

Technical Report

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Hydrochemical stability of groundwaters surrounding a spent nuclear fuel repository in a 100,000 year perspective

Edited by I Puigdomeneck

September 2001

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A project jointly supported by POSIVA and SKB

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.

ABSTRACT

This report is focussed on the effects of climate changes on the chemical composition of deep groundwaters. The aim of the work has been to assess the hydrochemical stability at nuclear repository sites in Finland and Sweden.

Sites investigated by SKB and POSIVA have been compared. The corresponding features are important in judging how sensitive a site might be to climatic changes.

Evidence for climate effects in the past on groundwater compositions has been reviewed, including isotopic and mineralogical data. There is for example evidence that glacial meltwaters are currently present at repository depths in the Fennoscandian Shield. No evidence has been found however that oxidising conditions have ever prevailed at depth, even if glacial meltwaters presumably had a substantial amount of dissolved O₂.

The depth distribution of different calcite types (and other fracture minerals) indicates stability in large-scale groundwater circulation over time. Information on past (and future) groundwater salinities has been sought after in the results of hydrological numerical models for Äspö in Sweden and Olkiluoto in Finland.

It is expected that groundwater salinities will change due to future climatic variations. The main effects will be from shoreline movements, permafrost and continental ice-sheets. In most sites the present reducing redox conditions will remain undisturbed during glacial cycles. The modelling indicated that most of the SKB suitability criteria will be met during the life-span of the repository and the groundwater composition will vary within what is observed in the samples collected today at various depths. The expected changes are therefore not judged to threaten the integrity and functioning of the repository. The major conclusion is that despite long-term hydrodynamic changes hydrochemical stability is expected to dominate at repository depth.

Keywords: Groundwater chemistry, groundwater modelling, salinity, redox conditions, hydrogeological modelling, glaciation, permafrost, climate scenario modelling.

FOREWORD

This report has been put together on the basis of the discussions and experiments carried out in the framework of the Äspö cooperation between SKB and Posiva. The Hydrochemical Stability project group consisted of

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1 INTRODUCTION

Hydrochemistry is central to the planning, design and construction of a long-term repository for the disposal of radioactive wastes. Suitable groundwater chemistry at depth will assist in maintaining the integrity of the engineered multi-barrier system to at least 10 000 years into the future. The ability to study the present-day hydrochemical system, and relate to past groundwater conditions (e.g. glacial events), provides a strong semi-quantitative basis to predict future changes (or lack of change) in groundwater chemistry within the range of repository safety and performance assessment timescales (thousands to tens of thousands of years). In addition, chemical evidence can provide qualitative information with which to support the development of, and output from, quantitative numerical models of groundwater flow.

Two main categories of hydrochemical parameters (pH, Eh, salinity, isotopes, trace elements etc.) are recognised in repository development depending on their intended use: 1) site characterisation and support for hydraulic flow models, and 2) repository safety and performance assessment. In performance assessment the importance of hydrochemistry will depend on the selected disposal concept, the repository materials used to house the various waste forms and, to some extent, the nature of the host rock. The major risk to all disposal concepts, however, is the possible incursion of groundwaters of extreme composition (i.e. brines and glacial melt water) during the lifespan of the repository (Smellie et al., 1999).

1.1 QUESTIONS AT ISSUE

- Will hydrochemical conditions still be suitable in the future at a nuclear repository site?
- Or will future climate changes induce important modifications in the hydrochemistry of a repository?
- What processes govern the hydrochemistry of groundwaters?
- Are these processes such that they will buffer against climate changes?
- Is it possible to state that hydrochemistry will probably be stable at a site, but perhaps less stable at another site?

These questions describe the issues that have been discussed at length within the frame of a joint SKB/POSIVA project named *Hydrochemical Stability*. Naturally, the focus of the group has been on granitic-rock sites in Sweden and Finland (see Figure 1). The results of these discussions and corresponding modelling work are presented in this report.

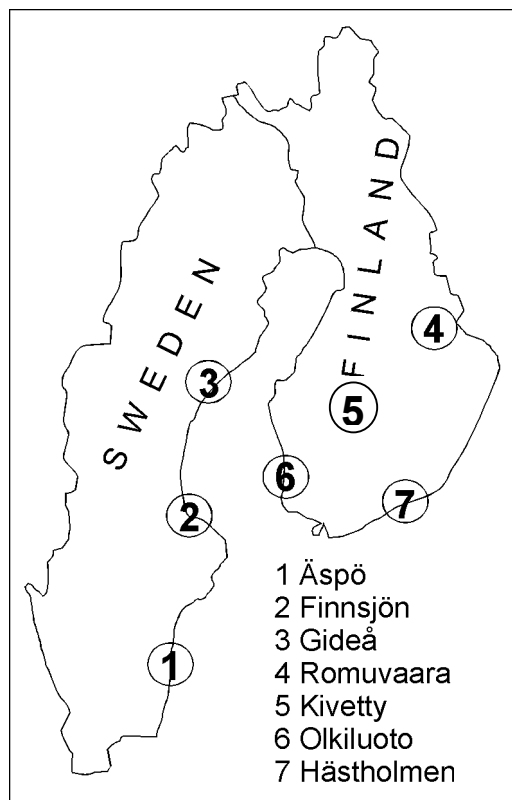


Figure 1. The map shows the location of the evaluated sites in Finland and Sweden.

Two hydrochemical factors have perhaps the largest dependence on climatic conditions, while at the same time have a large impact on repository performance: salinity and dissolved O_2 . These two aspects have therefore received special attention within this project.

The members of the *Hydrochemical Stability* group, co-authors of this report, are all well aware of not having the magical power of future predictions. Nevertheless, a review of the present knowledge on the relevant questions allows judgement on the possible stability (or instability) of hydrochemical conditions on any site for a nuclear waste repository in granitic rock in the Fennoscandian Shield.

1.2 BACKGROUND

Hydrochemical conditions are of importance for the durability of engineered barriers (canister and bentonite buffer) and for the solubility and migration of radionuclides. For example, *highly saline waters* may be detrimental for the corrosion of metals, for the solubility of radionuclides like Pu, and for the swelling properties of clay minerals. Disturbed *redox conditions*, like the presence of dissolved oxygen or high sulphide levels, are also detrimental for the corrosion of metals, and they may enhance the solubility of some radioactive actinide elements.

Taking this into account, SKB and POSIVA started the *Hydrochemical Stability Project*. The purpose of this joint venture was to try to answer questions like:

- Will the saline deep groundwaters, found now at depths of about 1000 m in several locations, reach repository levels in the future, and if so when and for how long? Or can it be assumed that due to density differences the saline groundwaters will remain at their present depths during the repository life?
- During a glaciation cycle it is possible that meltwaters reach repository depths. Will the O₂ contents of the infiltrating waters be consumed before they reach the repository, or will they create a redox perturbation, and if so, for how long time?
- Can microbial sulphate reduction in a repository site affect the function of the canister and buffer materials?

These questions are schematically illustrated in Figure 2.

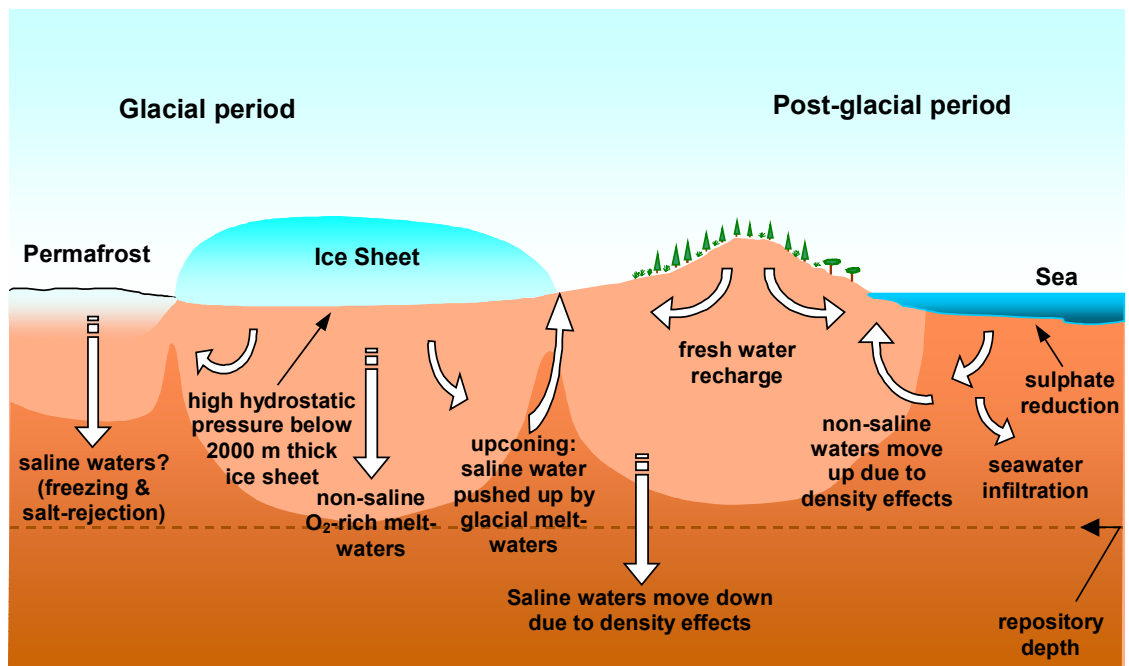


Figure 2. Processes affecting repository performance that may change over long periods of time:

- Glacial meltwaters, rich in dissolved O₂, might reach repository levels due to a high hydrostatic pressure.
- During postglacial periods the land might be covered by seas or lakes of varying degrees of salinity.
- Glacial rebound will eventually rise the repository location above the sea level and groundwater is recharged by precipitation.

The objective of the *Hydrochemical Stability Project* was therefore to study the general hydrochemical stability of repository sites in granitic bedrock. Particularly, the aims were:

- To describe the chemical processes and their effects as a result of the enhanced groundwater flow caused by draw-down into tunnels and shafts. This objective was addressed by the “Modelling Task #5” group (of the *Äspö Task Force on Modelling of Groundwater Flow and Transport of Solutes*).
- To quantify the chemical effects of remaining oxygen entrapped during the closure of the repository. This was resolved by the REX Project (see section 4.2.5.2).
- Develop and test methods for assessing the hydrochemical evolution at candidate repository sites, e.g. Olkiluoto in Finland.
- Obtain the most probable description of the hydrochemical conditions in the next 100 to 10 000 years
- Describe possible scenarios for hydrochemical evolution at Äspö over the next 100 000 years

In order to achieve these goals, the *Hydrochemical Stability Project* has had the following tasks:

- Re-sampling and analysis of groundwaters from KLX02, including also surface water sampling (wells, springs, percussion boreholes, etc.).
- Modelling groundwater evolution.
- Collection of information from Finnish and Swedish sites on deep groundwaters.

Furthermore, results from other projects were incorporated:

- EQUIP (Evidence from Qaternary Infills for Palaeohydrology, an EU project, see section 4.1.2).
- Äspö Task Force “Modelling Task#5” (Wikberg, 1998).
- The “Matrix Fluid” project, dealing with the chemical characterisation of groundwater in very low conductivity rock (Smellie, 2000).

1.3 SALINE WATERS IN BASEMENT AREAS

In a crystalline bedrock environment, recharge groundwaters initially react with the overburden (if present) and subsequently with the fracture surfaces during percolation through the bedrock to greater depths. Generally, hydrochemical profiles show that the groundwaters become more alkaline and rich

in dissolved salts (higher TDS^a) with increasing depth, in particular due to greater amounts of sodium and/or calcium chloride, and sometimes sulphate.

Fresh to brackish groundwaters tend to characterise the upper approximate 500 m or so, where groundwater flow is driven by head differences based on topographical variations, the presence of lakes or the sea, etc, and where there is a greater number of conducting fractures, and the mean residence times are relatively short (< 10 000 years). Groundwater mixing from different sources may also contribute to changing hydrochemical properties. Approaching 1000 m depth groundwater flow conditions usually change; flow rates are less active and tend to be associated with more discrete, isolated water-conducting fracture systems. In this environment groundwaters are often more saline in character. These waters, however, may be still to some extent influenced by surface-derived input components under favourable hydraulic conditions. For example, in the case of Fennoscandia from recent precipitation, ancient and modern marine waters (i.e. coastal localities) and cold climate waters (e.g. glacial meltwaters).

Mostly as a result of mining activities in the Canadian Shield and deep exploration drilling in the Fennoscandian Shield, saline waters (TDS 10 000-100 000 mg/L) and brines (TDS > 100 000 mg/L), are found to be relatively commonplace at depths greater than 1000 m (Figure 3). Saline groundwaters have also been found at depths below 500-600 m at the Finnish sites of Hästholmen and Olkiluoto. The maximum salinity found was about 75 g/l at depths \geq 800 m in Olkiluoto. The same salinity has been found at Laxemar in the Äspö area at depths below 1100 m. Many of these saline groundwaters are Ca-Na-Cl in type with a Ca:Na ratio of \approx 1.5-3.0 (e.g. Gravberg between 5453-6967 m has a value of 3) and some are extreme in composition, containing up to 6 g/L Ca, 5 g/L Na and 20 g/L Cl in the Canadian basement at depths of 1500 m (see compilation by Smellie, 1996). In some cases (e.g. Äspö, Sweden; Olkiluoto, Finland) the Ca:Na ratio is nearer one, and in other cases (e.g. Hästholmen, Finland) slightly less than one.

1.3.1 Origin of the Brines

The origin of saline groundwaters has been reviewed (e.g. Lampén, 1992; Raven and Clark, 1993). To explain the occurrence of saline waters several questions need to be answered. What is the origin of the salinity? Was it introduced into the bedrock (e.g. marine-derived waters), does it represent relict, ancient fluids in the bedrock (e.g. metamorphic fluids), does it derive from bedrock reactions with meteoric-derived waters, and what role does bedrock geochemistry play in determining the groundwater chemistry? Furthermore, what is the mean groundwater residence time, and how old are the saline waters?

^a TDS = Total Dissolved Solids.

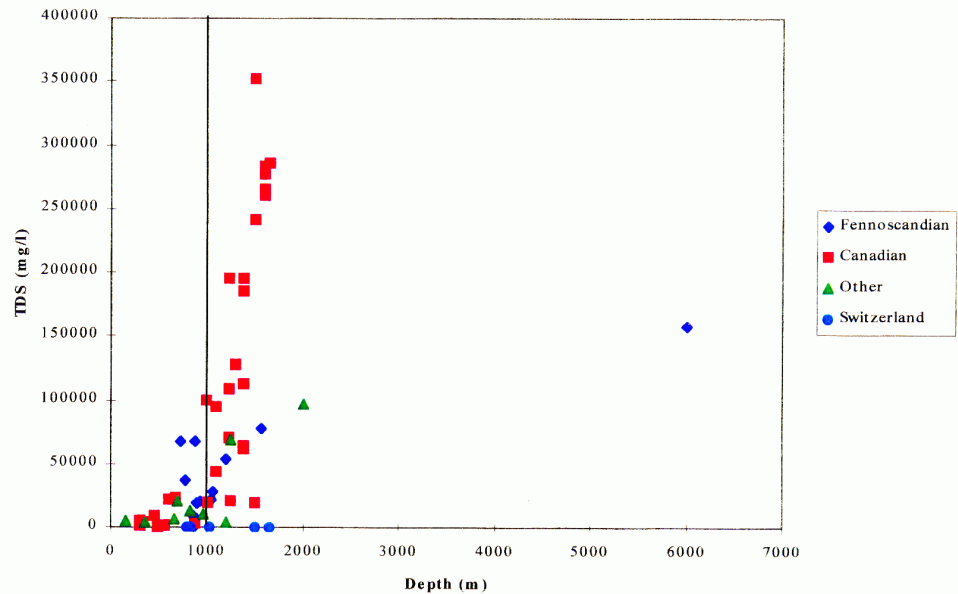


Figure 3. Compilation of TDS concentrations in groundwaters in crystalline rock down to 6 km depth (from Juhlin et al., 1998).

The main mechanisms whereby saline constituents can be introduced into the Fennoscandian Shield groundwater system are via:

1. Modern sea water or brackish water
2. Relict sea water
3. Leaching of marine sediments, e.g. marine clays
4. Enrichment of salt due to freezing of seawater or existing groundwater in the bedrock during glacial periods
5. Leaching of Palaeozoic or Proterozoic sedimentary rocks e.g. evaporites
6. Leaching of fluid inclusions
7. Water rock interaction processes

For waters with long residence times points 5, 6 and 7 become increasingly important compared with the other processes.

The processes involving freezing of seawater or groundwater during glacial periods has been paid more attention during recent years (e.g. Gascoyne, 2000; Herut et al., 1990) and it involves also the formation of sodium sulphate minerals that may be later leached causing high sulphate contents in the groundwater (cf. Palmottu, Blomqvist et al., 2000).

Water/mineral interaction processes that may constitute local salinity sources within the bedrock include:

- Hydrolysis of silicate minerals
- Release of salts from the rupture of fluid inclusions
- Radiolytic decomposition of groundwater

It is generally accepted, however, that no one process or source can account for the observed salinities in the basement shield areas; most reported samples seem to represent mixtures of meteoric water with a highly concentrated brine (Pearson, 1987), which may be an ancient relict sea water, basinal water or fluids genetically linked to geochemical processes occurring from rock/water interactions at various temperatures over long periods of geological time in the bedrock.

As pointed out in (Raven and Clarck, 1993), groundwater hydrochemical and isotopic data show the basement brines to be highly modified by low temperature alteration such that many of the primary chemical and isotopic signatures (e.g. stable isotopes) have been lost, thus making it impossible to differentiate whether the brines are meteoric in origin or syngenetic with the rocks themselves. Exceptions are the strontium isotopes which support a large-scale in situ water/rock origin for most of the cations. The solutes in the brines may thus be as old as the rocks themselves, giving ages of 10^6 to 10^9 years for the most concentrated brines.

^{36}Cl studies at Laxemar (Louvat et al., 1997) and Olkiluoto (Gascoyne, 2001) indicate a high degree of evolution over very long time scales, at least in the range of 1 million years. Calculations on isotope data for Laxemar (^{18}O , ^{13}C , ^{34}S and ^{87}Sr) show that even if the origin of the salinity can not be explained, there is evidence for silicate weathering (biotite, K-feldspar and plagioclase to a minor extent) over long periods of time (Wallin, 2001). Water-rock interaction involving silicate minerals under hydrothermal conditions is also supported by deviation from the Meteoric Water Line observed for the most saline groundwaters at Laxemar (Laaksoharju and Wallin, 1997), a phenomenon common also to the Canadian Shield brines.

Support for a bedrock origin has recently been shown from the Underground Rock Laboratory (URL) at Whiteshell, Manitoba (Gascoyne et al., 1996). At this site, long-term, in situ experiments (4-5 years) carried out in boreholes drilled into bedrock of low hydraulic conductivity, have revealed a close similarity in chemical composition between sampled pore/fissure fluids and deep brines. At Äspö on-going studies are focussed on sampling matrix fluids from low transmissive parts ($T < 10^{-10} \text{ m}^2\text{s}^{-1}$) of the bedrock (Smellie, 2000). Under such conditions long residence times are characteristic and the matrix fluids are considered to constitute the pore fluids in the rock matrix. However the accessibility of these fluids, and their ability to move through the rock matrix, will depend on whether or not the pore spaces are connected. Assuming a rock fabric of interconnected pores and fine fissures, and bearing in mind that rocks of low transmissivity constitute the major volume of the bedrock mass in any granite body, matrix fluids are suspected to contribute to the chemistry of deep formation groundwaters. Matrix fluids trapped in isolated pore spaces or in micro-fracture/fissure dead-ends will not contribute directly to the surrounding formation groundwater chemistry, but some contribution can be expected from long-term diffusion processes.

A conclusion from studies of deep mines in the Canadian Shield is that there is no clear correlation between major rock type and the groundwater chemistry. "In all cases, the brines and brackish groundwater are dominated by a Ca-Na-Cl facies, with similar maximum concentrations of specific species in the most concentrated brines" (Raven and Clarck, 1993). The results from Finnish groundwaters disagree however with the Canadian results (e.g. Blomqvist, 1999). In Finland saline groundwaters from mafic and ultramafic rocks show a strong Na-Cl tendency whereas a Ca-Na-Cl tendency is typical in felsic rock formations. In addition, clear differences can be observed in minor element concentrations between groundwaters in felsic rocks, for example, high Mg concentrations occur in saline groundwaters (Na-Ca-(Mg)-Cl type) from the Hästholmen rapakivi granite (Pitkänen et al., 2001), whereas Mg is low in saline Ca-Na-Cl type groundwater in the Olkiluoto mica gneiss-microcline granite migmatite. Similar differences are found for SO_4^{2-} concentrations and gas compositions, such as CH_4 and H_2 , all of which are important for repository safety.

There are fewer documented highly saline basement shield locations in Sweden compared to Finland, so it is unclear whether similar hydrogeochemical heterogeneities also occur. The data collected so far in Sweden and Finland support the important contribution of long groundwater residence times conducive to water/rock reactions, palaeohydrogeology (i.e. introduction and mixing of groundwaters of different origin), and present hydrogeological conditions (Blomqvist, 1999; Laaksoharju, 1999; Laaksoharju et al., 1999b; Pitkänen et al., 1999; Pitkänen et al., 2001).

