the U, HCO_3^- and Fe concentrations.

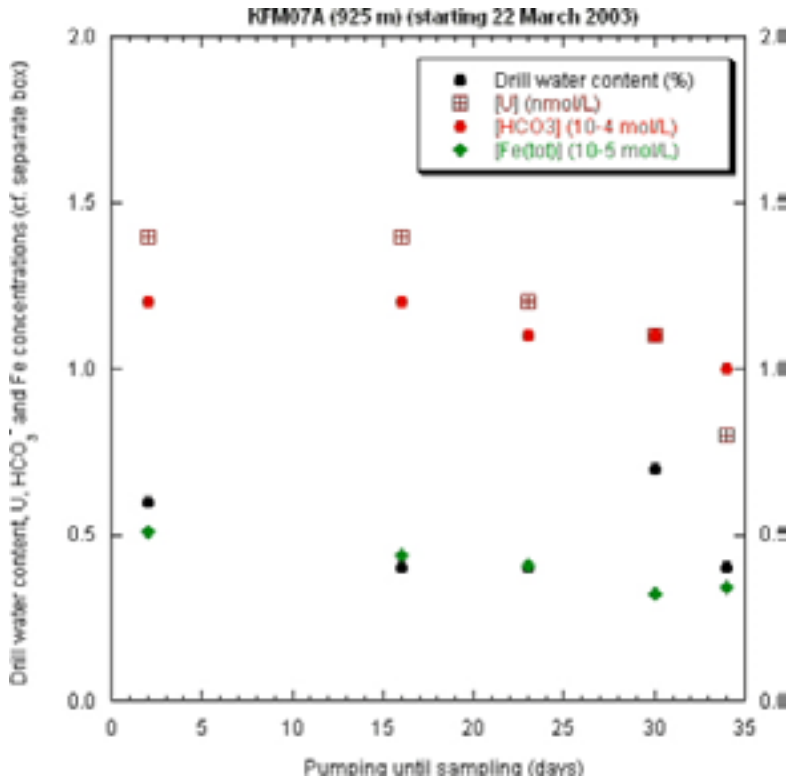


Figure G3-7. Concentrations of different indicators as a function of pumping/sampling time at campaign starting 22 March 2003 in KFM07A at 925 m depth.

G4 Overall analysis

In this section the groundwater samples are analyzed with respect to uranium and the influence of drill water content, depth, and possible co-reactions with Fe and Mn.

G4.1 Drill water content

Figure G4-1 shows the drill water concentrations as a function of depth. The drill water concentration varies within individual sampling campaigns. Nevertheless, the drill water content in sampling points around 100 m depth is relatively low, followed by an increase with increasing depth. At around 300 to 400 m depth, the drill water concentrations show one maximum.

With further increasing depth, to about 920 m, the drill water concentration decreases. Below this depth and down to about 1,000 m, the drill water content scatters widely, including very high numbers. This information is a prerequisite for analyzing the possible influence of drill water on the chemical behavior of uranium.

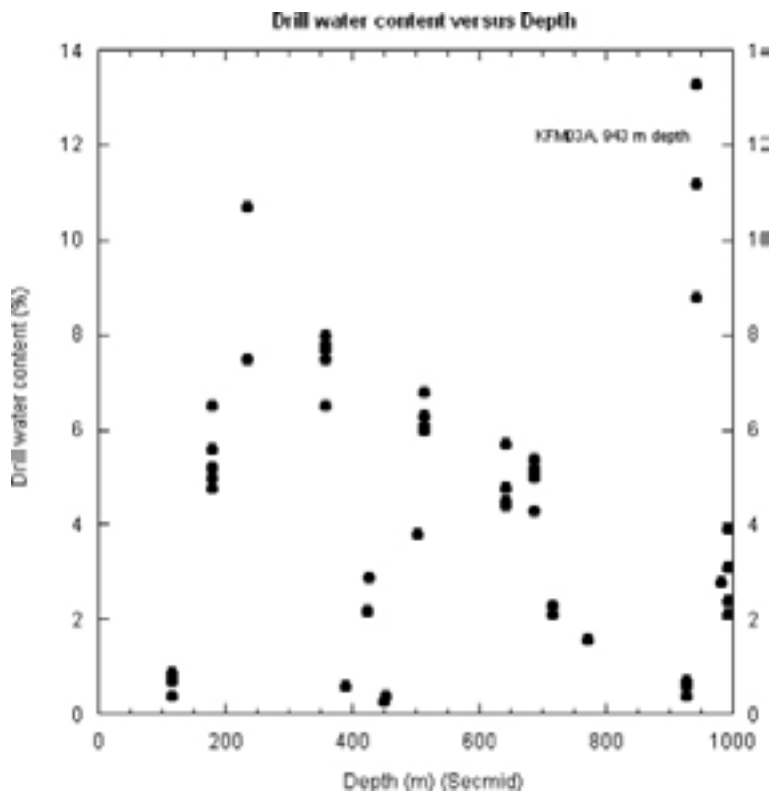


Figure G4-1. Drill water content versus depth for KFM groundwater.

G4.2 Uranium

In Figure G4-2, the uranium concentration is shown against the depth. For reference, also the drill water content is shown (Figure G4-1). As for the drill water content, the uranium concentrations are relatively low at 100 m depth, the maximum concentration increasing with increasing depth. It reaches a maximum at around 550 m depth. With further depth, the uranium concentration decreases and above about 700 m is a few nmol/L. As is the case with the drill water content, some samples fall below the general trend for maximum concentrations with depth. A very marked difference between the uranium and drill water concentrations as found at depths around 940 to 990 m. Also where the drill water concentrations are high, the uranium concentrations remain low. This shows that not only the drill water concentration determines the uranium concentration.

In Figure G4-3, the uranium concentration is shown as a function of the drill water content. High uranium concentrations are not found where the drill water concentration is low. The drill water thus appears to be a pre-requisite for high uranium concentrations. The dependency, however, seems to fall in two groups, where the strength of the drill water impact varies. As seen in Figures G4-1 to G4-2, the deep samples with drill water content beyond 8% do not show elevated uranium concentrations.

In Figure G4-4, the ratio between the uranium and drill water concentrations is shown against the sampling depth. At low depth, the uranium release with drill water impact is low, followed by an increase until about 500 to 600 m depth. Below this depth, the release of uranium with drill water decreases again. At 900 to 1,000 m depth the drill water normalized uranium release is negligible.

Based on these findings the following explanation is offered. At low depth, the accessible pore space is depleted from uranium by flushing with comparably oxidized water. Between about 700 and 1,000 m depth, the uranium is bound in a fashion where oxidative impact from drill water does not lead to a uranium release from the accessible pore space. In the intermediate range, the accessibility of uranium for oxidative release varies between very low and almost 400 nmol/L at 513 m depth.