1.4 CONCEPTUAL MODEL FOR THE EVOLUTION OF GROUNDWATERS

The assumed groundwater development at the Swedish sites is shown in Figure 4 as a conceptual postglacial model for the last 10 000 years (Laaksoharju, 1999). The evolution during the last 10 000 years at the Finnish sites are described in detail in (Pitkänen et al., 1999; Pitkänen et al., 2001) and further discussed in section 4.1.1. The developments of Hästholmen and Olkiluoto correspond roughly with those at Äspö (see locations in Figure 1). The Finnish sites of Kivetty and Romuvaara differ in that they have not been exposed to marine water bodies after deglaciation: the Kivetty site was a small island, and Romuvaara was located in the mainland well above the sea level after the last deglaciation. These sites would therefore plot on the left axes of the diagrams in Figure 4.

The major events, illustrated in Figure 4 and possibly affecting the groundwater composition, are as follows:

1. The continental ice melted and retreated and glacial meltwater was injected into the bedrock (>13 000 BP). At large depths (>800 m) glacial meltwater was mixed with old saline/brine groundwater in the bedrock. At the interface a saline groundwater with a glacial signature could have

been formed. A non-saline glacial water was present in the upper part of the bedrock. The hydraulic forces are believed to be greatest during the glaciation/deglaciation period.

2. The flushing out on the mainland started directly after deglaciation. However, for those sites that were below sea level, postglacial marine water affected the groundwater composition. The continuous land rise gradually elevated all sites to above sea level and the increased hydraulic driving force resulted in the flushing out and mixing of existing groundwater types. A mixture of glacial, brine and meteoric groundwater could occur at all sites, and marine waters might also be present in the sites that have been exposed to seawaters.

All the available evidence and the modelling results described in this report and elsewhere support in general terms this scheme of events.

At Äspö, Finnsjön and Gideå where the different seawater stages covered the bedrock at some point in time, the salinity of the seawater could have affected the groundwater in the bedrock by density turnover. The higher the salinity of the seawater the deeper the penetration depth. The land rise resulted in the formation of a freshwater aquifer at these sites. The fresh water flushed out the traces of older waters. The depth to which the waters were flushed out was determined by the prevailing hydraulic driving forces. The land rise gradually increased the penetration depth of meteoric water until a certain depth was reached where the hydraulic force could not remove a denser water such as a brackish-saline groundwater.

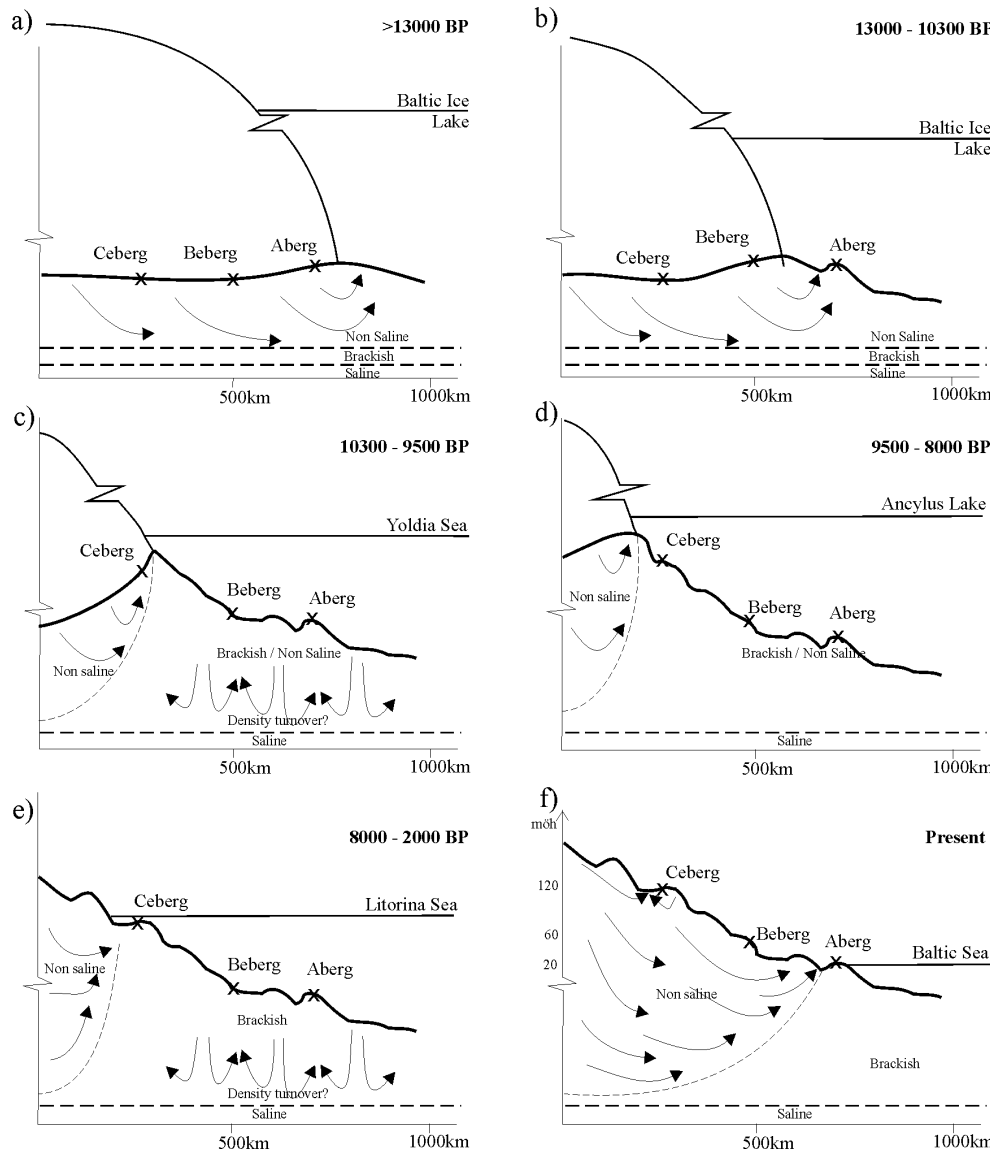


Figure 4. A conceptual postglacial scenario at the Äspö (Aberg), Finnsjön (Beberg) and Gideå (Ceberg) sites (for locations see the map in Figure 1). Possible relation to different known post-glacial stages and land uplift which have affected the hydrochemical evolution of the sites: flow lines, density driven turnover, non-saline, brackish and saline water interfaces are shown a) Injection of Glacial meltwater into the basement. b) Baltic Ice Lake stage, c) Yoldia Sea stage, d) Ancylus Lake stage, e) Litorina Sea stage and f) present day Baltic Sea stage situation (Laaksoharju, 1999).

2 SITE DESCRIPTION AND INTER-COMPARISON

In order to understand the processes that affect the hydrochemical stability of candidate repository sites, it is essential to have information on the characteristics of these sites, and the differences and the reasons for these differences between the sites.

The site inter-comparison presented here for Äspö, Finnsjön and Gideå in Sweden, and Olkiluoto, Kivetty, Hästholmen and Romuvaara in Finland (Figure 1) was based on the following:

- Compilation and summary of the geo-data
- Conceptual model of the groundwater evolution
- Groundwater evaluation of the sampled data

The results were used as background information for the modelling work described in chapter 5, and the aim for this inter-comparison was therefore not to describe the details but to summarise the major characteristics useful when modelling the groundwater features of the sites.

2.1 SITE INTER-COMPARISON SUMMARY

Table 1 gives a compilation of the site specific geo-data (Gurban et al., 2001). The information was extracted and compiled from published reports (Ahlbom et al., 1991; Ahlbom and Tirén, 1991; Anttila et al., 1999a; Anttila et al., 1999b; Anttila et al., 1999c; Anttila et al., 1999d; Laaksoharju and Wallin, 1997; Luukkonen et al., 1999; Pitkänen et al., 1999; Pitkänen et al., 2001; Rhén et al., 1997a; Rhén et al., 1997b; Ruotsalainen and Snellman, 1996; Walker et al., 1997).

The items compiled in the table are: topography, geology, fracture mineralogy, main fracture orientations, transmissivities of the fracture zones, mean hydraulic conductivity of intact rock, main water types and dominant groundwater reaction processes at the sites.

Table 1. Summary of geo-data obtained at the sites: Äspö, Finnsjön, Gideå, Olkiluoto, Kivetty, Hästholmen and Romuvaara. Data from almost a hundred boreholes with depths of 100-1700 m and about 800 groundwater samples have been evaluated (for groundwater chemical data see Gurban et al., 2001).

	Äspö	Finnsjön	Gideå
Area	S-E Sweden, on an island in the Baltic Sea, 1 km ²	E Sweden, 6km ²	N-E Sweden, 6km ²
Topography	~14 m.a.s.l.	~25 m.a.s.l. (± 15m)	~80-130 m.a.s.l.
Geology	quartz monzodiorite, medium grained granite, fine-grained granite, greenstone, mylonite	granite, greenstone, metavolcanics, gneiss-schist	veined gneiss (main rock type) and migmatite granite (subordinate rock type)
Fractures mineralogy	chlorite, calcite, epidote, fluorite, quartz, hematite/FeOOH, pyrite, clay minerals	epidote, calcite, prehnite, haematite, laumontite, chlorite, amorph. Fe ²⁺ oxy-hydrox. precip., pyrite, kaolinite, clay	calcite, chlorite, laumontite, pyrite, clay minerals (smectite and illite), epidote
Main fracture zone orientation	sub-vertical, steep; NE-1, NNW4, NNW1	zone 1 and zone 2	
Transmissivities of fracture zones	10 ⁻⁷ to 10 ⁻⁴ m ² /s	10 ⁻⁷ to 10 ⁻⁴ m ² /s	10 ⁻⁹ to 10 ⁻⁶ m ² /s
Mean hydraulic conductivity of intact rock	10 ⁻⁸ m/s	10 ⁻⁷ m/s	10 ⁻¹⁰ m/s
Origin of main water types	meteoric, marine, marine sediment, glacial, brine	meteoric, brine	meteoric, glacial
Dominant processes	inorganic redox reactions, calcite precipitation/dissolution, ion exchange, methanogenesis, microbial sulphate reduction, silicate dissolution	inorganic redox reactions, calcite precipitation/dissolution, ion exchange	inorganic redox reactions, calcite precipitation/dissolution, ion exchange

(continued on next page)

Table 1. (Continued)

	Romuvaara	Kivetty	Oikiluoto	Hästholmen
Area	N-E Finland, 7km ²	Central Finland, 6km ²	S-W Finland, on an island in the Baltic Sea, 7 km ²	S-E Finland, on an island in the Baltic Sea, 0.75 km ²
Topography	~227m.a.s.l. (d=10-30 m)	~154-219 m.a.s.l.	~5m.a.s.l. (highest point= 18m)	~16 m.a.s.l. (highest point)
Geology	gneisses, with cross-cutting migmatizing leucocratic and mafic dykes	porphyritic or equigranular granodiorites, granites and quartz monzonites	migmatitic and veined mica gneisses, quartzitic gneisses, granites, schists, pegmatites	wiborgite/pyterlite, even-grained and porphyritic rapakivi granite
Fractures mineralogy	calcite, iron sulphides, iron oxyhydroxides and clay	calcite, iron sulphides, iron oxyhydroxides, clay minerals and iron oxides and quartz	calcite, iron sulphides and clay	calcite, dolomite, clay minerals, iron oxides and oxyhydroxides
Main fracture zone orientation	inclined-vertical	vertical	sub-horizontal	horizontal – sub-horizontal
Transmissivities of fracture zones	10 ⁻⁸ to 10 ⁻⁴ m ² /s	10 ⁻⁷ to 10 ⁻⁴ m ² /s	10 ⁻⁹ to 10 ⁻⁵ m ² /s	10 ⁻⁷ to 10 ⁻⁴ m ² /s
Mean hydraulic conductivity of intact rock	10 ⁻¹¹ m/s	10 ⁻¹¹ m/s	10 ⁻¹² m/s	10 ⁻¹² m/s
Origin of main water types	meteoric, glacial	meteoric, glacial	meteoric, marine, glacial, brine	meteoric, marine, glacial, brine
Dominant processes	oxidation of Fe(II) compounds in recharge zone, silicate hydrolysis, calcite precipitation/dissolution, ion exchange, microbial sulphate reduction	inorganic redox reactions, silicate hydrolysis, calcite precipitation/dissolution, ion exchange, microbial sulphate reduction	inorganic redox reactions, silicate hydrolysis, calcite precipitation/dissolution, ion exchange, methanogenesis, microbial sulphate reduction	inorganic redox reactions, silicate hydrolysis, calcite precipitation/dissolution, dedolomitisation, ion exchange, microbial sulphate reduction

2.2 GROUNDWATER EVALUATION

The M3 code, developed for SKB, was used to evaluate, compare and model the groundwater types at the different Swedish and Finnish sites.

2.2.1 M3 Description

The new method named Multivariate Mixing and Mass balance calculations (abbreviated to M3, see Laaksoharju et al., 1999a) uses statistical procedures to analyse variations in groundwater compositions so that the mixing components, their proportions, and chemical reactions are estimated. The method evaluates the contribution to hydrochemical variations by mixing of groundwater masses in a flow system by comparing groundwater compositions to identified reference waters. Subsequently, contributions to variations in non-conservative solutes from reactions are calculated. The modelling assumes the following:

1. the compositions of the groundwaters being studied are predominantly determined by mixing of a number of chemically-distinct water types or 'reference waters',
2. deviations from this mixing model are assigned to chemical/microbial reactions,

The features of the model are:

- It is a mathematical tool which is adapted to evaluate groundwater field data, to help construct a conceptual model for the site and to support expert judgement for site characterisation;
- It uses the entire hydrochemical data set to construct a model of geochemical evolution, thus providing an important complement to standard thermodynamic equilibrium models that simulate reactions or predict the reaction potential for a single water composition;
- The results of mixing calculations may be integrated with hydrodynamic models, either as a calibration tool or to define boundary conditions;
- Experience has shown that to construct a mixing model based on physical understanding often requires more information than available especially at site scale. M3 results can provide additional information of the major flow paths, flow directions and residence times of the different groundwater types which can be valuable in transport modelling;
- The numerical results of the modelling can be visualised and presented for non-expert use;

The M3 model consists of 3 steps where the first step is a standard principal component analysis (PCA), followed by calculations of mixing proportions, and finally mass balance calculations (for more details see Laaksoharju, 1999; Laaksoharju et al., 1999a). The uncertainties have been handled in M3 by assuming an uncertainty of 0.1 in mixing units (with a confidence interval of 90%, that is, 10% of the observations could have a higher uncertainty)

and stating that a mixing portion <10% is under the detection limit of the method. In this work, M3 code was used to make PC-plots (principal component plots), for all the sites simultaneously and site by site, in order to compare the hydro-chemistry of the seven Finnish and Swedish sites (see Section 2.2.2) and to make scenario modelling by altering the calculated mixing proportions (see Chapter 5). In this report the following two modelling steps were employed:

(1) Principal Component Analysis (PCA)

A standard multivariate technique called Principal Component Analysis (PCA) is used for the clustering of the data in order to summarise the information and to construct an *ideal mixing model* for the site. The starting point is the measurement of various chemical variables for a number of groundwater samples (“variables 1, 2, 3...n”). Generally the major solutes Cl, Ca, Na, Mg, K, SO₄ and HCO₃ in combination with the isotopes $\delta^2\text{H}$, $\delta^{18}\text{O}$ and ^3H are measured. By using PCA the samples can be visualised as corresponding to points in a multi-dimensional space where the number of dimensions equals the number of different constituents. The PCA rotates the coordinate system in this space to find the optimum orientation to display the largest possible resolution of the different point clusters.

The PC-plot (Principal Component plot) is used to visualise the clustering of the data as well as to identify reference waters. Reference waters are water compositions that are selected as the component waters from which the sampled groundwaters can be derived by mixing. A reference groundwater can be any water composition but generally extreme waters or end-members such as rainwater or deep water are assigned. There are no limitations concerning how many reference waters can be selected in the modelling, but the general rule is to use as few as possible to describe the observed variations. The number of reference waters can also be guided by the type of modelling to be performed or by a conceptual model of the site.

Lines are drawn in the PC-plot between the reference waters so that a polygon is formed. The polygon defines the observations that can be described by the selected reference waters. By definition, samples inside the polygon can be described by the selected reference waters.

(2) Calculations of Mixing Proportions

The mixing proportions describe the contributions of each reference water composition to the observed water. They are inversely proportional to the distance of a sample to the selected reference waters in the plot. On a two-dimensional surface, a mathematically unique solution is only obtained from mixing proportions containing a maximum of three reference waters. If there are more than three reference waters, a centre point P is created at the weight point of the polygon. By using this centre point, mixing proportions can be assigned when there are more than three reference waters in a two-dimensional plot (Laaksoharju et al., 1999a). For a polygon containing, say, five reference waters, M3 would suggest that a sample plotting at the centre point consists of 20% of each reference water.

2.2.2 PC-Plots and Selection of End-Members

PC-plots are useful tools to compare groundwater samples collected at different sites. Figure 5 shows the PC-plots of all the sites together: Äspö, Finnsjön, Gideå, Olkiluoto, Kivetty, Hästholmen and Romuvaara (“Scandinavian” data represents groundwater data available from other sites in Sweden). A complete data set is published elsewhere (Gurban et al., 2001). In Figure 6 the sites are shown one at the time, with the data from all the sites as background information.

The reference waters (end-members) were selected so that the samples can be described. The criteria are by definition that a sample inside the polygon can be described by the selected end-members. The closer to an end-member a groundwater observation plots in the PC-diagram the more of that end-member the water likely contains. The selected end-members for the M3 modelling are (for more details see Laaksoharju, 1999):

- *Precipitation*; corresponding to the precipitation and infiltration of meteoric water from 1960. Modern meteoric water with a modelled high tritium content (2000 TU) was used to represent precipitation from that period. For modelling purposes the mean $\delta^{18}\text{O}$ (-10.5 ‰ SMOW) value from Äspö was used.
- *Marine sediment*; is an extracted pore water composition from marine sediments adjacent to Äspö. The major component chemistry in the pores resembled modern Baltic Sea values except for sulphate and bicarbonate. Based on this knowledge the modern isotope values measured from the Baltic Sea water were used since the isotopes were not analysed in the pore water.
- *Litorina Sea*; represents a modelled ancient Baltic sea water composition (8000-2000 BP) with a Cl concentration of 6100 mg/L and was modelled based on $\delta^{18}\text{O}$ analysis of microfossils from marine sediments and on measurements of interstitial water in postglacial black clays (Kankainen, 1986; Sjöberg et al., 1984). The other constituents were calculated based on dilution of ocean water to the appropriate Cl concentration.
- *Glacial meltwater*; represents a possible meltwater composition from the last glaciation >13 000 BP. Precipitation water composition was used for the major elements and the $\delta^{18}\text{O}$ isotope value (-21 ‰ SMOW) was based on measured values of $\delta^{18}\text{O}$ in calcite surface deposits (Tullborg and Larson, 1984). The $\delta^2\text{H}$ value (-158 ‰ SMOW) is a modelled value based on the equation ($\delta\text{H} = 8 \times \delta^{18}\text{O} + 10$) for the meteoric water line. However, it should be noted that the observed isotopic glacial signatures in groundwaters could also have been derived by oxygen isotope fractionation caused by gradual freezing during the development of permafrost (e.g. Gascoyne, 2000).
- *Brine water*; which represents the deep brine type (Cl = 47000 mg/L) of water found in KLX02: 1631-1681m.

Table 2 gives the analytical data for the end-members used in this study, and Figure 7 shows the location of these reference waters on a PC-plot.

The reason for building PC-plots for all the sites simultaneously, and using the same end-members, is that a larger amount of information for the different groundwater systems can be obtained, and at the same time approximate geochemical comparisons between the sites are possible. The PC-plots show similarities/differences between the sites, grouping the sites by water types, as following:

- Äspö, Hästholmen and Olkiluoto: marine sites located near the Baltic Sea, the same water types occur: marine, marine sediment, precipitation, glacial and brine.
- Finnsjön: transitional site, water types: meteoric and brine.
- Kivetty, Gideå and Romuvaara: meteoric sites the dominating water types: precipitation and glacial.

However, certain dissimilarities are observable between marine sites, particularly between saline end-members such as proportions of brine and marine water. This may result partly from differences in end-member compositions and from differences in hydraulic and geological properties of the host rocks leading to different groundwater compositions from water-rock reactions during history.

The existence of general end-members is supported by the conceptual post-glacial scenario model in Figure 4. Differences in the end-member compositions between the sites are however expected, e.g. differences in sulphate:chloride ratios in the saline groundwaters at Äspö and Olkiluoto. Therefore, the results from the mixing calculations presented here should be used cautiously, because the same end-members have been used for all sites in order to make comparison between the sites possible (see also the discussion on model uncertainties at the end of section 5.1). A more detailed modelling would require a selection of individual end-members for all the sites, but would also lead to site specific mixing calculations which are not necessary for a comparison between the sites.

Table 2. Composition of the end-members used as reference waters in the M3 modelling.

	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	HCO ₃ (mg/L)	Cl (mg/L)	SO ₄ (mg/L)	³ H (TU)	δ ² H ‰	δ ¹⁸ O ‰
Brine	8500	45.5	19300	2.12	14.1	47200	906	4.2	-44.9	-8.9
Glacial	0.17	0.4	0.18	0.1	0.12	0.5	0.5	0	-158	-21
Precipitation	0.4	0.29	0.24	0.1	12.2	0.23	1.41	2000	-80	-10.5
Litorina	3180	154.1	152.0	379.6	146.0	6100	527.3	0	-35	-5
Marine sediment	2144	91.8	103	258	793	3383	53.1	0	-61	-7

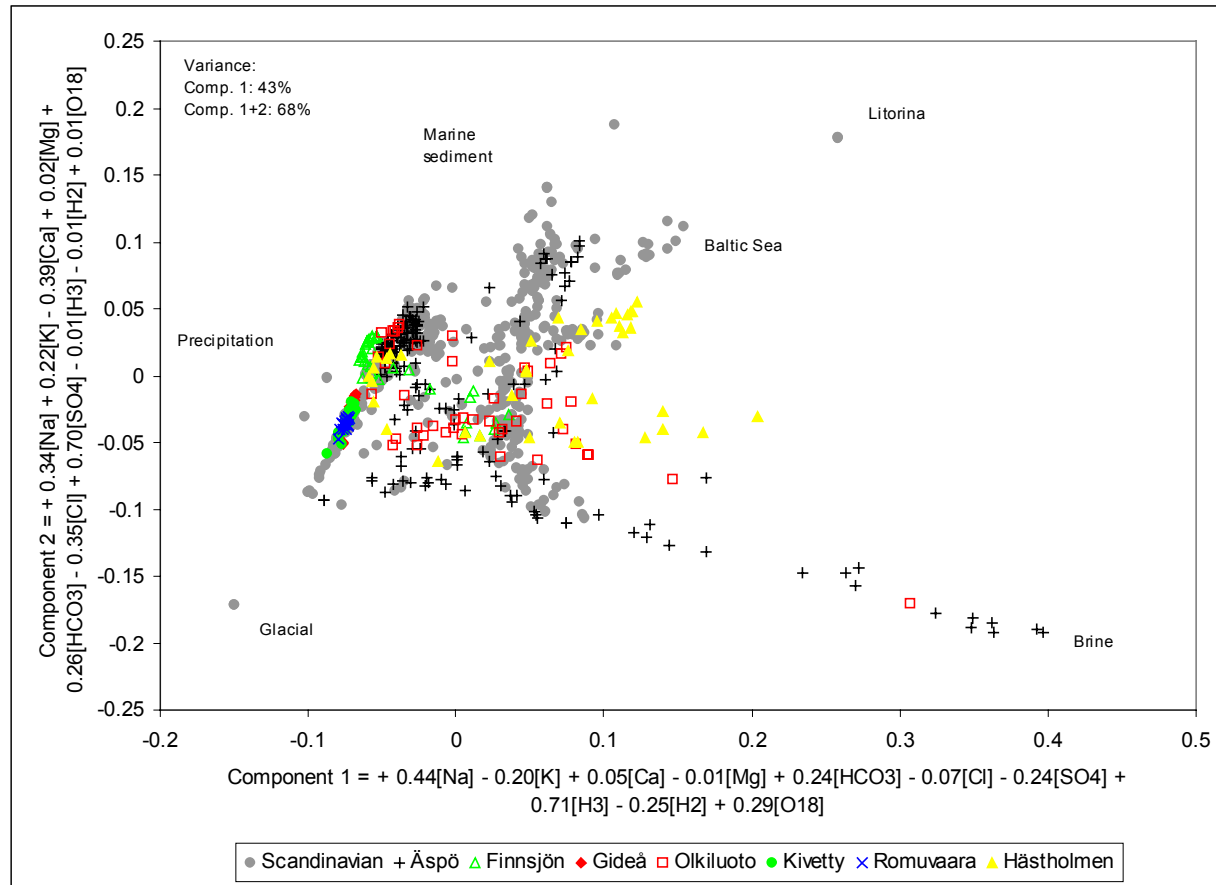


Figure 5. PC-plot, identification of end-members and of samples belonging to the different sites (“Scandinavian” = other Swedish sites sampled by SKB). The first and second principal components are based on the following chemical constituents: Na, K, Ca, Mg, HCO₃, Cl, SO₄, ³H, ²H and ¹⁸O. The location of a sample in the plot is determined by its composition: similar groundwater samples cluster close to each other but far away from samples with a very different composition. A sample plotting close to an end-member is modelled to contain more of that water than of an end-member plotting far away. The plot is therefore a convenient way to compare, summarise and model analytical groundwater data.

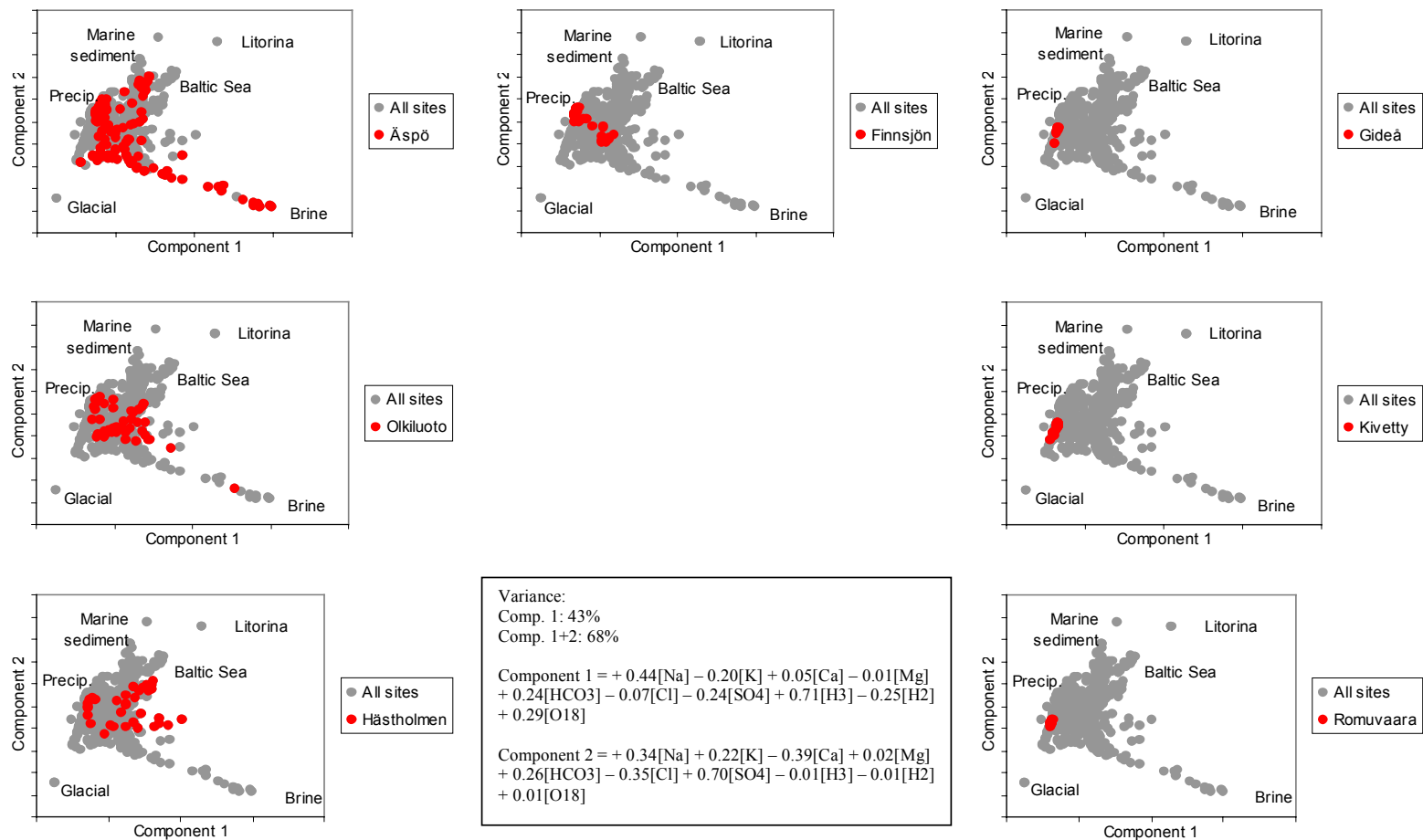


Figure 6. PC-plot for all waters with data from each of the seven sites distinguished. The coastal sites Äspö, Olkiluoto and Hästholmen seem to contain contributions from many of the end-members. The Finnsjön site seems to be a transition site where only a few end-members contribute to the obtained water composition. The inland sites such as Gideå, Kivetty and Romuvaara seem to be affected by meteoric water and plot therefore between the Precipitation and Glacial end-members.

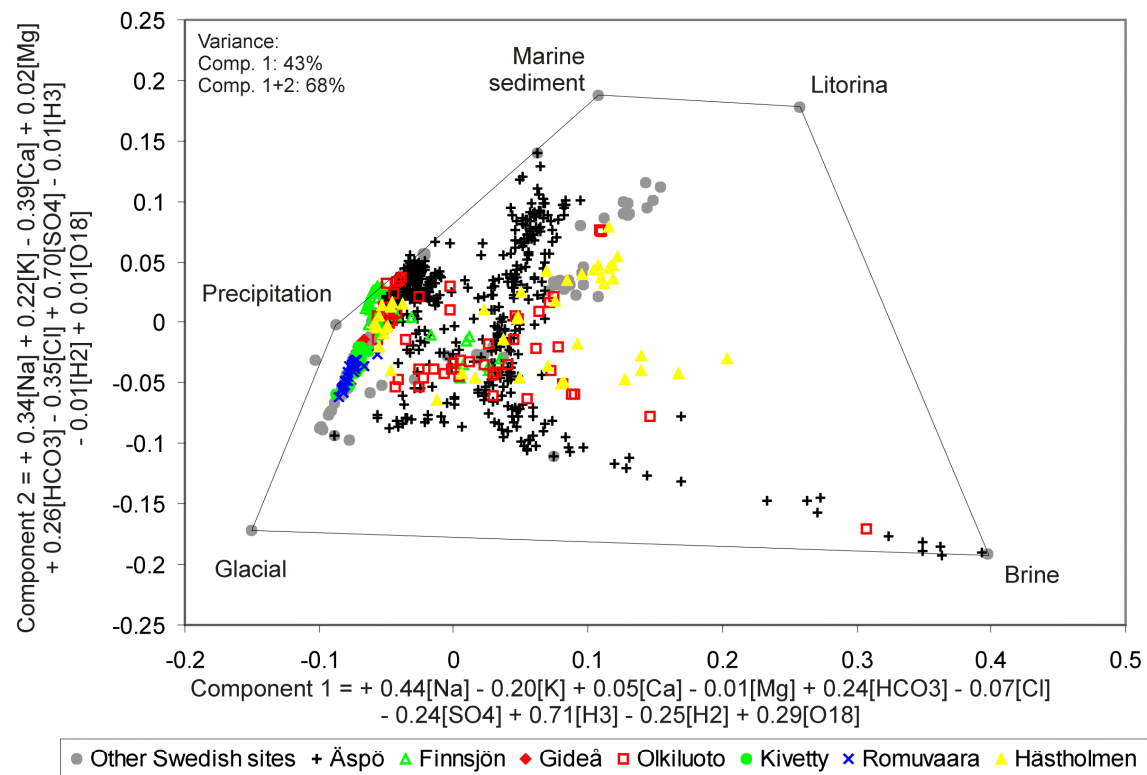


Figure 7. PC-plot, identification of the reference waters used in the mixing modelling. The polygon defines the modelled area and the observations inside the polygon are assumed to be mixtures where the selected reference waters Brine, Glacial, Precipitation, Marine sediment and Litorina contribute in various mixing portions to the observed composition (dependent of the distance from the sample in the plot to the reference water). The first and second principal components are based on the following chemical constituents Na, K, Ca, Mg, HCO₃, Cl, SO₄, ³H, ²H and ¹⁸O. "Other Swedish sites" = other sites sampled by SKB.

2.3 CONCLUSIONS FROM THE SITE INTER-COMPARISON

Geo-data from Äspö, Finnsjön and Gideå sites in Sweden, and Olkiluoto, Kivetty, Hästholmen and Romuvaara in Finland have been compiled.

A simultaneous summary analysis (PCA) has been used in order to compare the hydrochemistry of the sites. In addition, for each site a PC-plot was made, highlighting the data from each site against background data from all the sites. The diagrams show how the end-members plot with respect to the samples used for the mixing modelling (chapter 5). The plots show the similarities between the sites, by grouping the sites with respect to water types affected by the location.

The major conclusion is that site elevation and the positions of the sites with respect to post-glacial sea levels, together with water-rock interactions, play a central role in determining the water types found at each site, since the compilation of geological data (section 2.1 and Table 1) showed considerably similarities concerning geological features. This is due to the fact that the site elevation over the sea level can affect the prevailing hydrogeology at the site, which in turn determines how much of the older water types (e.g. glacial, or ancient sea water) have been flushed out and to what depth.^a This flushing out is naturally dependent on many factors, such as local and regional hydrogeology, topography, fracture frequency and orientation, rock type, etc.

As an example the mixing fractions resulting from M3 calculations at the different sites was examined in Figure 8 for the repository depth of 500 ± 100 m. The coastal sites generally show more traces of older water types such as Brine, Glacial, and Litorina at repository depth. The inland sites show generally a domination of precipitation type of water at repository depth. However, it is important to note that despite the hydrodynamic changes that have been active the groundwater can still be a relatively old meteoric water and therefore be hydrochemically stable. This type of water can thus still be favourable from the hydrochemical point of view for a final repository.

For modelling purposes the mean $\delta^{18}\text{O}$ (-10.5 ‰ SMOW) value from Äspö was used for the meteoric reference water. However, this value represents precipitation at the southern part of Fennoscandia; in the northern part the $\delta^{18}\text{O}$ mean value is -14 ‰ SMOW. This simplification results in an underestimation of meteoric water proportions and overestimation of glacial water proportion when the northern sites are modelled with M3. Nevertheless the error is within the uncertainty of the M3 method.

^a It should be noted however, that there are exceptions to this general trend. For example, the most saline groundwaters observed in Finland are at the Miihkali site (Blomqvist, 1999) situated 150 m over the sea at the eastern part of the country near the highest shoreline of post-glacial seas.

The inverse modelling results on the effects of past climatic changes (section 4.1.1) were produced using a different number and type of reference waters. The two models are therefore substantially different, and the results shown in Figure 8 (M3 results) and those in Figure 18 and Figure 19 (inverse model) can not be directly compared. Nevertheless, both procedures conclude with models for groundwaters consisting of mixtures of pre- and post-glacial waters, and qualitatively both models conform with the conceptual model presented in section 1.4.

Depth below ground surface 500m \pm 100m

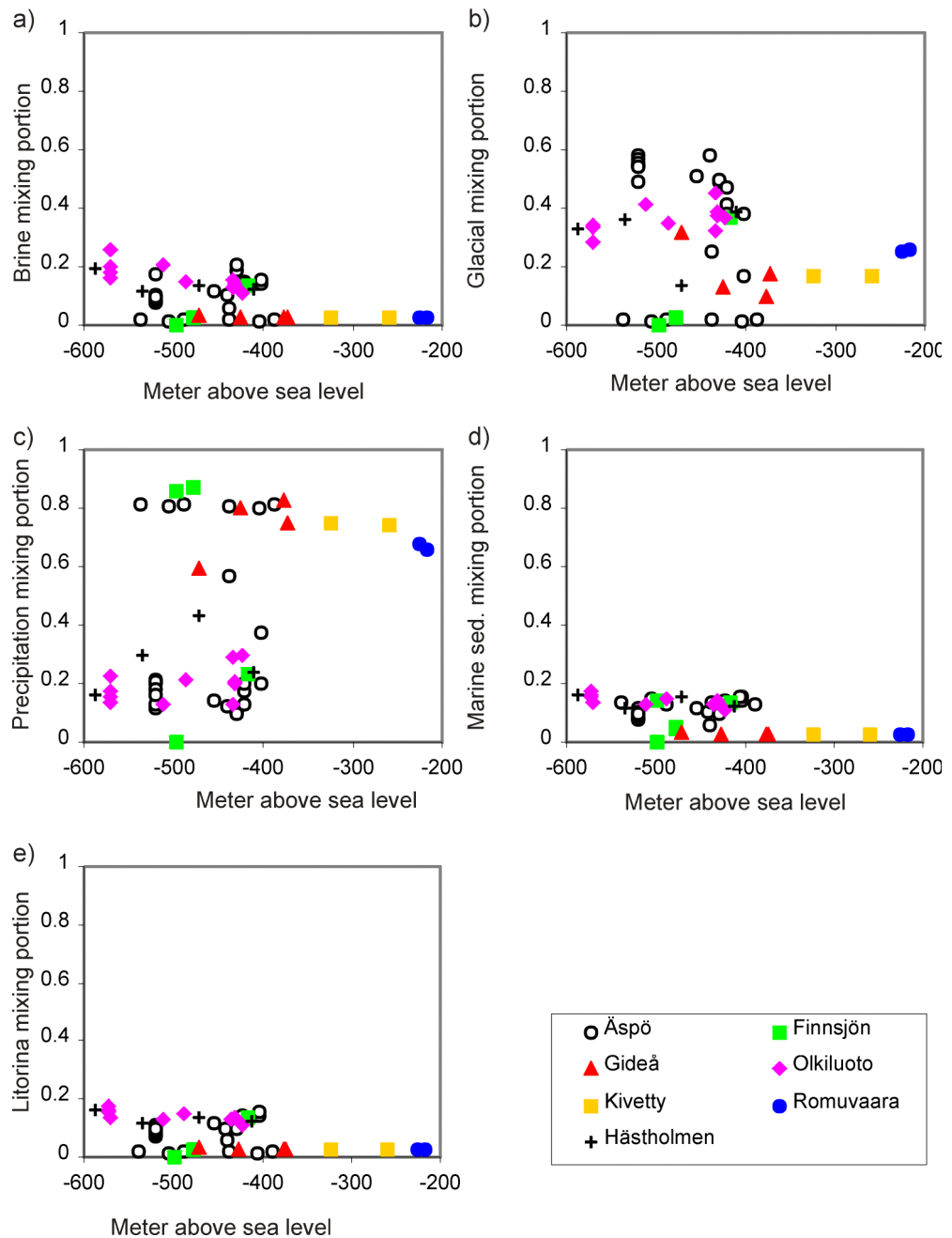


Figure 8. The dominating mixing proportions calculated by using M3 of different water types at the different sites at the repository depth of 500 \pm 100 m. In order to be able to compare the sites the depth is in relation to the actual sea level. The inland sites such as Romuvaara, Kivetty and Gideå show dominating mixing proportions of Precipitation type of water and less mixing proportions of Brine, Glacial, Marine sediments and Litorina Sea water. The coastal sites such as Hästholmen, Olkiluoto and Äspö (dependent of where the sample is taken, at the island or at the Laxemar mainland) and to some extent Finnsjön (dependent of the fracture zone sampled) show generally smaller mixing proportions of Precipitation type of water and traceable mixing proportions of Brine, Glacial, Marine sediments and Litorina Sea waters at repository depth.

3 HYDRODYNAMIC EFFECTS FROM CLIMATIC CHANGES

Climate affects the hydrodynamic conditions of a repository site (Boulton et al., 2001; SKB, 1999):

- temperate climate: the most significant effects are (related to shore-line displacements) caused by land uplift in coastal regions
- permafrost: very limited groundwater recharge due to decreased precipitation and frozen ground. Groundwater flow is mostly limited to depths where the ground is not frozen
- glaciation: possible large influx of meltwater and compression of the bedrock

The performance of a repository during the first few thousand years is most important, because this is the period of highest radiological toxicity and when radioactive decay is most intense within the spent fuel. Temperate or boreal climatic conditions are expected during this period. Numerical simulations for the Äspö and Olkiluoto sites indicate that it may be possible to model in detail the effects of climatic changes on the hydraulic conditions of these two sites during this time span. The results of some model calculations are presented below.

During periods of permafrost and glaciation the hydrodynamic conditions will be quite different from the present situation. *Upconing* is expected to take place close to the ice-sheet limit. In a simplified (simplistic?) manner upconing might be described as the upwards displacement of dense brine-type groundwater that has to compensate, with the weight of its water column, for the high hydraulic pressure created by the meltwater and the presence of some thousand metres thick ice sheet. The results of numerical calculations on this phenomenon are illustrated in Figure 9 (details may be found in the original report: Svensson, 1999a). During the evolution of the ice sheet, and the corresponding movement of the ice front, high salinities due to upconing are expected at a repository location for periods of at most a few thousand years (depending on the progression rate of the ice front)

Chemical data indicate that Glacial water (which is meltwater from inland ice sheets) is currently found at depths of a few hundred metres at Äspö (Laaksoharju et al., 1999b; Smellie et al., 1995). When this fact was realised some time ago, many questions arose, and some theories had to be revised.