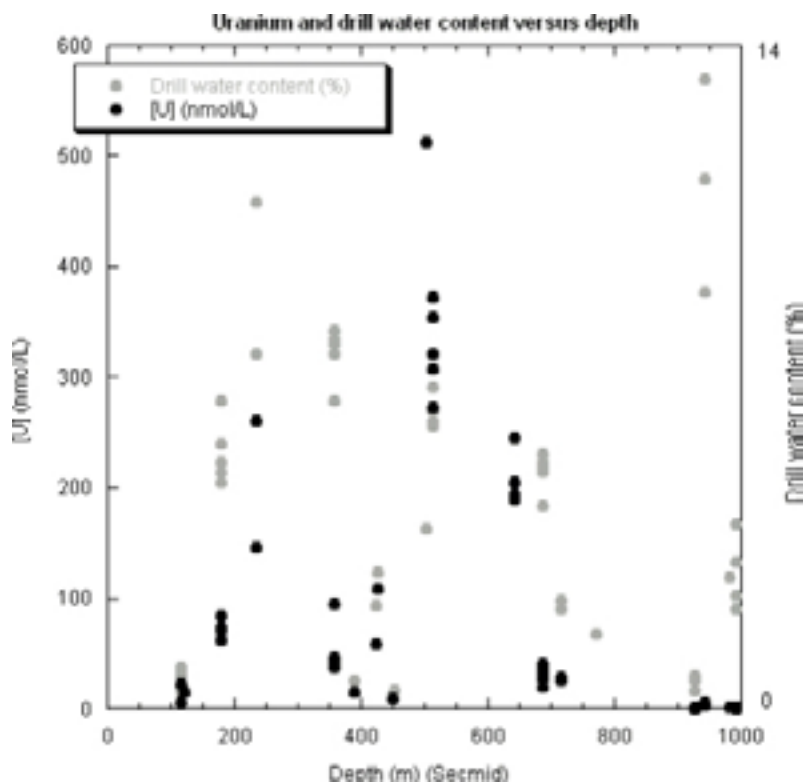


Figure G4-2. U content versus depth for KFM groundwater, compared to drill water content (cf. Figure 8-1).

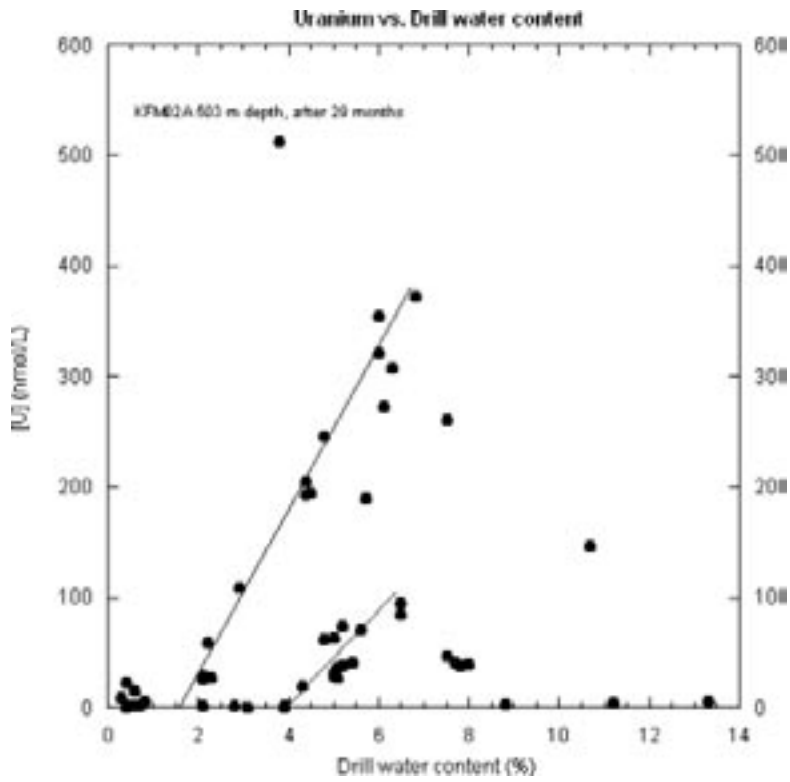


Figure G4-3. Uranium content versus drill water content for KFM groundwater.