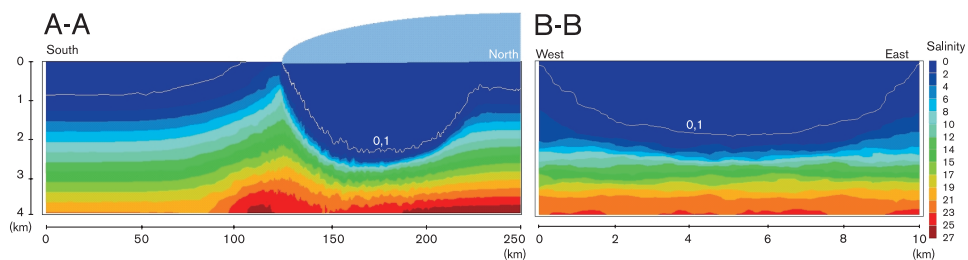
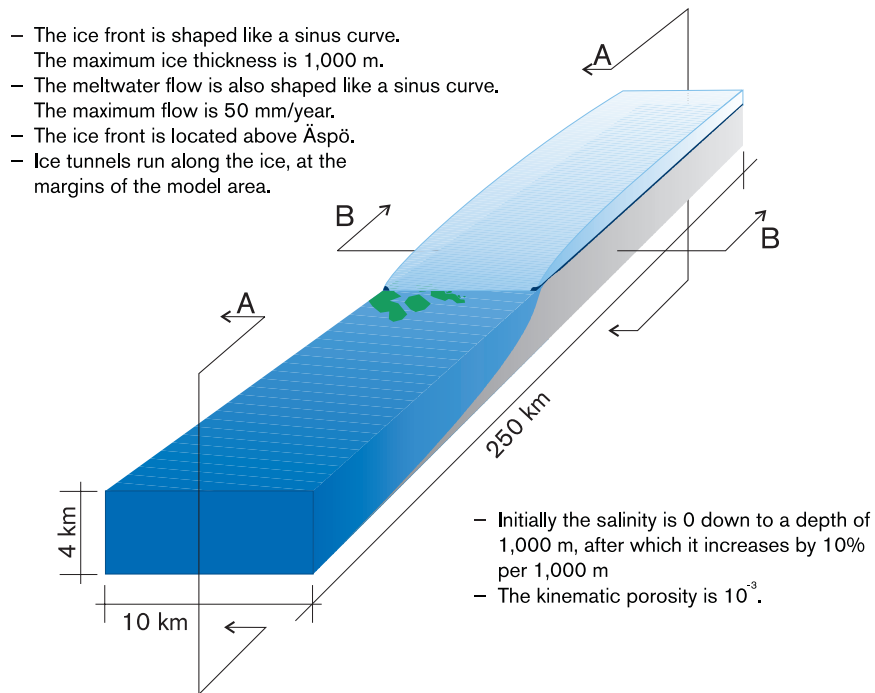


Figure 9. Salinity distributions in two vertical section showing the upconing effect when the ice front is located above Äspö (Svensson, 1999a). The east-west section (B-B) is located 25 km from the ice margin and the north-south section (A-A) in the middle of the domain.

The last inland ice left the area about 12 000 years ago and it is not clear why this water has not been replaced by younger water types. Up to about 4 000 years ago Äspö was under the Baltic Sea and exposed to seawaters of varying salinities. The period with the highest salinity, $\approx 1.2\%$, was the Litorina period at about 7 000 years ago. According to recent studies the salinity of the Litorina Sea was at least 8‰ during the time-span from 7500 BP to 2500-2000 BP (Donner et al., 1999) while the present Baltic Sea has a salinity of about 5-6 ‰. Due to the fact that seawaters were denser than glacial meltwater, hydraulic reasoning leads to the conclusion the lighter glacial waters should have been almost completely replaced by heavier seawaters, in contradiction with chemical data (see also section 3.1.3). A possible explanation for this apparent contradiction has been proposed: numerical calculations showed that both old brines and glacial meltwaters might be stored in confined vertical or sub-vertical fractures due density/gravitational effects (details for this possible mechanism may be found in Svensson et al., 2001).

3.1 A NUMERICAL SIMULATION OF THE ORIGIN AND COMPOSITION OF THE GROUNDWATER BELOW ÄSPÖ

3.1.1 Background

In chapter 2 it was concluded that it is useful to characterise the composition of the groundwater below Äspö (past, present and future) in terms of water types classified with respect to origin. As a complement to the hydrochemical analysis, it is useful to also estimate the water composition from a hydrodynamical transport model. Such simulations have been described in (Svensson, 1999b) and a brief account of that work will be given here.

An attempt was made to calculate the origin (in the time and space) of waters found below Äspö. It was assumed that the present water compositions are due to the conditions prevailing after the last glaciation (initial conditions) and the hydrological events after this time (resulting in transient boundary conditions). The total time span simulated was from 10 000 years BP (Before Present) to 5 000 AP (After Present).

The different water types were tracked by solving an advection/dispersion equation for each of the identified water types (i.e. end-members as defined by the M3 model). This novel technique is called the ‘fluid population method’ and is a simple and straightforward computational technique.

The main objective of the study was to evaluate if simulations of the kind indicated (long-term transient, 3D in space, many variables, etc) could be performed. The study was thus a feasibility test and all results presented here should be interpreted with care.

3.1.2 Conceptual and Mathematical Models

The computational domain was the same as that used in the regional model study (Svensson, 1997); a volume of $10 \times 10 \times 3 \text{ km}^3$, centred on Äspö, was considered.

During the period 10 000 \rightarrow 0 years BP the sea level and salinity of the Baltic have varied considerably, while conditions may be expected to be less dramatic during the next 5 000 years. In Figure 10 the salinity during the period is shown and the names of the different stages of the Baltic are introduced. Also the water level and groundwater recharge were considered to vary during the period. More assumptions and concepts were needed to formulate a simulation model but in this context only the main conceptual assumption will be given:

- The water composition 500 m below Äspö is determined by the conditions prevailing after the last glaciation (initial conditions) and the hydrological events after this time (resulting in transient boundary conditions).

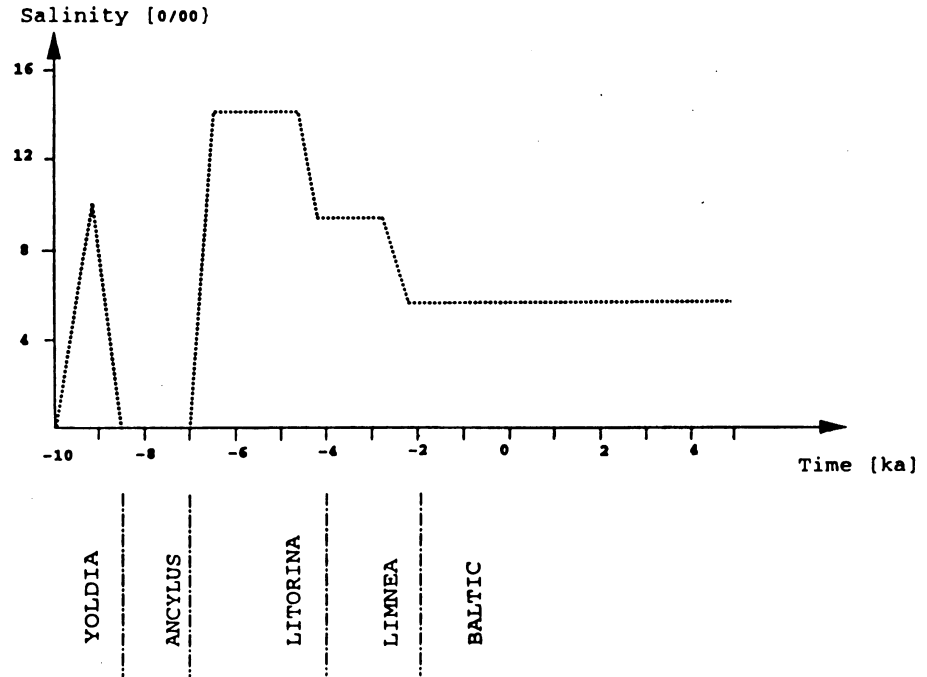


Figure 10. Assumed salinity in the Baltic for the period 10 000 years BP to 5 000 years AP.

Arguments for this statement can be found in (Svensson, 1999b).

The key elements of the mathematical model can be summarised as follows:

- Flow velocities are determined from the Darcy's law.
- Conservation equations are solved for mass and salinity.
- An equation of state relates the density to salinity.
- In order to track the various components of the groundwater an advection/dispersion equation is solved for each component:

$$n \frac{\partial c_i}{\partial t} + \frac{\partial u_j c_i}{\partial x_j} = \frac{\partial}{\partial x_j} \left(D_c \frac{\partial c_i}{\partial x_j} \right), \quad i = 1, k$$

where c_i is the marker for water type i , u_j velocity and n kinematic porosity. We will not consider dispersion effects in the present context and D_c is hence zero. To track the component that originates, say, from 8 000 to 7 000 BP (Before Present), we put the upper boundary condition to 1.0 for the relevant c -variable. The initial condition for the c is zero, which is also the boundary value for all other time intervals.

3.1.3 Results from the Numerical Simulations for Äspö

The main water types at 7 000 years BP are shown in Figure 11. From Figure 10 it is clear that only two stages of the Baltic Sea, i.e. the Yoldia and Ancylus periods, have been active at this time. However, one may of course also find water types set as initial conditions (Brine and Glacial meltwater) and Meteoric water (fresh recharge water). The Glacial meltwater fraction was found to be very small at 7 000 BP, which means that it can not dominate at later times either. The general impression from Figure 11 is that the Yoldia water dominated at this time. Meteoric water is found below Laxemar and water from the Ancylus period is found below the Baltic Sea.

The present conditions are shown in Figure 12. According to this figure the water below Äspö, at a depth of 450 metres, is composed of Meteoric and Brine water; a result that does not totally agree with existing chemical data, and it indicates that the model should be improved in the future. The Baltic water around Äspö can not penetrate into the ground as Äspö and the sea around Äspö is a discharge area. The discharge water originates from the Laxemar area and brings up the Brine water due to the circulation in the freshwater lens.

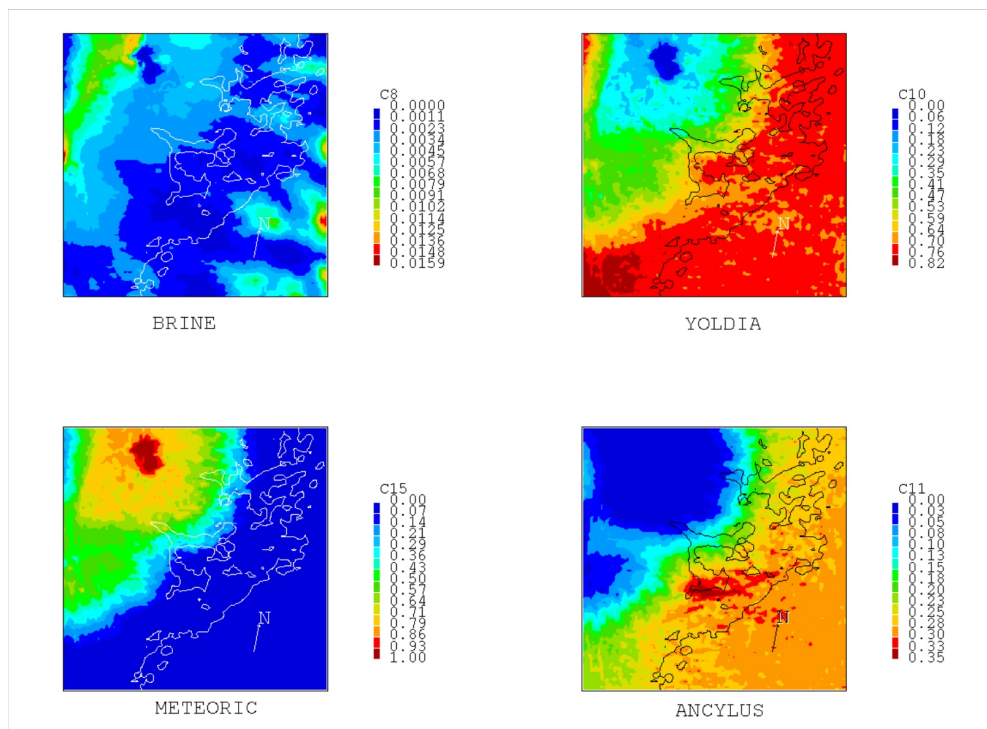


Figure 11. Horizontal sections at a depth of 450 metres, showing the volume fractions of the dominant water types. Time: 7 000 years BP.

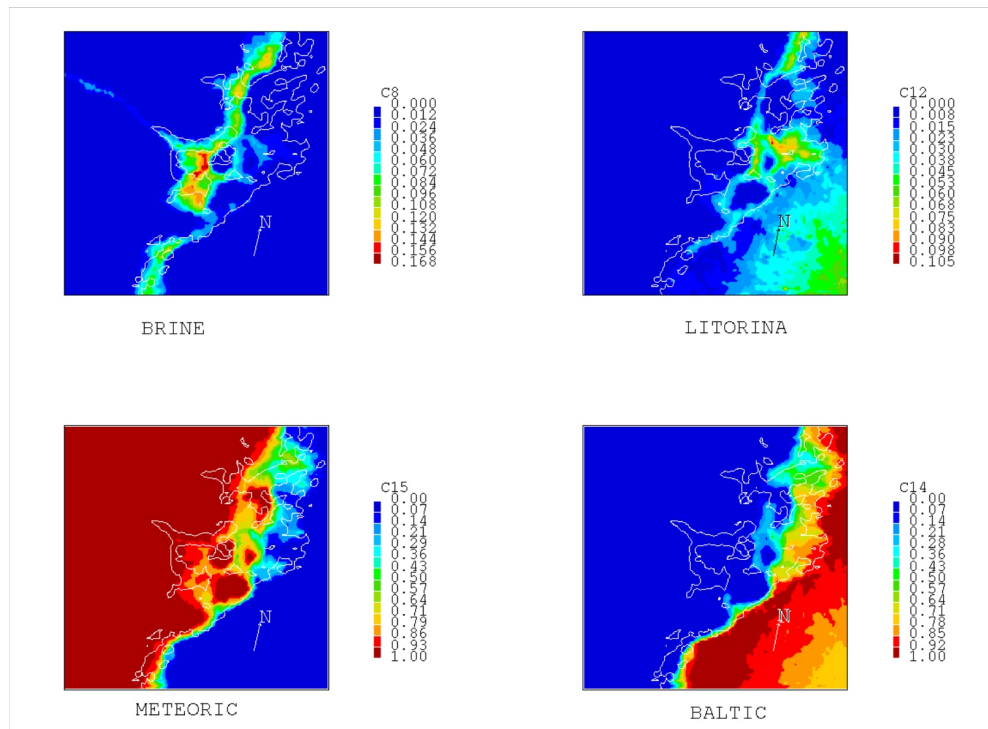


Figure 12. Horizontal sections at a depth of 450 metres, showing the volume fractions of the dominant water types. Time: 0 years BP

3.1.4 Concluding Remarks from the Numerical Simulations for Äspö

It should be kept in mind that the results presented correspond to a feasibility study. Several aspects of the simulations need to be discussed and, probably, improved. In the study of the Olkiluoto site (following section in this report) the dual-porosity concept is used to provide a mechanism for storage of water. This is certainly something that this study needs also to consider. Preliminary work on the storage problem may be found in (Svensson, 2001).

The tentative conclusion from the study in (Svensson, 1999b) is that it is technically possible to simulate the origin and composition of the groundwater below Äspö, considering a time period from 10 000 BP to 5 000 AP. However, the uncertainties about the basic conceptual model and the boundary conditions do not presently make a direct comparison with field data meaningful.

3.2 GROUNDWATER FLOW SIMULATIONS AT THE OLKILUOTO SITE

This section describes numerical groundwater flow simulations for Olkiluoto on the site scale that were performed under the EQUIP project (Bath et al., 2000). The objective of the study was to characterize the evolution of groundwater flow conditions at Olkiluoto during the postglacial period since early Litorina Stage. In addition, the impacts of the land uplift and matrix dif-

fusion on the flow deep in the bedrock in the vicinity of potential repository are evaluated. The numerical simulations have been carried out from 7500 years B.P. up to the present day. The main result quantities in this study are the salinity distribution of the site as well as the driving force and the amount of water flowing in the vicinity of potential repository.

3.2.1 Salinity Distributions at Olkiluoto

The evolution of the salinity field during the last 7500 years is illustrated in Figure 13, in which contours of concentration are presented at a SW-NE vertical cross-section located at the centre of the Olkiluoto island. Initially, the upper part of the bedrock was assumed to be saturated with brackish groundwater, which is a mixture of subglacial groundwater and glacial meltwater (Pitkänen et al., 1999). At the beginning of the simulation saline (Litorina) sea water starts to infiltrate into the bedrock through the sea bottom. The density differences result in a flow, which mixes the recharging and deeper saline waters gradually with the former brackish water. The results indicate that the mixing process is relatively fast, because groundwater in the upper part of the bedrock is nearly saline by 7000 years B.P. From about 6000 years B.P. the salinity field is practically in a steady state due to the absence of any driving forces, until the highest hills of Olkiluoto rise above the sea level due to the postglacial land uplift at about 2900 years B.P. The contours in Figure 13 show how the salinity field is evolving, when the land is gradually rising from the sea. The postglacial land uplift causes fresh water to replace brackish and saline water below the widening area of the island. Fresh water not only pushes brackish and saline water deeper in the bedrock but also along horizontal and upward directions in some areas below the sea. The computed results on the cross-section show that the present groundwater in the bedrock in the middle of the island is fresh down to the depth of the intersection of the sub-horizontal fracture zone R20HY. Figure 14, in which average salinity concentrations are presented at the depths of 150 and 400 metres in boreholes KR1-KR5, illustrates how the infiltration of sea water and fresh water affect the salinity field in the upper part of the bedrock by increasing concentration at early stages of the simulation and decreasing it at later stages.

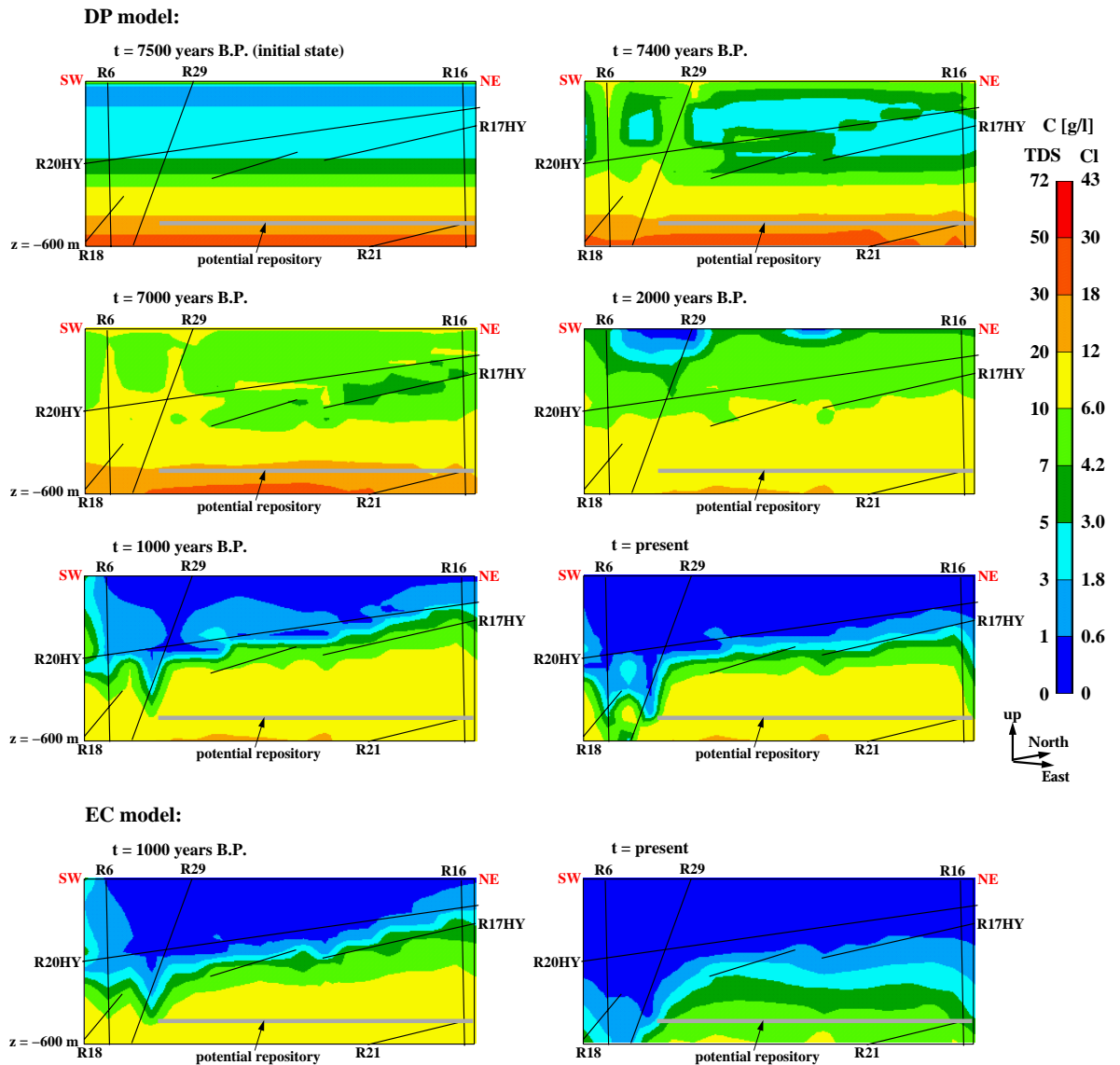


Figure 13. Evolution of salinity concentration (DP and EC model) at a SW-NE vertical cross-section located at the centre of the Olkiluoto island and extending to the depth of 600 metres.