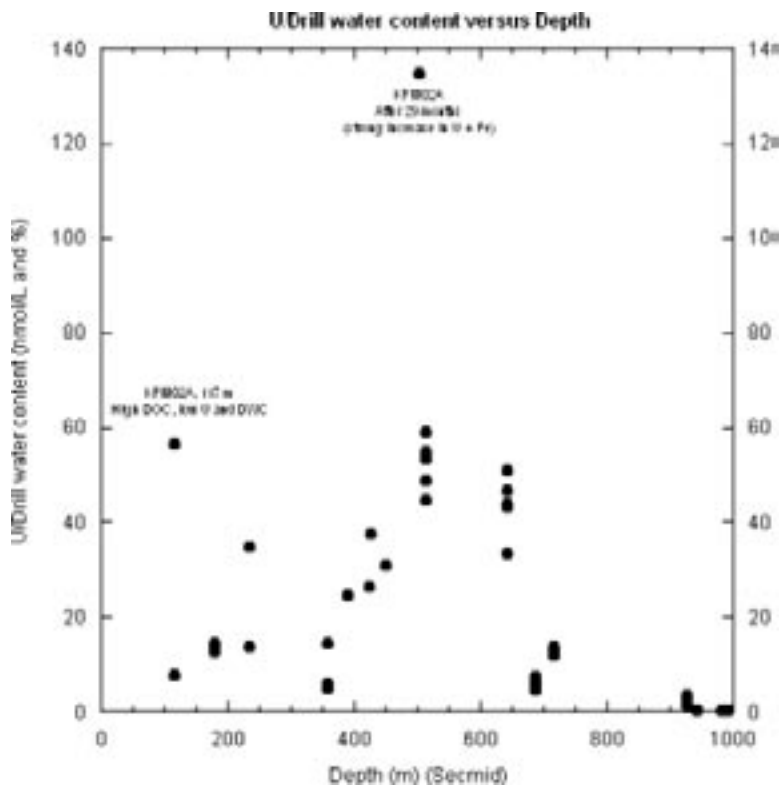


Figure G4-4. Uranium concentration over drill water content versus depth for KFM groundwater.

G4.3 Uranium and Iron

The question then is how uranium is bound in the accessible pore space. Discussions above revealed that in some cases Fe shows release in association with uranium. In Figure G4-5, the Fe(tot) and U concentrations are shown against each other. The picture is relatively complex, but some observations can be made. In the figure the samples from the different campaigns are distinguished and shown together with the respective sampling depth.

A first general observation is that there is basically no significant release of U without release of Fe. Secondly, at depths between 925 and 991 m, despite partly high drill water concentrations, there is no significant release of either U or Fe. Surface near waters show a high release of Fe without an associated release of U. In the depth range between about 180 and 450 m depth, there is a relatively high and variable release of Fe associated with a moderate release in U. Between about 500 and 700 m, a correlation between the Fe and U release may be identified with a mol ratio in the order of 80 Fe/U. KFM05A at 717 m depths has a drill water content about 2%, shows a very high release of Fe, however, not associated with a corresponding release of U.

Another way of identifying relation between the Fe and the U in the KFM groundwater samples is given in Figure G4-6. This figure gives the U/Fe and Fe/U atom ratios for the different sampling wells and depths. The vertical dotted line represents the Fe/U atom ratio of 80 as also shown in Figure G4-5, corresponding to 0.125 U/Fe. Higher U/Fe ratios are found in a sequence of samples at 642–643 m depth in KFM03A. The U/Fe ratios increase with increasing pumping time (6, 16 and 19 days). Revisiting the well at this depth after 16.5 and 21 months, however,