In this study, the hydraulic characteristics of fractured rock mass are modelled conceptually with two alternative approaches: the equivalent-continuum (EC) and the dual-porosity (DP) approach (see e.g. Löfman, 2000). Concentrations presented in Figure 14 and Figure 15, which represent the values in the water-bearing part of the bedrock, indicate that up to 3000 years B.P. the results are about the same regardless of the conceptual model employed, but flow of fresh water into the bedrock results in differences in the computed salinities. Concentrations computed with the DP model tend to be higher than those of the EC model. In contrast to the EC model, in which the solution domain is assumed to contain flowing water only, the DP model in addition includes matrix blocks, which contain essentially stagnant water. Thus, in the DP approach the diffusion of solute particles from matrix blocks, which act as a storage, feed the water-bearing fractures retarding the trans-

port of solutes along with the flowing water and resulting in higher concentrations than in the EC approach. The differences are clear especially deeper in the bedrock.

In addition, Figure 15 shows that the DP model results compare better with the field values than the ones computed with the EC model. Thus, matrix diffusion is one possible explanation for the high salinities observed at Olkiluoto, although the agreement between simulated and measured values is not very good to the depth of about 200 metres. However, too far-reaching conclusions from the comparison between the simulated and measured values should not be drawn, because the simulated values represent the concentration of mobile water, while it is uncertain how the measured values are related to mobile and/or stagnant water. In addition, there are important input parameters relating to solute transport such as flow porosity, for which the field data are scarce and so they are subject to high uncertainties.

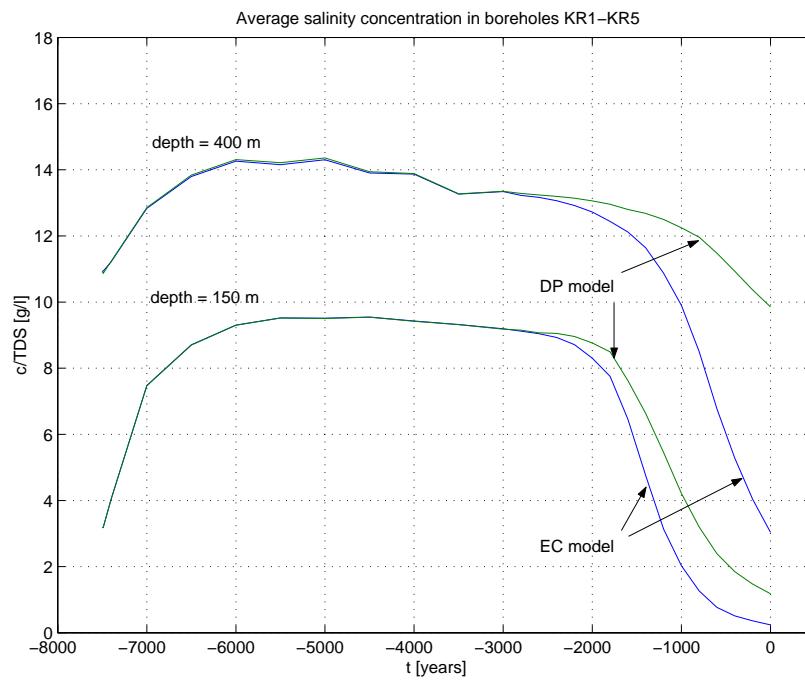


Figure 14. Average salinity concentration at the depths of 150 and 400 metres in boreholes KR1-KR5.

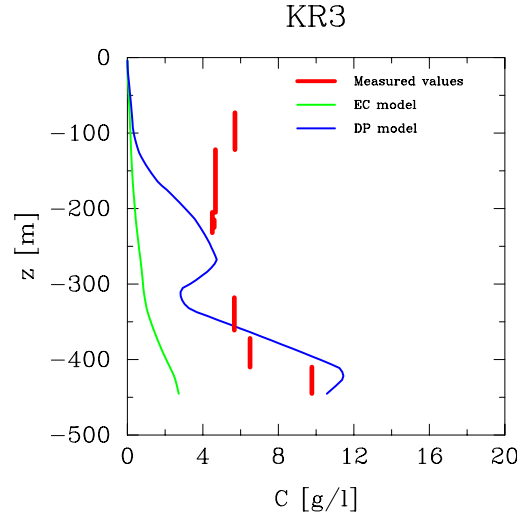


Figure 15. The measured and simulated salinity concentration in borehole KR3 presently.

3.2.2 Driving Force at Olkiluoto

In the latest site scale groundwater flow analysis at Olkiluoto (Löfman, 1999) one objective was to compute the magnitude of the driving force from the present day up to 10000 years into the future in the sparsely fractured rock (called intact rock in this study) between the repository and the nearest fracture zones. The repository was located at the depth of 500 metres and the driving force was computed within the distance of 100 metres to the repository. Because of the varying salinity concentration, the driving force was given by the combination of the residual pressure (the total pressure without the hydrostatic component of fresh water) gradient and the gravitational force as

$$driving\ force = \left| \frac{1}{\rho g} (\nabla p_r + (\rho - \rho_0)g \nabla z) \right|,$$

where p_r is the residual pressure [Pa], ρ is the density of water [kg/m^3], ρ_0 is the density of fresh water [kg/m^3], g is the gravitational acceleration [m/s^2], and z is the elevation relative to the sea level [m].

Although the repository is not included in the simulations carried out for this study, the computed driving force near the potential repository can still be used to characterise the evolution of the flow conditions deep in the bedrock. The evolution of the average driving force is presented in Figure 16. At the beginning of the simulation the infiltration of saline sea water into the bedrock results in a flow driven purely by density differences and an increase in the driving force, which stabilises to the level of 0.1 % as soon as the hydraulic conditions (i.e. salinity field) are not changing enough to have an effect on the driving forces. Regardless of the slight fluctuation the driving force remains substantially the same from about 6000 years B.P., until the highest hills of Olkiluoto rise above the sea level at about 2900 years B.P. As the land rises and shoreline moves further on, the driving force starts to increase

sharply reaching the level of 0.55 % (EC model) and 0.85 % (DP model). Up to 2900 years B.P. the results are about the same regardless of the conceptual model employed, but after that the DP model produces higher values than the EC model. The relative difference increases with time, being at its greatest (about 35-40%) during the last 1000 years. The higher driving forces produced by the DP model can mainly be attributed to the higher concentration gradients resulting from the opposite effects of the land uplift, which pushes fresh water deeper and deeper into the bedrock, and the matrix diffusion, which retards the transport of solutes (Löfman, 2000). The driving forces discussed here represent the values deep in bedrock, and, for comparison, it can be mentioned that the highest computed values encountered near the surface of the model are about 4-5 %.

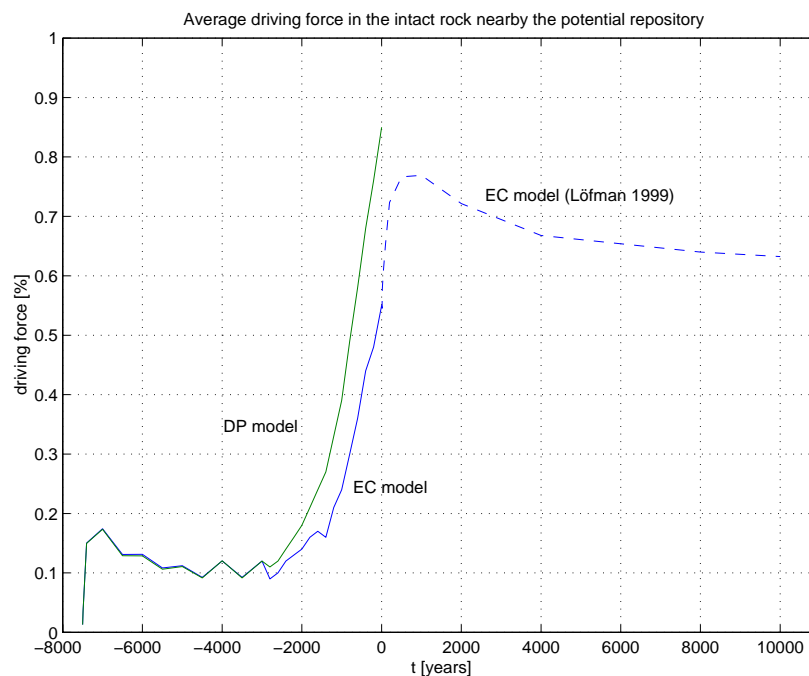


Figure 16. Average driving force in the intact rock nearby the potential repository at the depth of 500 meters.

3.2.3 Flow Rates at Olkiluoto

In the latest site scale groundwater flow analysis at Olkiluoto (Löfman, 1999) the repository and the surrounding disturbed zone were modelled as a two-dimensional plate. Due to the simplified modelling the flow distribution inside the repository could not be described in detail. However, the main characteristics of the groundwater flow in the repository could be considered by placing an enclosed control box closely around the plate representing the repository and disturbed zone, and by computing the flow rates through the faces of the box as

$$Q = \int_A \mathbf{q} \cdot d\mathbf{A},$$

where Q is flow rate [m^3/a], \mathbf{q} is the Darcy velocity [m/s] and A is the area of the face [m^2].

Like the driving forces, the computed flow rates can also be employed to estimate the flow conditions in the bedrock. The total flow rates through the control box are presented in Figure 17. Because the driving force affects directly the amount of water flowing in the bedrock, the flow rates follow quite closely the driving forces presented in Figure 16. Up to 2900 years B.P. the flow rates remain approximately on the level of $5 \text{ m}^3/\text{a}$, but after that they increase strongly and the amount of water flowing through the control box is about $33 \text{ m}^3/\text{a}$ (EC model) and $48 \text{ m}^3/\text{a}$ (DP model) presently. Again, after 2900 years B.P. the flow rates computed with the DP model are higher than the ones computed with the EC model.

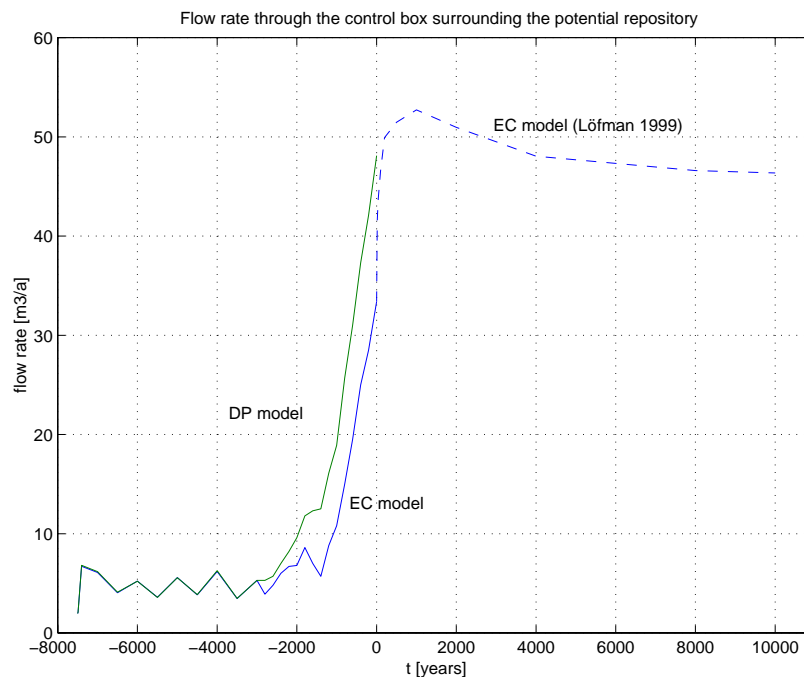


Figure 17. Flow rate through the control box surrounding the potential repository at the depth of 500 metres.

3.2.4 Summary and Conclusions from the Olkiluoto Hydrodynamic Model

At early Litorina stage at about 7500 years B.P. saline seawater starts to infiltrate into the upper part of the bedrock saturated with brackish groundwater. The higher concentration of seawater results in a driving force, which mixes the recharging and deeper saline waters gradually with the former brackish water. Because of the absence of any other driving forces, ground-

water flow is driven purely by density differences, until the highest hills of Olkiluoto rise above the sea level due to the postglacial land uplift at about 2900 years B.P. As the land rises, the driving force starts to increase sharply and fresh water starts to recharge into bedrock pushing brackish and saline groundwater deeper.

Concentrations computed with the DP model tend to be higher than those of EC model. In addition, the DP model produces higher driving forces than the EC model due to the higher concentration gradient. Thus, matrix diffusion is not only retarding transport of solutes but also having effect on flow.

4 POSSIBLE HYDROGEOCHEMICAL EFFECTS FROM CLIMATIC CHANGES

Hydrochemical effects are coupled to the hydraulic changes discussed in chapter 3. Three main climate scenarios are expected during the next 100 000 years (Boulton et al., 2001; SKB, 1999):

- Temperate and boreal: shoreline movements will affect the salinity of the groundwater.
- Permafrost: the main expected chemical effects are,
 - Salt exclusion caused by freezing might increase the salinity.
 - The solubility of carbonate minerals increases with decreasing temperature, and this might affect the fracture filling minerals at shallow depths. On the other hand, increased salinity caused by freezing would cause calcite oversaturation instead.
 - Low temperatures might reduce significantly the rate of microbially mediated redox reactions, and low biological production will decrease the infiltration of dissolved organic carbon (DOC).
- Glacial:
 - As in the case of permafrost, low temperatures will in general reduce the rates of many chemical reactions, especially microbial processes.
 - Erosion and the lack of biological activity will result in an almost complete decrease in the infiltration of dissolved organic carbon (DOC)
 - Zones under the ice-sheet where the ground is frozen: the situation will be quite similar to that of a permafrost climate described above
 - Zones where melting occurs at the ice-ground interface: meltwaters will decrease the salinity under the ice-sheet, while upconing might increase the salt content in the ice marginal zone. Meltwaters might be O₂-rich because of reduced biological activity in the sub-glacial soil, and these waters might penetrate at depth through conductive vertical fracture zones.

Temperature and salinity effects (with a salinity remaining within the limits of present day groundwaters at the sites) are not expected to endanger the functionality and integrity of the bentonite barriers and copper canisters. All the repository systems and engineered barriers should perform properly at least at groundwater salinities ranging from fresh waters to TDS = 35 g/L (Vieno, 2000). However, for saline groundwaters having TDS \geq 35 g/L there is a need to develop alternative tunnel backfill options to those in the present KBS-3 reference backfill system. Furthermore permafrost might have an effect on the performance of the backfill. In order to be able to estimate the future evolution of groundwater salinities, it is necessary to consider past climatic effects on groundwater compositions and any evidence for these effects in fracture infills.

The infiltration of O₂-rich meltwaters, which has been postulated as a mechanism by which oxidising conditions could reach repository depths, has been debated on speculative and modelling grounds in several reports (Gascoyne, 1999; Glynn et al., 1999; Guimerà et al., 1999; Puigdomenech et al., 2001). Therefore the emphasis here has been on reviewing experimental evidence on whether such oxidising environments may have occurred in the past.

4.1 CLIMATIC EFFECTS ON MIXING AND SALINITY

4.1.1 Effects of Past Climate on Contemporary Groundwaters

Before attempts to predict how future climatic changes could affect the groundwater compositions currently found in the research sites there is a need to understand how past climatic changes have affected the groundwater compositions.

Calculations of mixing proportions of reference water types in sampled groundwater have contributed substantially to the present understanding of past climatic effects on these groundwaters. The problem of finding the mixing proportions can be solved both by principal component analysis (see section 2.2) and with the inverse modelling approach (see e.g. Parkhurst, 1995; Parkhurst et al., 1980; Plummer et al., 1983; Wolery, 1979). The latter technique is illustrated here using three examples: Olkiluoto, Hästholmen and Äspö, which outline how the Quaternary climatic changes have affected the distribution of the reference groundwater types. Details on these models have been published elsewhere (Luukkonen, 2001; Pitkänen et al., 1999; Pitkänen et al., 2001). The depth distributions shown in the figures below illustrate the undisturbed bedrock conditions, i.e. conditions before tunnel and shaft excavations.

Figure 18 shows the approximate reference water type distributions in the coastal Olkiluoto and Hästholmen islands. On both island areas recharge of meteoric water to shallow depths is taking place. Groundwater sampling programmes have been concentrated below the islands. Therefore, the diagrams do not give indications on how the Baltic Sea water has infiltrated into bedrock below the sea areas surrounding the islands. In both sites at depths around 100-600 m the residual Litorina Sea water (around 100-300 m) and sub-glacial^a types (below 300-400 m) are dominant. In the 100-600 m depth interval the proportion of Pleistocene glacial melt is frequently 10-30 % in both sites. According to the Olkiluoto and Hästholmen interpretations the glacial melt contamination gradually vanishes at depths around 700 m and 1000 m, respectively. At the same time the proportion of saline reference water grows almost linearly practically to 100 %.

^a Pre-glacial groundwater modified during a glacial period e.g. by permafrost

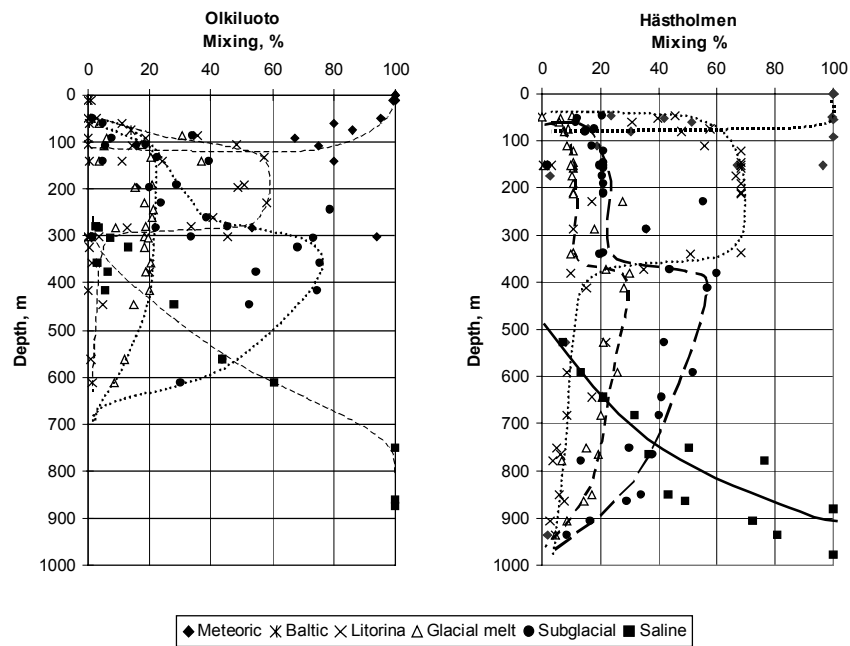


Figure 18. Depth distributions of reference water types in Olkiluoto and Hästholmen (Pitkänen et al., 1999; Pitkänen et al., 2001).

Figure 18 indicates that *in the site scale* there are no clear signs of density turnover phenomenon where the Litorina Sea water would have infiltrated through earlier recharged fresh or brackish reference water type layers. As Table 1 indicates the sub-horizontal/horizontal fracture systems are dominant features both in Olkiluoto and Hästholmen, and these fracture systems may have hindered or slowed down the turnover process. It may be possible as well that the density differences between seawater and the groundwater mixture receiving it during the Litorina recharge were not large enough to cause effective density turnover.

Figure 19 represents the estimated reference water type distribution diagrams for Äspö. The results from inverse modelling calculations lead to similar results as in Olkiluoto and Hästholmen. In this case also, the pre-investigation undisturbed groundwater sampling in Äspö was concentrated in the bedrock below the island. The illustrated Baltic Sea water proportion is based on samplings from sea-connected sub-vertical fracture zones. The geochemical interpretation of groundwaters from Äspö differs from Olkiluoto and Hästholmen in that it contains an additional postglacial altered seawater type (i.e. altered marine, see section 2.2.2). In the modelling calculations this altered seawater type stood for seawater that has infiltrated through biologically active sea bottom during the Äspö postglacial history.

There are a couple of differences between Olkiluoto and Hästholmen (Figure 18), and Äspö (Figure 19). It seems that both the meteoric and fresh Baltic Sea reference waters in Äspö have infiltrated to deeper depths than in

Olkiluoto or Hästholmen. However, the infiltration depth of glacial melt seems approximately similar between Äspö and Hästholmen, while it is significantly less in Olkiluoto. At least partially, these differences can be addressed to the differences between the fracture zone systems. The prevailing fracture zone orientation in Äspö is steep or sub-vertical (Table 1). There are clear differences in the saline reference type composition as well. In the case of Äspö (TDS 24.1 g/L) and Hästholmen (TDS 31.8 g/L) the most saline undisturbed samples found below the islands were chosen as the saline reference. In the case of Olkiluoto (TDS 35.2 g/L) the saline reference was chosen discarding the most highly saline sample found.

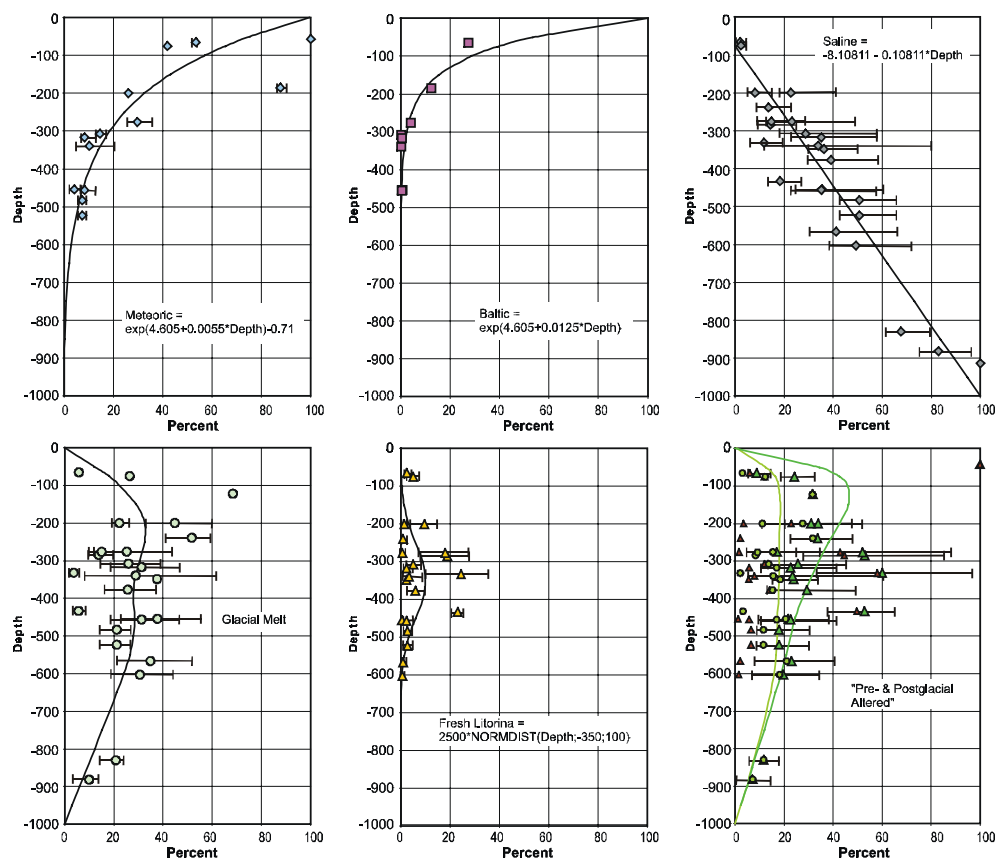


Figure 19. Depth distribution of reference water types in Äspö (Luukkonen, 2001). Observed mixing fractions of meteoric (blue diamonds), fresh Baltic (violet squares), saline (grey diamonds), glacial melt (light green circles), fresh Litorina (orange triangles), "preglacial altered" (green circles) and postglacial altered (red triangles) references in studied samples. Cumulative extreme mixing fractions stemming from analytical uncertainties of Cl and $\delta^{18}\text{O}$ are shown with error bars. The sum of "pre- and postglacial altered" fractions are marked by dark green triangles. Depth distribution regressions are shown with solid lines.

The results from the inverse geochemical modelling presented in this section and those from the M3 analysis (section 2.3) can not be compared directly, but they agree in general terms with the conceptual model presented in section 1.4: both consider the sampled groundwaters as mixtures of pre- and post-glacial waters. The agreement is surprisingly good when taking into account the differences in the approaches, and in the number and compositions of the reference-waters. The choice of the saline reference water has a particularly large effect on the results of the models (Luukkonen, 2001).

Both the general information about the past climatic events (Eronen and Olander, 1990) and the data from geochemical tracers sampled in the groundwaters become increasingly blurred back in time. These facts make the detailed geochemical interpretation of the sites beyond the Quaternary impossible with present knowledge. However, in the case of Olkiluoto (Pitkänen et al., 1999) and Hästholmen (Pitkänen et al., 2001) the highly saline groundwater compositions at depth suggest that elevated temperature processes occurred early in the history of the sites. These indications set the approximate maximum interaction depth for the Quaternary events illustrated in Figure 18. Keeping in mind the coastal topographic positions and structural differences between the sites it seems that the maximum depth to where the Quaternary climatic changes can be tracked down is about 1000 m depth in Hästholmen and somewhat less than 1000 m in Olkiluoto. In the case of Äspö, detailed brine composition studies can not be performed due to lack of information. It was assumed that the saline reference chosen was sampled deep enough (914 m deep) for justified mixing calculations indicating similar Quaternary coverage depth as in the Finnish sites.

4.1.2 Evidence for Climatic Effects in the Past from Fracture Filling Minerals at Äspö: Calcite

4.1.2.1 The EQUIP project

The EQUIP project (Bath et al., 2000) studied the ‘Evidence from Quaternary Infills for Palaeohydrogeology’ and had a 3 year duration, finishing in January 2000.

The main part of the studies investigated recently-formed secondary minerals that occur in the fractures of crystalline rock ('Quaternary infills'). The study sites for these investigations were Sellafield in the UK, Äspö/Laxemar in Sweden, Olkiluoto in Finland, and Vienne in France. The first three of these sites were covered by ice sheets and also had prolonged periods of permafrost during Quaternary glacial periods.

In addition to the studies of deep groundwater systems by fracture-filling minerals, some studies of evidence for past environmental change in the near surface have been carried out at sites in Spain and England. These have involved various approaches including studies of fossil microfauna and geochemical evidence in Quaternary clastic and organic sediment deposits and studies of carbonate deposits ('speleothem') in shallow karst systems. The work carried out in EQUIP comprised:

- Review of palaeoclimate, hydrogeology and geochemistry information for the study sites, and of conceptual models for palaeohydrogeology;
- Characterisation of fracture minerals in drillcores from the crystalline rock study sites, using petrographic methods to identify the most recently formed minerals (especially calcite);
- Detailed petrographic and geochemical analyses of the recently-formed calcites, and interpretation of geochemical environments in which they formed;
- Studies of sediment deposits in Spain and of speleothem in England to obtain information about past climate and hydrological environments in the Quaternary;
- Interpretation of palaeohydrogeological significance of geochemical/mineralogical information, and evaluation of the general approach.

4.1.2.2 *Synthesis of results from Äspö*

Calcite from open fractures mainly at Äspö and Laxemar, sampled at depths ranging from 25 to 1600 m, have been analysed. Results show that several generations of calcite can be identified, chemical zoning is common, and the influence on calcite precipitation of fresh or marine water decreases with depth. It can be concluded that fine scale zoning, possible dissolution/redistribution of calcite, and the disturbances caused by drilling (where loose material probably containing young calcite precipitates was lost), introduce difficulties in the separation of different calcite generations. Thus, the timing of different calcite generations is hard to establish.

The compilation (Bath et al., 2000) of the existing data results in identification of 6 calcite generations precipitated in different environments (see also Figure 20):

- a) Low temperature;
 - 1) Possible recent meteoric,
 - 2) Brackish,
 - 3) Marine,
 - 4) Glacial
- b) Increased temperatures
 - 5) Warm brine
 - 6) Hydrothermal (oldest).

Occurrence of calcite types 1 to 4 decrease with increasing depth, whereas calcite of type 6 and to some extent calcite of type 5 increase with depth. Calcite generations of type 5 and 6 constitute the thickest precipitates (mm thickness) whereas the low temperature calcite constitutes extremely thin coatings or rims (μm thickness) on older hydrothermal calcite precipitates. Reliable age determinations of the low temperature precipitates are therefore very difficult to obtain.

It is remarkable that calcites precipitated from brackish and marine water are only found down to ca 500 m depth whereas calcites with meteoric/cold climate recharge signatures can be traced to larger depth, possibly as deep as

1000 m. One explanation for this may be differences in hydraulic head: during phases when Äspö/Laxemar is covered by sea (brackish or oceanic) the lack of hydraulic driving force does not allow deep penetration of the marine water. The penetration depth for marine water is partly determined by the difference of the density of the penetrating water and the water in the rock. The penetration stops when the difference is equalled out. In contrast when the area is situated above sea level the hydraulic situation is more in favour of recharge to large depths. The topography (with higher elevations at Laxemar and lower at Äspö) should also suggest a difference in hydrogeology at these two areas, which is also indicated in the results from EQUIP: the calcites with meteoric signatures can be traced to greater depth at Laxemar than at Äspö.

A tentative model of the past and present groundwater circulation is shown in Figure 21. Three different zones can be recognised. The upper 0-100 metres are characterised by a dynamic situation including dissolution and precipitation of new calcite. During some phases, biogenic activity has been significant, producing reducing conditions, whereas during others phases oxidising conditions may have prevailed. At depth below 100 m down to ≈ 700 m (or possibly down to 1000 m) mainly precipitation (or recrystallisation) of calcite is detected. Several generations are common at these depths. Redox conditions have probably been stable and reducing, and contributions of biogenic carbonate is detected in terms of low carbon isotope values and high contents of Mn, La and Ba. At even larger depth recent calcite precipitation is rare and the biogenic input seems to be insignificant.

The observed distribution pattern of the different calcite generations is the net effect of calcite/fluid interactions (and also of subsurface microbiological activity during long periods) during the entire geological history of the Äspö granitoids. The hydrothermal calcite (type 6) is the most widespread fracture calcite precipitation. It is probably related to the regional hydrothermal alteration along fractures and fracture zones that occurred early in the geological history of the granitoids at Äspö. The subsequent dissolution and replacement of the hydrothermal calcite by calcite from younger groundwater regimes have been repeated during long time periods since then. When the sedimentary cover on the shield was thick the temperatures may have been high enough to precipitate calcite from a brine type of water (calcite 5). It is expected that the present rock surface has been exposed since the Late Tertiary if not before.

The depth distribution of different calcite types indicates stability in large-scale groundwater circulation, but in detail large variations in depth may have occurred. For example, attempts to correlate calcite/groundwater pairs from specific borehole locations indicate that there is no equilibrium with the present groundwater. Nevertheless, the large-scale pattern of calcite types and the groundwater chemistry are in rough correspondence.

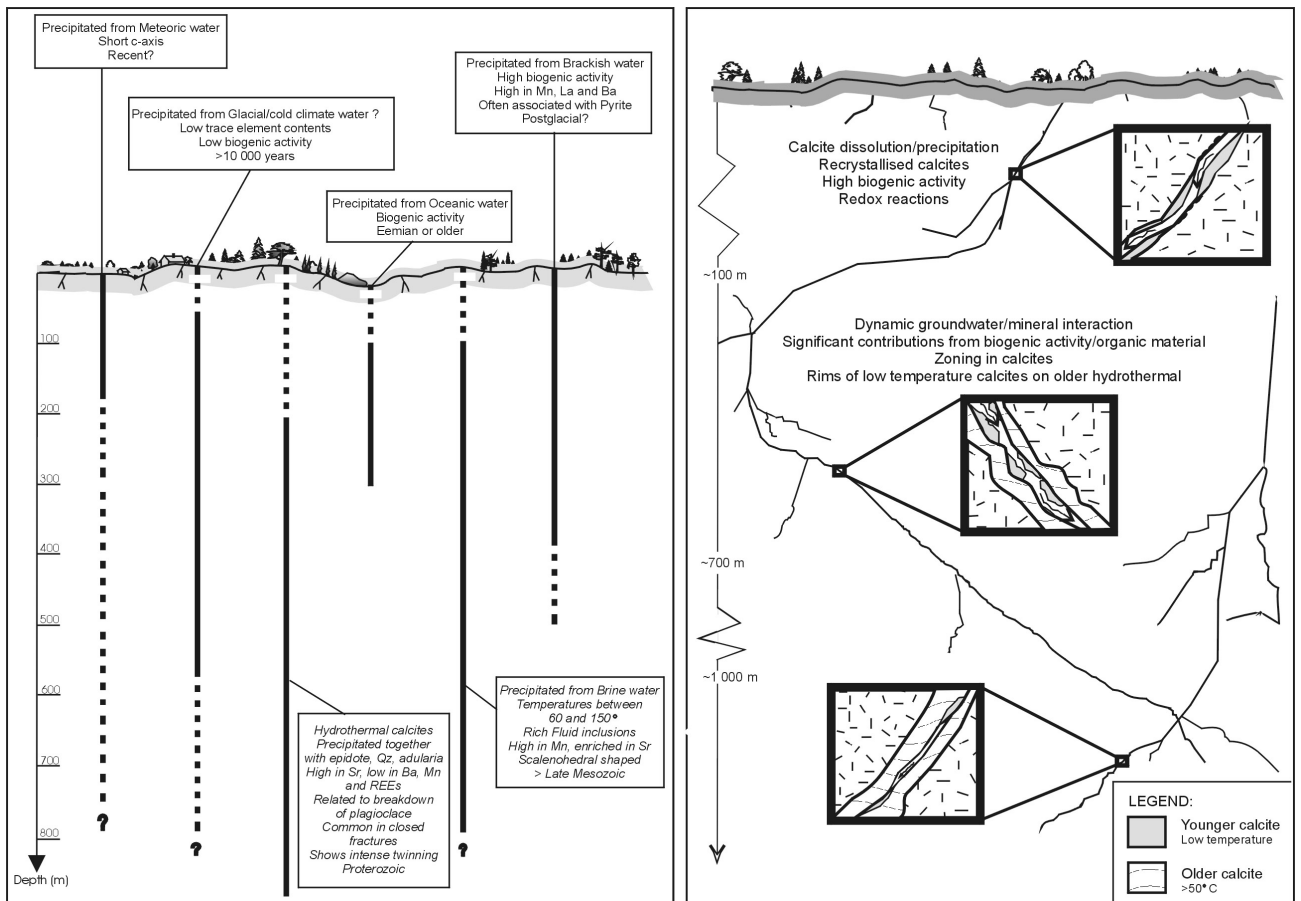


Figure 20 (left). Depth distribution of different calcite types at Äspö. Classification is based on stable isotope data supported by all other available information (trace elements, morphology, fluid inclusions etc).

Figure 21 (right). Tentative sketch of calcite/groundwater interaction at various depths at Äspö (refer to text).

The chemical, isotopic and morphological information from Äspö/Laxemar show that water of varying salinity has been involved in the calcite precipitation processes (Bath et al., 2000). One generation of calcites, rich in two-phase fluid inclusions with a high salinity was interpreted as precipitates from brine water. These calcites show scalenohedral shape (indicative of precipitates from water with salinities over 1000 ppm in Cl; Milodowski et al., 1998) and temperature estimates from fluid inclusion together with $\delta^{18}\text{O}$ mostly in the range of -10 to -17 ‰ SMOW, elevated Sr ratios (100 to 250 ppm), indicate possible formation temperature in the range of 60 to 150°C. This type of calcite is probably older than late Mesozoic (100 million years) and younger than 1400 million years, and is interpreted to originate from allochthonous source fluids (sedimentary brine water) when the shield was covered with sedimentary rocks during Riphean or Palaeozoic eras.

Also younger saline water can be traced in the low temperature varieties of calcite where brackish and marine origins can be traced down to 500 m depth.

4.2 REDOX CONDITIONS AND O₂ INTRUSION/UPTAKE

4.2.1 Use of Fracture Mineral Frequencies and Compositions for the Determination of Redox Fronts

Surface waters contain dissolved oxygen whereas groundwaters are mostly reducing and have no measurable content of dissolved O₂. This means that oxygen in the recharge water is consumed either in the soil cover or in the fractures in the bedrock. These redox reactions mostly involve iron, sulphur and carbon and can be dominantly biogenic or inorganic. Microbes use organic carbon present in the soil to consume oxygen very rapidly in the groundwater.

If organic material is transported into the bedrock aquifer anaerobic respiration using Fe³⁺ or SO₄²⁻ to oxidise the organic carbon may take place. In such cases Fe²⁺ minerals and sulphides (e.g. FeS) are produced instead of being consumed and the reducing capacity thus increases along the fractures. In other areas where the soil cover is thin or poor in organic material, oxidising water will reach the bedrock and cause oxidation of Fe²⁺ minerals and sulphides along the fractures down to different depths depending on the hydrogeological conditions.

In both cases fracture minerals like FeOOH, pyrite and calcite, will be influenced. The presence of Fe-oxyhydroxide in fractures at depth may be interpreted as result of recent oxidation (Glynn et al., 1999) but may also have a hydrothermal origin, it is therefore important to study these fracture precipitates in detail in order to get more information about their history, formation conditions, etc.

Therefore mineralogical site characterisations might indicate past occurrences of redox events, and they can give an indication on the sensibility for future intrusions of O₂-saturated waters. This is exemplified here by comparing the Klipperås and Äspö sites.

4.2.1.1 *Klipperås*

The Klipperås area (Figure 1) is located within granitoids belonging to the Transscandinavian Igneous Belt (TIB) i.e. the same rock type as at Äspö. The metamorphic history is also similar in the two areas. However the Äspö area is situated close to the anorogenic 1.4×10⁹ years old Götemar intrusion. The interpretations of the origin of the different generations of fracture fillings are given in (Tullborg, 1989). The topography of the Klipperås area is quite flat at an altitude of 170-200 m.a.s.l., which means that it is situated above the highest Late Weichselian shoreline. Outcrops are almost missing in the area and the geological mapping is based on drillcores and geophysical measurements (Olkiewicz and Stejskal, 1986). The Quaternary deposits are primarily of till mainly consisting of small boulders and gravel. The mean soil

depth is 4.2 m. In depressions the till is covered by peat bogs. Hydraulically the site is a recharge area with local discharge in the lower parts.

The groundwater chemistry has been evaluated in (Smellie et al., 1987). Seven sections in three boreholes at vertical depths from 326 m to 860 m, were selected for groundwater sampling. All groundwaters sampled showed freshwater characteristics. Only three of the sections were considered as representative based on water budget calculation and content of drilling fluid (Smellie et al., 1987). Two groundwater types were indicated; near-surface origin (Ca-HCO₃⁻-type) and intermediate type (Na-Ca-HCO₃⁻-type). The intermediate water type showed a somewhat higher Cl⁻ content although all waters sampled had Cl⁻ values below 51 mg/L. Tritium was below detection limit in the representative samples. The ¹⁴C content in two samples, Kl 1:406 m and Kl 9:696 m was very low (2-3 pmC) and the δ¹³C between -17.0 to -15.7 ‰. Two alternative interpretations were given in (Tullborg, 1989): *a*) the carbon isotopes indicate a very long residence time for the water or *b*) they are a result of repeated dissolution and precipitation of calcite which cause apparent high ¹⁴C ages and might perhaps yield low δ¹³C as well.

Results presented in (Tullborg, 1989) show that oxidising surface waters, unsaturated in respect to calcite have affected the fractures in the upper part of the bedrock at Klipperås. The absence of calcite and pyrite corresponding to a presence of Fe-oxyhydroxide was observed to a depth of between 20 to 50 m, and in fracture zones as deep as 120 m. Fe-oxyhydroxide was also found in fracture zones at even larger depths (200 to 700 m). This was not attributed to recent oxidation since it was related to the presence of hematite and no dissolution of calcite was observed. Two alternative explanations are given in (Landström and Tullborg, 1990); the Fe-oxyhydroxides may have been formed as a result of low temperature water/rock interaction in the hematite-bearing, hydraulically conductive fractures or may have been formed during the last phase of the hydrothermal event when the hematite was formed.

The oxidised character of the fractures in the upper part of the bedrock together with the absence of calcite emphasise the sensitivity in such an area for example to acidification, and the low reducing capacity, which might be important in case of injection of e.g. glacial meltwater saturated with O₂.

4.2.1.2 Äspö

The hydrological situation at Äspö (Figure 1 and Table 1) is characterised by a low hydraulic gradient. The recharge/discharge takes place mainly in tectonic zones and major fractures of which the EW-1 zone is the major recharge feature (Smellie et al., 1995). The surface geology is characterised by outcrops, depressions with peat bogs or clayish gyttja. Surface related dissolution of calcite is indicated in the upper 10 m, and in fracture zone EW-1, down to ≈ 50 m depth (Tullborg, 1988). However, calcite is not totally removed even in the shallowest parts and trace element analyses in calcites

from 25-30 m depth in the EW-1 zone show negative Ce-anomaly which mirrors the chemistry of the water from which the calcite precipitated and in turn points to closeness to a redox front (Bath et al., 2000). Generally, the low hydraulic gradient together with the organic/microbial activity creates a reducing water chemistry at shallow depth and prevents calcite dissolution.

4.2.1.3 Comparison between Klipperås and Äspö

Characteristics and critical parameters of the two areas Klipperås and Äspö are summarized in the following table.

	KLIPPERÅS	ÄSPÖ
Rocktype	Granitoids belonging to TIB ^a	Granitoids belonging to TIB ^a
Soil cover	Till (2-5 m)	Outcrops and in parts gyt-tja, clay and peat bogs
Hydrogeological character	Above highest shoreline ^b , large scale recharge	Coastal area, large scale discharge
Groundwater chemistry	Fresh water to 700 m depth	Complex system with fresh water down to 50-80 m depth and below this brackish and saline waters.
Depth of surface related oxidation spotted as FeOOH	50 m	10 m
Depth of surface related calcite dissolution, in general	Complete dissolution down to max. 50 m	Lower frequency down to 10 m.
Depth of surface related calcite dissolution in fracture zones	120 m	50 m
¹⁴ C content in groundwater	Very low; 2 to 3 pmC	Extremely variable with high values in fresh and brackish waters (60 to 97 pmC)
Extreme $\delta^{13}\text{C}$ values (<-25 ‰ or >+1 ‰) in fracture calcites	Not found	Present in fractures down to at least 450 m depth

a: TIB = Transscandinavian Igneous Belt

b: Late Weichselian highest shoreline

The data in the table indicate that the Klipperås area is much more exposed to acidification and that water saturated with O₂ can be transported into the bedrock aquifer to a larger depth than at Äspö.