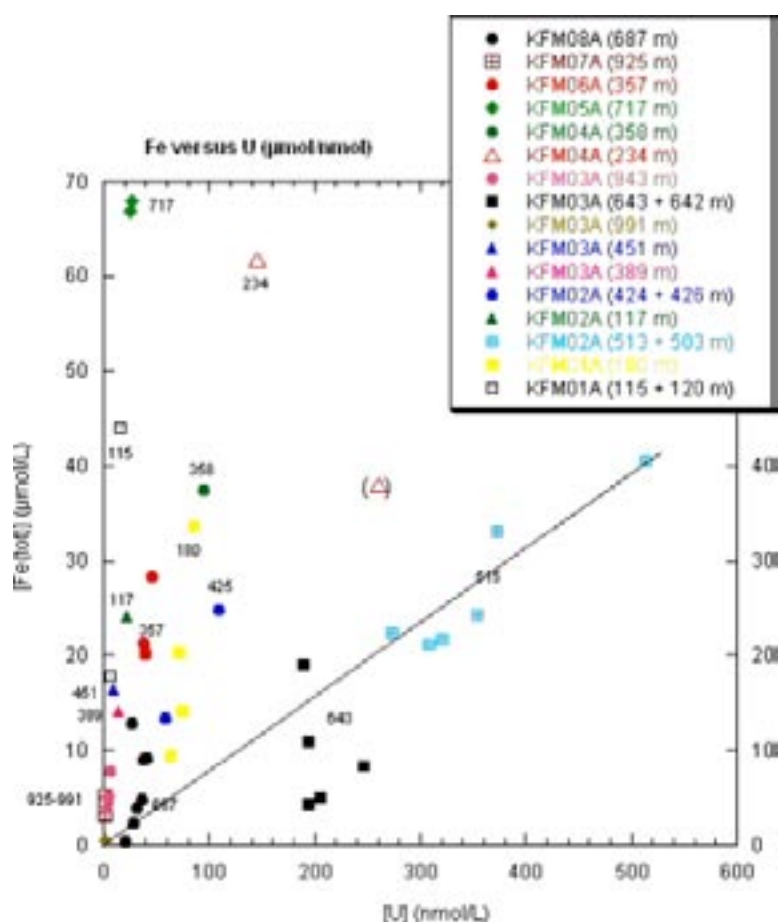


Figure G4-5. Fe(tot) versus U concentration for KFM groundwater.

the values decrease and after 21 months fall below the vertical line of 80 Fe/U. The highest U/Fe ratio is found in one sample of the well KFM08A at 687 m depths. This value is found after 7 days and is related to an exceptionally low Fe content. The samples taken afterwards fall on the vertical line and continuously decrease with increasing sampling time.

The overall impression that the chemical behavior of U is related to that of Fe remains. The deduced upper U/Fe atom ratio of around 0.0125 (or Fe/U ratio of 80 or higher) is valid for all samples where the sampling time is sufficient. A deeper understanding of the dependency between Fe and U would benefit from geochemical modeling of all individual samples by an expert in this field.

G4.4 Iron and Manganese

The interrelationship between U and Fe indicates that redox reactions could be important. In Figure G4-7 the concentration of Fe is shown against those on Mn. A general trend towards a correlation may be identified. In Figure G4-8, the Fe and Mn concentrations are shown for different sampling depths. Neglecting numerous extreme values, the Fe and Mn concentrations appear to increase with decreasing depth but show a large range between about 100 and around 250 m depth. The chemical behavior of these elements appear to be interrelated, however, a deeper understanding will require geochemical modeling of individual samples.

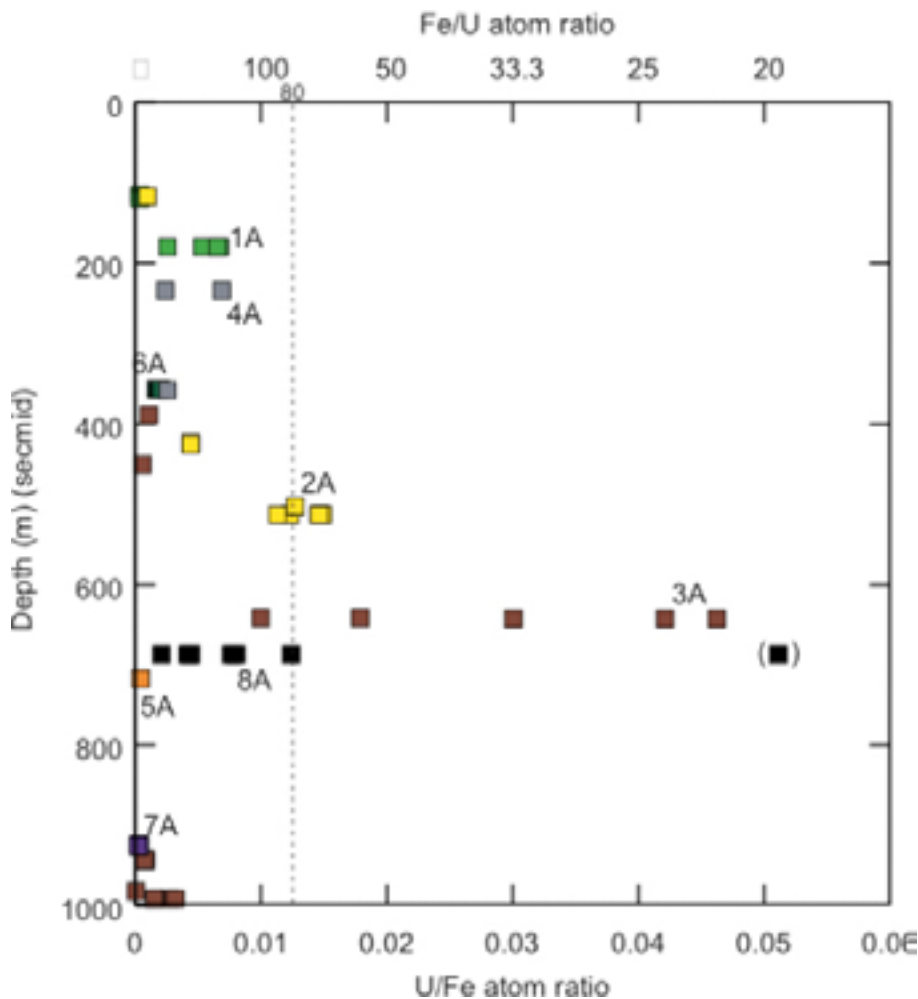


Figure G4-6. U over Fe atom ratio for KFM groundwater at different depth.

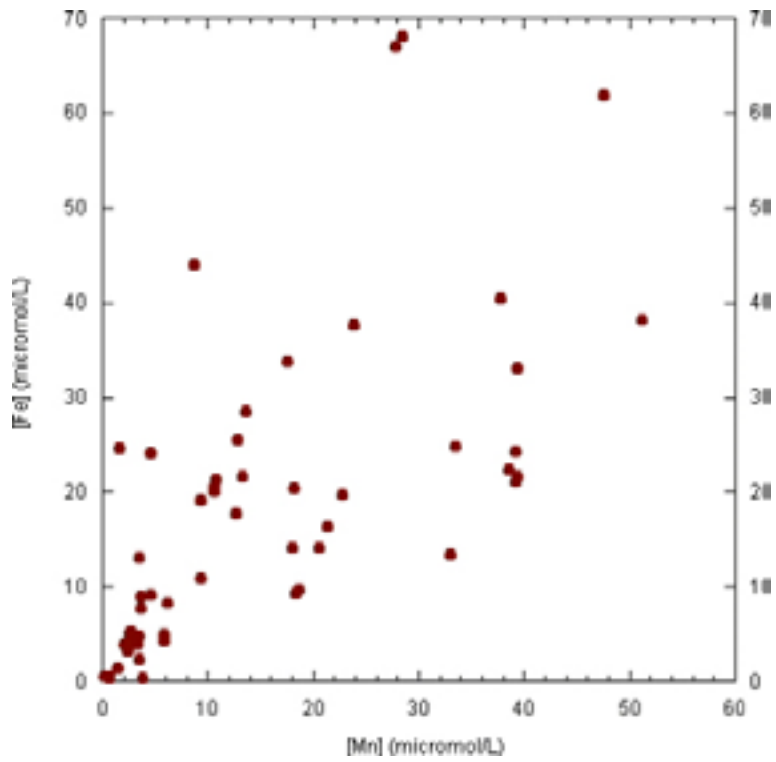


Figure G4-7. Fe(tot) versus Mn concentration for KFM groundwater.