4.2.2 Evidence for Oxidising Glacial Meltwater Effects in Drillcores at Äspö

It has been argued that glacial meltwaters may have a high contents of dissolved O₂. Different estimates and calculations of oxygen contents and reactive agents and their reaction rates have been reported (e.g Ahonen and Vieno, 1994; Gascoyne, 1999; Glynn et al., 1999; Puigdomenech et al., 1999). Therefore indications of depth penetration of oxygenated water during glacial periods have been paid special attention. The problem in interpreting redox fronts from mineral paragenesis is the lack of age constraints. Uranium, in common with iron, is sensitive to oxidising conditions and therefore U-series analyses can give an indication of uranium mobilisation (oxidising conditions) or uranium deposition (reducing conditions) within the time span of approx. one million years to 10 thousand years ago, depending on which uranium isotope ratios are interpreted. However to fully exploit the use of uranium series isotopes a combination of analyses including other trace elements is preferable.

The effects of hydrothermal and subsequent low temperature alteration and glacial/post-glacial weathering have been the subject of a pilot study (Landström et al., 2001) in two drillcores of quartz monzodiorite, cf. Figure 22:

- One core (YA 1192) was drilled into the hydrothermally altered rock wall of a water-conducting fracture exposed at 170 m depth in the access tunnel to the Äspö Hard Rock Laboratory.
- The other core (BAS-1) was drilled from a surface outcrop with a glacially polished surface, 1 km north of the YA 1192 site, on northern Äspö.

Both drill cores were sectioned into mm thick slices perpendicular to the core axis. The fracture fillings of the YA 1192 core, the weathered surface of the BAS-1 core and the different slices were analysed for major and trace elements and isotopes of U and Th, aiming to identify past and present diffusion of elements and natural radionuclides into the rock wall adjacent to a water-conducting fracture, and to study the possible influence of glacial meltwater on redox conditions. In order to disclose low-temperature diffusion components, U-series disequilibrium studies were included (confining processes during the recent 1 million years) and comparative studies of low-temperature glacial/post-glacial weathering.

The fracture surface of the YA 1192 core has probably been in contact with groundwater during long periods of time, in hydrothermal as well as in low-temperature regimes. Mineral/water reactions have affected a narrow (2-3 cm) zone of the wall rock adjacent to the fracture and have formed coatings on the fracture wall, with chemical and mineralogical compositions that strongly differ from those of the rock. Alteration of plagioclase (plagioclase → albite + sericite + epidote) dominates, and has resulted in a higher porosity and in the formation of secondary minerals with high sorption capacity (e.g. sericite). Br, Cs and the ²³⁴U/²³⁸U activity ratio are increased in the altered zone, relative to the host rock, indicating saline water (Br) in con-

nected pores and microfractures (i.e. indirectly the presence of a diffusion medium) and diffusion of U and Cs from fracture groundwater and subsequent sorption. The U migration is geologically recent (< 1 million years).

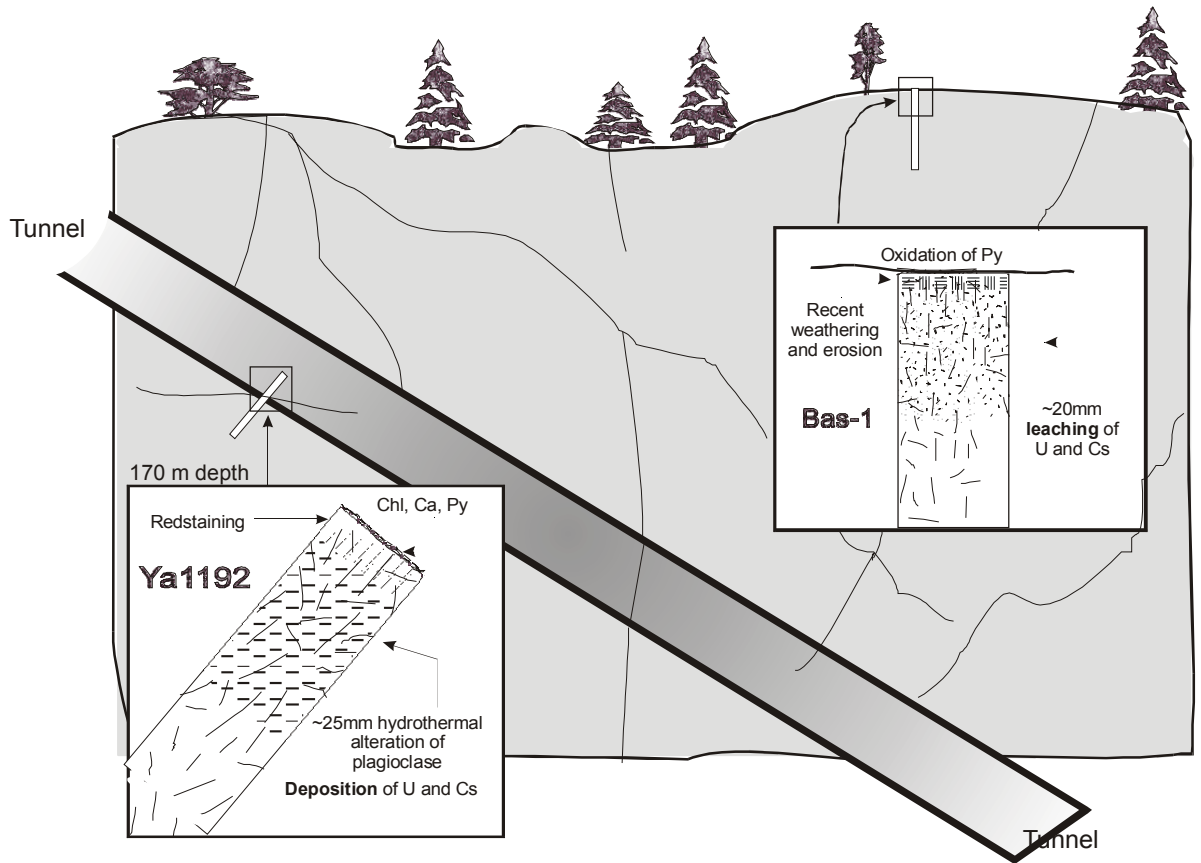


Figure 22. The location of drillcores YA 1192 and BAS-1 (Landström et al., 2001).

In contrast, the bedrock surface at BAS-1 was intensely worked by the ice during the late Weichselian glaciation, covered by till and Baltic sediments after deglaciation and exposed to air, precipitation and snow cover during the last 4 000 - 5 000 years. Pre-quatarnary weathered zones as well as weathered zones from earlier quaternary glaciations have been removed. The weathering effects now observed in the BAS-1 core are restricted to a narrow rim of the bedrock surface (approx. 0.2 - 0.5 cm thin weathered surface rim and depletion of Ca, U and Cs in a 2-cm zone below the surface) and are therefore most probably confined to the late glacial/post-glacial period. Mass balance calculations for the thin weathered rim (based on immobility of K) indicate that mechanical erosion has dominated over chemical dissolution processes (is roughly 10 times greater). The chemical weathering has affected mainly plagioclase and chlorite resulting in slight dissolution of these minerals. Quartz and K-feldspar have remained almost unaltered. Oxidation of pyrite (with rims of FeOOH on cores of pyrite) is documented in the upper 2 mm of the drill core whereas at 15 mm depth pyrite is fresh. Besides the thin weathered surface rim, the upper 2 cm of the core shows slight al-

teration of plagioclase, and decrease in the U and Cs concentrations, relative to unaltered rock. This indicates increased porosity and leaching of U and Cs, probably in glacial/postglacial time.

The recent deposition of U (< 1 million years as indicated by the $^{234}\text{U}/^{238}\text{U}$ activity ratio) in YA 1192 coincides with repeated glacial, interstadial and interglacial periods, which significantly changed the hydrogeological and geochemical environment at Äspö. For example, loading/unloading of huge ice sheets on the bedrock may have affected the fracture systems and large amounts of glacial meltwater were released at the deglaciations. The bedrock surface at BAS-1 has certainly been in contact with glacial meltwater during the Weichselian glaciation. The potentially high content of O_2 and low content of dissolved solids in such water and subsequent meteoric water, may have caused oxidation and mobilisation of U as well as desorption of Cs explaining the decrease in concentrations of these elements in the upper zone at BAS-1.

In contrast to the situation at the outcropping surface at BAS-1, the results from the YA 1192 core show deposition of uranium ($^{234}\text{U}/^{238}\text{U} > 1$), unaltered pyrite in the fracture coating and pore water salinity similar to, or higher than, the present salinity in fracture groundwater at corresponding depth. This implies reducing conditions and, importantly, no evidence of intrusion of oxygenated glacial meltwater.

The results from BAS-1, and data from the sites of Palmottu (see section 4.2.3) and Lac de Bonnet (Gascoyne and Cramer, 1987) suggest that alteration of pyrite and bulk leaching of U are common results of interaction between oxygenated water and the uppermost surface of the bedrock or in near surface fractures in areas exposed to the last glaciation. Depletion of U, $^{234}\text{U}/^{238}\text{U} \cong 1$, $^{230}\text{Th}/^{234}\text{U} > 1$ and alteration of pyrite (and formation of FeOOH) may thus be used as indicators of interaction with oxygenated surface waters (e.g. glacial meltwater during glaciation/deglaciations and meteoric water during interstadial/interglacial periods). Therefore, it may be concluded that the accumulation of U in the wall rock of YA 1192 fracture and the presence of fresh pyrite in its outermost coating implies that intrusion of oxygenated surface water has not occurred in the YA 1192 fracture (170 m depth).

Components of groundwater with glacial meltwater signature ($\delta^{18}\text{O}$ values varying from -15.8 to -13.6 ‰) found at depths from 134 to 450 m at Äspö (Laaksoharju et al., 1999b) are not associated with oxidation processes at these depths as evidenced by results from (Landström et al., 2001) and mineralogical data compiled in (Tullborg, 1997, and references therein). This means that previous suggestions about a high O_2 content in glacial meltwaters may be over-estimated or that the O_2 was consumed already in the near surface zone.

4.2.3 Evidence from Uranium Disequilibrium Studies at Palmottu

Uranium-series disequilibria ($^{234}\text{U}/^{238}\text{U}$, $^{230}\text{Th}/^{234}\text{U}$) have also been used to obtain information on redox-fronts in the near-surface crystalline bedrock at the Palmottu U-deposit in Finland (Blomqvist et al., 2000; Suksi and Rasilainen, 2001; Suksi et al., 2001). U-series disequilibrium may provide important information of geologically recent low-temperature in basement in contrast to ferric oxyhydroxides, which may also have formed during hydrothermal alteration.

Disequilibria were studied around water-conducting fractures and the rock matrix next to the fracture surface. Drill core samples for analysis, about 50 mm long and perpendicular to fracture surfaces were sampled from oxic bedrock conditions close to ground surface (≈ 30 m depth) and deeper from anoxic conditions (> 50 m).

In the samples from shallow depths preferential removal of U was clearly seen in the relative enrichment of immobile ^{230}Th against ^{234}U up to 30 mm depth in the rock matrix whereas the $^{234}\text{U}/^{238}\text{U}$ ratios were nearly at equilibrium. It was suggested that oxidising conditions have penetrated into these rocks and U isotopes have been congruently dissolved in the vicinity of the fractures. Diffusion estimations indicated that it took $\approx 10\,000$ years for an oxic front to reach 30 mm in the Palmottu rock, i.e. O_2 intrusion should have started during deglaciation in the area.

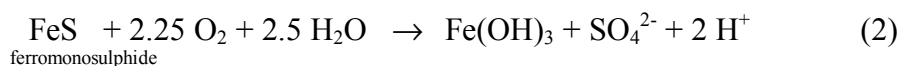
In the deeper Palmottu samples, where anaerobic conditions currently prevail, the Th-U activity ratios did not indicate oxidative loss of ^{234}U within the last 300 000 years, whereas the ratio of U isotopes showed clear release of ^{234}U . This preferential ^{234}U release should have occurred at a rate compatible with the $^{230}\text{Th}/^{234}\text{U}$ equilibration rate, because the release could not be seen in this ratio. The selective release of ^{234}U under anoxic conditions was explained by the different valence state of the U isotopes, ^{234}U being mostly in the more soluble U(VI) state due to α -recoil (Suksi and Rasilainen, 2001).

4.2.4 Evidence from Groundwater Isotopes at Olkiluoto

Brackish groundwaters from 100-400 m depth at Olkiluoto show strong depletion in stable isotopes of water, particularly the deeper (250-400 m) non-marine Na-Cl type layer located below the upper sulphate-rich Litorina derived groundwaters (see Figure 18). This has been interpreted as a signature of recharged glacial meltwater (e.g. Pitkänen et al., 1999). Similar depletions have been observed in almost all studied sites in Finland and Sweden (e.g. those given in Figure 6). The maximum portion of glacial melt has been assessed to be currently about 30 % in Finnish sites, i.e. Olkiluoto and Hästholmen (see Figure 18 and Pitkänen et al., 1999; Pitkänen et al., 2001), but the amount in the upper part of the bedrock has probably been higher, maybe about 50 % before Litorina seawater descended into bedrock. It has been discussed that glacial meltwater may contain relatively significant amount of dissolved O_2 , and may penetrate into great depths due to the high hydraulic

gradient and the potential organic inactivity in the recharge zone as compared with current conditions (e.g. Ahonen and Vieno, 1994). Ferrous iron, sulphide and organic carbon (reduced carbon) compounds are the major reactants that may consume O₂ in deep bedrock groundwater conditions. Iron and sulphide compounds are mainly in solid form (iron sulphide minerals and ferrous silicates) whereas biodegradable organic carbon is in dissolved form such as methylated substances (e.g. acetate) and methane. The following reactions generally consume O₂ in the groundwaters in bedrock environments, but also in the overlying till, through which meltwater usually infiltrates before reaching the rock (if the advancing ice has not removed the till).

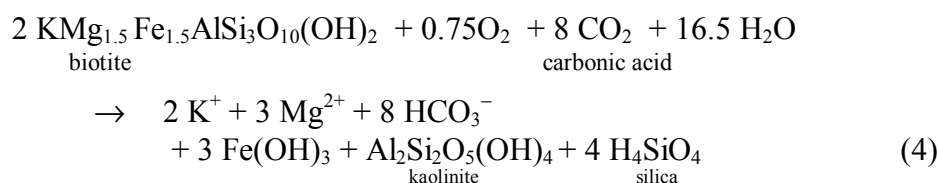
Iron sulphides react easily with oxygen producing significant amounts of acidity:



If organic matter is available, for instance in till, carbonic acid is formed



Carbonic acid and/or acid released from sulphide reactions also aids the oxidative weathering of ferrous silicates:



In Olkiluoto methane may have been present to a large extent in SO₄-free groundwater, even in the shallow bedrock, particularly during glaciation when interaction with the atmosphere was restricted and marine water may have been absent. Methane concentrations are significant in deep saline groundwaters and in the deeper non-marine brackish groundwater layer. δ¹³C data from fracture calcites studied within the EQUIP-project (e.g. Karhu, 2000) also indicated methanic environments in the upper brackish groundwater layer at depths of 100 to 250 m, where SO₄²⁻-rich Litorina derived groundwater dominates today at Olkiluoto (see Figure 18).

Methanotrophs can oxidise methane:



It has been estimated that the maximum content of O₂ in meltwater should not exceed 45 mg/L, i.e. 1.4 mmol/L (Ahonen and Vieno, 1994; Puigdomenech et al., 1999, p.81). The consumption of oxygen (reactions 1 to 5) is relatively large compared with the reaction products formed, which also may have other reaction sources. Therefore, it may no longer be possible to identify the products from O₂ reduction other than ferric precipitates,

which may, however, dissolve if conditions change to reducing (e.g. there are no observations of Fe(III) compounds in deep bedrock at Olkiluoto). Isotopic effects may however be distinguishable, particularly if the system is closed, i.e. if only primary oxidation has occurred. Isotopic and chemical effects can be divided into primary (direct oxygenation) and secondary (anaerobic reactions) in an open system.

4.2.4.1 *Primary isotopic signatures from O₂ intrusion*

Pyrite oxidation

Pyrite is a frequent secondary mineral at Olkiluoto, probably also formed at low temperature by microbial reduction of SO₄²⁻ (Pitkänen et al., 1999). Microbially mediated sulphide should have a clearly negative δ³⁴S value that decreases the δ³⁴S signature in dissolved SO₄²⁻ if pyrite has been oxidised. This isotopic effect (max. contribution should be 0.74 mmol/L) may be distinguishable as decreased values compared to marine background data. Sulphur isotope data is unfortunately scarce (e.g., there are no data available for any sulphide mineral) and δ³⁴S(SO₄) values are mainly from Litorina-derived groundwaters. However, no depletion can be observed on the data available. On the contrary the increased δ³⁴S signatures observed correspond to SO₄²⁻ reduction.

Iron monosulphide (pyrrhotite) oxidation

Iron monosulphide typically represents high temperature precipitation from a primary sulphur source as well as from pyrites. The sulphur isotopic signature is around 0 ‰ in this case (e.g. Fontes et al., 1989), which corresponds fairly well to the signature in overburden groundwaters (3 ‰) at Olkiluoto, reflecting recent oxidation. Possible SO₄²⁻ derived from FeS oxidation caused by meltwaters (max. contribution 0.62 mmol/L) has not been observed and it is probably difficult to distinguish in sulphate-rich waters.

Oxidation of organic matter

The δ¹³C signature derived from the oxidation of organic matter (around -25 ‰) by meltwater is, unfortunately, impossible to differentiate from later respiration of organic matter and mixing from other carbonate sources.

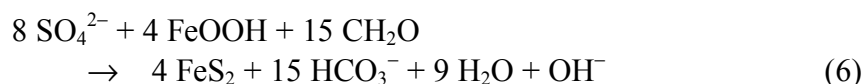
Methane oxidation

The oxidation of CH₄ (δ¹³C is less than -40 ‰ in Olkiluoto) should have a strong decreasing effect on the δ¹³C signature of dissolved carbonate. The isotopic data contain one sample with a very low, potentially CH₄-based value (-36.3 ‰ in a sample from the transition zone between two brackish groundwaters: the upper SO₄²⁻-rich and the deeper non-marine type). However, chemical and isotopic data from this sample indicate anaerobic oxidation of CH₄ connected to SO₄²⁻ reduction rather than oxygenation in this sample.

4.2.4.2 *Secondary isotopic signatures*

Ferric precipitates, which are a probable result from any oxygen intrusion into the water-rock system, may be reduced and dissolved by iron reducing

bacteria during anaerobic respiration of organic matter. If limonite coatings had been formed by meltwater e.g. in the depths where SO_4^{2-} -rich groundwaters are now found or even deeper, ferric iron may have subsequently disappeared but the iron concentration in groundwater should have increased. Significant iron enrichment in groundwaters has not been observed at Olkiluoto. However, iron could have precipitated as pyrite if sulphate reduction had taken place in the system:



In this case respiration of organic carbon decreases the $\delta^{13}\text{C}$ of dissolved carbonate, particularly due to low carbonate content ($\ll 1 \text{mmol/L}$) in brackish and saline groundwaters at Olkiluoto and even strongly if methane is the electron donor. If reaction (1) takes place in a closed system (assuming 1.4mmol/L O_2 produces 0.37mmol/L of $\text{Fe}(\text{OH})_3$), $\delta^{13}\text{C}$ will decrease near -25% with organic matter mineralisation or near -40% if methane is used in reaction (6). These types of shifts were observed in two samples that were from the lower part of the SO_4 -rich layer. One sample from Na-Cl type groundwater with the lowest $\delta^{18}\text{O}$ values also showed a fairly low $\delta^{13}\text{C}$ value (-21.75%). However, carbonate content of this sample is very low (0.3mmol/L), thus the O_2 content in the water could not be significant if the isotopic value is derived from secondary oxidation. In addition, if significant ferric iron mass transfer was involved in a reduction process at Olkiluoto, it should be possible to find late-stage fracture-filling calcites with depleted $\delta^{13}\text{C}$ values, i.e. clearly below -20% . However, this type of calcite has not been observed so far in Olkiluoto (Blyth et al., 2000; Karhu, 2000).

If the system is open, i.e. groundwater moves significantly, the isotopic signatures or the concentration of dissolved Fe(II) (if not precipitated) may have been diluted by mixing. However, SO_4^{2-} reduction may have occurred along the flow path, so the low carbon isotope signature should be still observable, particularly methane based. In addition the very low alkalinity in brackish Na-Cl type water and deeper groundwaters in Olkiluoto should reveal the depletion of $\delta^{13}\text{C}$, if significant SO_4^{2-} and Fe reduction has occurred.

The arguments discussed in this section show how difficult it is to make any clear conclusion to the magnitude of oxygen intrusion during deglaciation. However, according to the $\delta^{13}\text{C}$ data it seems that the deeper brackish ^{18}O depleted Na-Cl type groundwater beneath the Litorina-derived SO_4 -rich layer and deep saline groundwaters in Olkiluoto could not have contained significant amounts of oxygen.