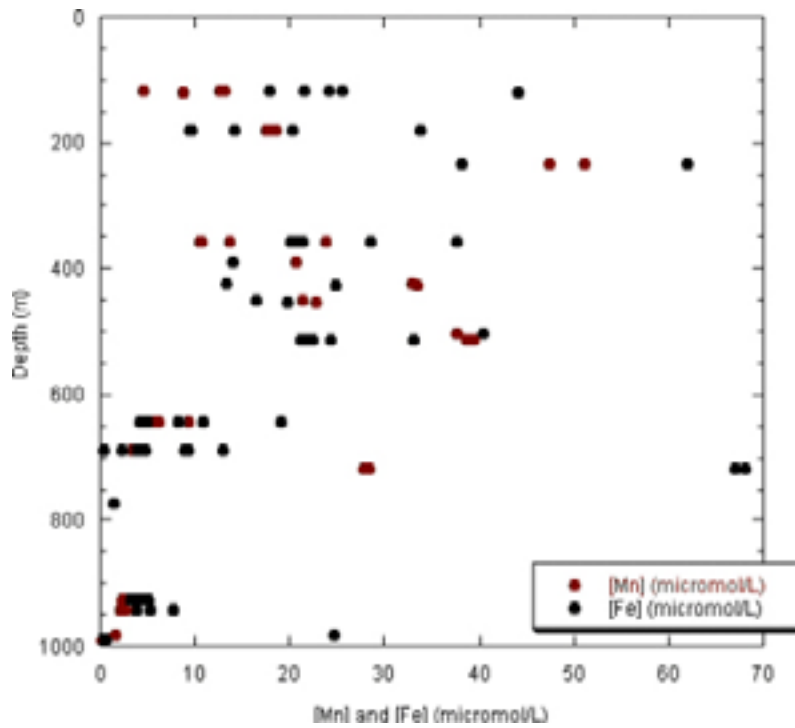


Figure G4-8. Fe(tot) and Mn concentrations versus depth for KFM groundwater.

G5 Summary and conclusions

The Forsmark KFM groundwater samples are analyzed, especially in view of their U concentrations, the possible impact of sampling artifacts and the correlation with the behavior of other redox sensitive groundwater constituents. Individual sampling campaigns show that the water bearing fractures are frequently contaminated with considerable amounts of drill water. Upon pumping, these concentrations in some cases decrease, in other cases they do not decrease significantly. Waiting for more than 3.5 years for a subsequent sampling campaign does not lead to groundwater free of drill water. This may be related to different explanations, such as

- Excessive contamination with drill water where the drill water is distributed over different flow accessibilities and released slowly.
- Cross contamination in periods where sampling at a specific horizon does not take place.
- Problems with drill water content analysis.

Other explanations may also be possible.

Depending on the depth, drill water impact leads to release of widely different amounts of U. This release is associated with the release of Fe. The chemical behavior of Fe also shows a possible interrelation to that of Mn. The overall findings would suggest that:

- U is associated with the chemistry of Fe bearing minerals, deposited in the accessible pore space.
- U is washed out in surface near oxidizing horizons.
- In deep horizons, U (and Fe) are stable, or not present in the accessible pore space.
- High U concentrations are sampling artifacts.

G6 Outlook

It appears that the unexpected high U concentrations are, amongst others, related to sampling artifacts, mobilizing uranium in Fe bearing minerals in the accessible pore space, especially in the intermediate depth range. If desired, the suggested explanation may be supported by additional investigations. Such investigations may focus on examination of drill cores from different depth with respect to:

- i. Concentration, redox state, chemical form and spatial distribution of U and associated minerals (especially Fe).
- ii. Controlled U leaching experiments, monitoring also the release of other elements (especially Fe). Special emphasis should be on the impact of oxidation and the release time function. The latter would give information on differences in diffusion-controlled accessibilities of the relevant minerals.
- iii. After leaching experiments, the drill core material should be characterized again (cf. i).

In addition, one should consider geochemical modeling of individual samples in combination with analysis of the redox potential.

G7 Acknowledgement

The work has been conducted within a project with SKB and within the EC Integrated Project “Fundamental Processes of Radionuclide Migration” (FUNMIG).

Forsmark 2.1 hydrogeochemical data

This data set is stored in the SKB database SIMON