4.2.5 Buffers Against Future Intrusions of O_2 in Glacial Meltwaters

Processes that may act as redox controls in deep granitic rocks have been discussed at length elsewhere (e.g. Gascoyne, 1999; Puigdomenech et al., 1999 and section 4.2.4). In this section the results from two recent studies will be reviewed: a numerical model coupling water transport and chemical

reactions, and experimental investigations performed within the Äspö International Cooperation.

4.2.5.1 *Models of O₂ Intrusion by Glacial Meltwaters: The GLOX Project*

The GLOX project (Guimerà et al., 1999) attempted to model numerically the depth extent of penetration of an oxidising front due to the infiltration of meltwater during a glacial period.

The main chemical processes considered were pH-buffering by calcite dissolution, release of Fe(II) from chlorite and biotite, and O₂ reaction with dissolved Fe(II) and pyrite. Chlorite was assumed to be present as fracture filling mineral while biotite and pyrite were supposed to be present in the rock matrix.

The simulation time in the calculations was set to about 5000 years, and an infiltration rate of 50 L·m⁻²·year⁻¹ with a dissolved O₂ content of 45 mg/L for the meltwater were used. Multicomponent reactive transport was modelled with the ARASE code using both one- and two-dimensional geometries. The numerical models reached to the depth of a repository: 500 m. For hydrodynamic details of the calculations see (Guimerà et al., 1999).

The calculations showed that groundwater reaching the repository level, after mixing and reactions with minerals, should be in general still anoxic after periods of thousands of years. However, the groundwaters could become oxic in some extreme cases. The alkalinity was not affected due to the calcite buffering capacity.

Two parameters were deemed crucial for the model results: the reactive surface area of the redox controlling minerals and the velocity of the groundwater. Hydrodynamic parameters, such as dispersion, were relevant to determine the first arrival times of infiltrating waters, but they were not crucial in terms of final values of the redox state. The reactive surface area determined the value for the steady state redox potential, while groundwater velocity controlled the time at which a certain state may be reached. The reducing capacity (in terms of Fe(II) minerals) of the rock remained largely unaffected, while in the fractures substantial decreases of reducing capacity might take place.

The assumptions made in the GLOX project and the modelling work within SITE-94 (sponsored by SKI, see e.g. Glynn et al., 1999 and Glynn and Voss, 1999, Part II, chapter 4) were later reviewed in (Gascoyne, 1999). The main conclusions of that review were: *a)* that the reducing capacity of fracture filling minerals might be lower than assumed in (Guimerà et al., 1999); *b)* the models used in SITE-94 were extremely conservative; and *c)* the assumptions of a warm-based ice-sheet and of a high O₂-concentration for meltwaters at a repository site are over-conservative.

4.2.5.2 *The Deep Biosphere*

Independent scientific studies have demonstrated that microbial life is present in most deep geological formations down to depths of several kilometres. In the Fennoscandian igneous rock groundwaters the average total number of unattached microbes is generally within 10^8 - 10^9 cells/L (Pedersen, 2000). The REX project established the importance of microbial activities for keeping reducing conditions around nuclear repositories: The oxidation of CH_4 and H_2 was found to be significant processes for O_2 reduction (Kotelnikova and Pedersen, 1999; Puigdomenech et al., 2001). These processes are activated when intruding O_2 -rich surface waters are mixed with deeper groundwaters which contain reductants such as CH_4 and H_2 that emanate from deeper sources.

Figure 23 illustrates how microbes in the geosphere hinder O_2 from reaching a nuclear repository (Pedersen, 2000). While the repository is open and after its closure (left and middle parts of the figure) O_2 will be transported with recharging waters into the basement rock and it will also diffuse from the tunnel air into the rock matrix. The recharging groundwater will however contain organic matter, which will be used by microbes to reduce O_2 . Furthermore, anaerobic microbes in the host rock may use organic matter to reduce Fe(III) , Mn(IV) , and SO_4^{2-} . The reduced products (Fe(II) , Mn(II) and HS^-) may also react with oxygen, for example when the groundwater reaches the tunnel walls of the repository.

During a glaciation there will be no input of organic carbon with the infiltrating glacial melt. However, the findings from the REX project demonstrated that microbes might use methane and hydrogen for O_2 reduction. The flow of these gases from deeper parts of the mantle will not depend on surface climate.

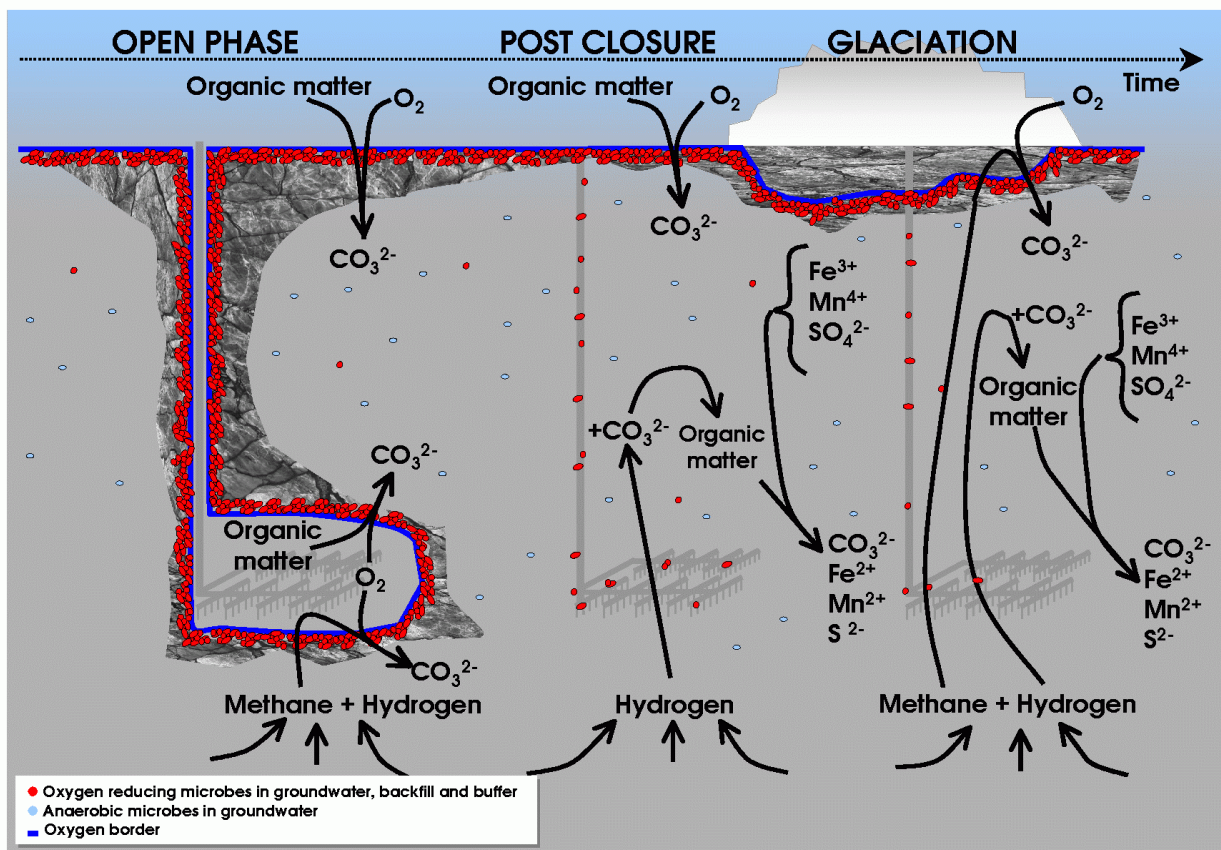


Figure 23. Schematic model of how microbes in the geosphere hinder O_2 from reaching a nuclear repository and keep the groundwater redox potential at low levels (from Pedersen, 2000). Microbes (here symbolised with red rounded shapes) are concentrated at the interface between oxidising and reducing environments, and they gain energy from mediating in redox reactions.

4.3 SULPHATE REDUCTION AT ÄSPÖ

Since sulphide can corrode copper canisters in reducing environments, the process generating sulphide has to be known in such detail that a repository can be located without the risk of extensive sulphide generation at the copper canister surface. The M3 methodology (section 2.2.1) was used to trace the effects from sulphate reduction that produce sulphide at Äspö HRL (Laaksoharju et al., 1995).

Sulphate reduction is indicated by the presence of Sulphate Reducing Bacteria (SRB) or by analysing the amount of sulphide generated in the groundwater. The sampling and identification of SRB cannot generally be done due to economical and practical restrictions. The reactivity of HS^- leads to special requirements for sampling and analysis. The lack of HS^- data from the boreholes in the Äspö HRL tunnel in combination with relatively few samples of

bacteria made it necessary to search for additional signs of bacterial sulphate reduction.

The SRB can reduce sulphate to sulphide using organic substances in natural groundwater as reducing agents (electron donors) according to the reaction:



This means that sulphate reduction in the groundwater is indicated by an abnormally *low* dissolved SO_4^{2-} content and an abnormally *high* HCO_3^- content (as compared, for example, with values expected from mixing models). The effect from mass transport mixing on different groundwaters, which can also give a similar $\text{SO}_4^{2-}/\text{HCO}_3^-$ ratio, was compensated for by the M3 calculations so that obvious microbiological sulphate reduction could be identified in the Äspö groundwaters. It was assumed that this had most probably taken place when the deviation ratio from the M3 model between bicarbonate and sulphate was larger than 1.27 (expressed as mole ratio $\Delta[2\text{HCO}_3^-] / \Delta[\text{SO}_4^{2-}] > 1.27$, the SO_4^{2-} deviation being negative, and the HCO_3^- being positive, cf. Laaksoharju et al., 1995). Sulphate reduction can also be identified from sulphur and carbon isotopic data, from the occurrence of HS^- , from late stage pyrite precipitates, etc.

The microbial results and the M3 modelling seemed to correlate. The mixing calculations show that water affected by sulphate reduction can be transported to other locations in the HRL tunnel especially in the tunnel sections under the Baltic Sea or in the near vicinity. Sulphate reduction occurs most prominently in the tunnel section passing below the sea but also occasionally at depth in the tunnel spiral. A high content of organic material (>10 mg/L) in combination with a salinity (Cl) interval of 4000-6000 mg/L seemed to correlate with samples having obvious biological sulphate reduction. However, SO_4^{2-} reduction also occurs at a lower organic content where the substrate might be hydrogen gas; in this case excessive HCO_3^- production does not occur. The obvious sulphate reduction has in a few cases been seen to give bicarbonate concentrations of above 1000 mg/L (some of this alkalinity might have originated from other sources than SO_4^{2-} reduction) and a corresponding decrease of sulphate from above 500 mg/L to less than 100 mg/L (Laaksoharju et al., 1995). The more vigorous sulphate reduction is believed to take place in association with the "Marine sediment" type of water (section 2.2.2).

In conclusion, in most sites SO_4^{2-} reduction may occur in many places, although the conditions are more favourable in marine bottom sediments or in their proximity. It is expected that sulphate reduction might produce substantial amounts of sulphide, but the solubility of metal sulphides is very low. Relatively high levels of Fe(II) may be expected in groundwaters under the reducing conditions required for the existence of sulphide, and under such environments the solubility of iron(II) sulphides keeps the levels of dissolved HS^- below the analytical detection limit.

5 APPROACHES TO MODELLING CHEMICAL CHANGES

5.1 METHOD

An attempt to estimate future chemical changes was performed using a modelling approach that included the following:

- *Criteria:* present groundwater compositions from the sites were used, and the SKB groundwater suitability criteria were applied on these observations.
- *Scenarios:* the SKB future climate scenario was used in order to model the future groundwater changes.
- *Mixing:* mixing portions of the groundwaters were modified to simulate future changes.

The above concepts are described in detail below:

Criteria. SKB has determined the criteria of the parameters regarded to be of importance for the stability of groundwater and the safety of the repository (Andersson et al., 2000). Groundwaters not meeting these criteria can affect the stability of the canisters, the stability of the bentonite clay surrounding the canisters or change the transport properties of the groundwater. The groundwater criteria are: Eh < 0 mV, pH 6-10, TDS < 100 g/L, DOC < 20 mg/L, colloids < 0.5 mg/L and Ca+Mg > 4 mg/L. These criteria were applied to the measured groundwater compositions from the sites in Sweden and Finland. PC-plots (see Figure 25 to Figure 30) are convenient to use in this type of modelling and therefore the samples or the water types meeting (or alternatively not meeting) the criteria were identified and the corresponding area was labelled with different line types corresponding to the different criteria. From these plots the samples meeting (or not meeting) the various criteria can be identified and it is also possible to examine how close or far away the individual samples are from meeting (or not meeting) a given criteria. In addition the type of criteria that a sample may not meet can be identified visually on the figures.

Scenarios. During the lifespan of a repository (up to 100 000 years and longer), major climate changes are expected to take place. Over such time scales in the past Fennoscandia has had major climatic changes that resulted in permafrost, ice sheets, stages of glacial meltwater, marine and fresh water and also land uplift. The future climate scenarios are described in (SKB, 1999, Vol.II, pp. 344-357). These scenarios were used in the modelling by incorporating the following time periods: present time, 20 000 - 30 000, 30 000 - 40 000, 60 000 - 70 000, 70 000 - 80 000 and 100 000 - 110 000 years shown in Figure 25 to Figure 30.

Mixing. In order to model future changes of the groundwater conditions at repository depths at Äspö, Finnsjön, Gideå, Olkiluoto, Kivetty, Hästholmen and Romuvaara, a scoping calculation was made. A representative groundwater sample (at Finnsjön two samples labelled “2a” and “2b” in the maps on Figure 25 to Figure 30) from each site representing repository depths (500±100 m) was selected. The mixing calculations of the obtained water chemistry were used as a starting point for the modelling. This step is of importance since the past and present hydrodynamic conditions have determined the obtained mixing portions and tend therefore to determine future changes also. Depending on the SKB climate scenario to be modelled the mixing portions of the Glacial water or Sea water (of Litorina Sea type) were added in steps of 50 % (see Figure 24) to reflect the changes due to new climate conditions. The added 50 % is regarded as a worse case modelling scenario. By knowing the mixing contributions from the reference waters, i.e. Brine, Glacial, Precipitation, Marine sediment and Litorina new water, compositions could be calculated for all the climate scenarios (see Table 3). This new values were added to the PC-plots and the resulting composition compared with the initial water compositions (the advantage is that the predicted composition could be compared with other measured samples and their properties) and how suitable the sample was in relation to the SKB criteria (see Figure 25 to Figure 30). The last step was used to investigate if the modelled changes of future effects could affect the hydrochemical stability of the groundwater surrounding the final repository.

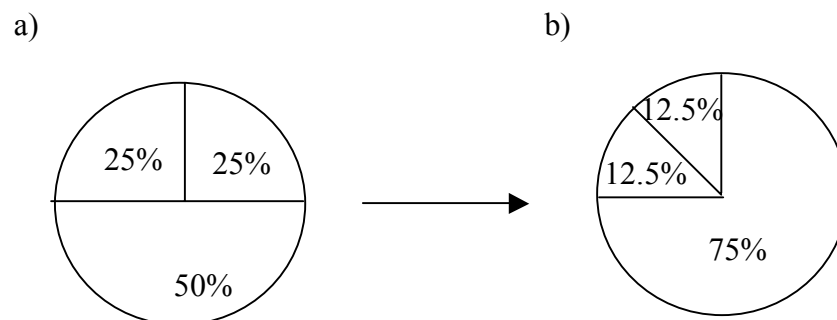


Figure 24. A schematic presentation of how the scenario modelling is performed, shown here on a sample consisting of a mixture of three water types: a) the calculated mixing proportions on the initial groundwater composition: 50% water of water type 1, and 25% of water types 2 and 3 (the sum of the mixing portions for the sample equals 100%). b) the effect of changing the mixing proportions where water type 1 is increased with 50% the new groundwater composition will consist of the following: water type 1 = 75% and water type 2 and 3 = 12.5% (the sum of the mixing portions of the new water composition equals 100%). By knowing the composition of the reference waters and the mixing proportions it is possible to calculate the elemental composition for the modelled groundwaters.

Table 3. Example of the modelling based on the SKB climate scenario. Mixing portions of the Glacial water or seawater (of Litorina Sea water type) was added in steps of 50% to the obtained water composition in order to obtain a new composition. In case that the water composition in the bedrock had a higher salinity than the intruding seawater the bedrock water was left unaffected since density overturn could not take place (see the examples in this table for Äspö and Olkiluoto). The samples to be modelled were collected at the repository depths (500±100 m) from: Äspö, Finnsjön (two samples: 2a and 2b), Gideå, Olkiluoto, Kivetty, Hästholmen and Romuvaara. “Secup” and “Seclow” stand for the packer positions (m) in the borehole when sampling. The major components are in mg/L, tritium in TU, deuterium and oxygen-18 in ‰ (SMOW).

Area		Idcode	Secup	Seclow	Na	K	Ca	Mg	HCO3	Cl	SO4	H3	H2	O18
Glacial		Glacial			0.17	0.4	0.18	0.1	0.12	0.5	0.5	0	-158	-21
Litorina		Litorina			3180	154	152	380	146	6100	527	0	-35	-5
1 Äspö	Present	KAS02	530	535	2100	8.1	1890	42	10	6410	560	8	-97.2	-12.3
1 Äspö	50% Glacial	KAS02	530	535	1050	4	945	21	5	3205	280	0	-128	-17
1 Äspö	50% Litorina	KAS02	530	535	2100	8.1	1890	42	10	6410	560	0	-97.2	-12.3
2a Finnsjön	Present	BFI01	439	459.1	1700	13	1650	110	47	5500	370	3	-88.7	-11.81
2a Finnsjön	50% Glacial	BFI01	439	459.1	850	7	825	55	24	2750	185	0	-123	-16
2a Finnsjön	50% Litorina	BFI01	439	459.1	2440	84	901	245	97	5800	449	0	-62	-8
2b Finnsjön	Present	KFI07	511	516	275	2	142	17	278	555	49	8	-89	-11.9
2b Finnsjön	50% Glacial	KFI07	511	516	138	1	71	9	139	278	25	0	-124	-16
2b Finnsjön	50% Litorina	KFI07	511	516	1727	78	147	198	212	3328	288	0	-62	-8
3 Gideå	Present	KGI04	404	406.7	105	1.9	21	1.1	18	178	0.1	8	-99.4	-13.63
3 Gideå	50% Glacial	KGI04	404	406.7	53	1	11	1	9	89	0	0	-129	-17
3 Gideå	50% Litorina	KGI04	404	406.7	1642	78	87	190	82	3139	264	0	-67	-9
4 Romuvaara	Present	3/T1	415	476	45	2.6	35.6	1.36	61	109	1.21	1.4	-99.6	-13
4 Romuvaara	50% Glacial	3/T1	415	476	23	2	18	1	31	55	1	0	-129	-17
5 Kivetty	Present	1/T4	515	555	18	0.82	12.7	0.65	86.0	2.05	1.15	0.8	-90.4	-12.6
5 Kivetty	50% Glacial	1/T4	515	555	9	1	6	0	43	1	1	0	-124	-17
6 Olkiluoto	Present	5/P1	446	558	3325	14	2255	65	7	9500	3.1	0.8	-89.3	-11.8
6 Olkiluoto	50% Glacial	5/P1	446	558	1663	7	1128	33	3	4750	2	0	-124	-16
6 Olkiluoto	50% Litorina	5/P1	446	558	3325	14	2255	65	7	9500	3	0	-89	-12
7 Hästholmen	Present	HH-KR5	590	595	1980	21	970	123	64	5140	135	0.8	-96.8	-13
7 Hästholmen	50% Glacial	HH-KR5	590	595	990	11	485	62	32	2570	68	0	-127	-17
7 Hästholmen	50% Litorina	HH-KR5	590	595	2580	88	561	251	105	5620	331	0	-66	-9

The modelling is based on several assumptions and it is therefore quite uncertain, and it should be regarded as a preliminary modelling. The main restrictions are:

- The mixing calculations presented here are a worse case modelling. A more realistic mixing modelling should be obtained by using a detailed hydrodynamic modelling as a guideline. Another possibility would be to make “titration” calculations with a thermodynamic code. For example, the capabilities of PHREEQC (Parkhurst, 1995) might be used to examine the effect of increasing amount of infiltrating water types by performing a series of geochemical simulations.
- The calculations do not include chemical reactions that tend to equilibrate disturbances caused by mixing two different waters. Equilibration would affect mostly pH and Eh. This problem could probably be avoided using thermodynamic modelling.
- In a PC-plot two samples looking alike might contain significant differences in single parameters, even in those which are used in PC calculations (i.e. adding another principal component would scatter the sample points above and below the paper sheet). This is a general limitation of the PC-methodology. Tests performed on the present data set indicate that the 1st and 2nd principal component summarise about 70% of the information in the data. A 3rd principal component summarises 10% of the information.
- The end-members “Marine sediment” and “Brine” defined in section 2.2.2 have been used in the modelling, both for Swedish and Finnish sites. These two end-members correspond however to waters sampled at the Äspö site. For the Marine sediment reference water, the average composition of the porewaters in Baltic sediments is expected to differ from site to site, but these variations have negligible effects on the results from this preliminary modelling.

In the case of the Brine end-member, variations are also expected to occur, for example between the groundwaters sampled at Laxemar and those at Olkiluoto. For other sites, like Gideå etc, there is no information available. Most of these “brines” are of the Ca-Na-Cl type as described in section 1.3. The salinity is nevertheless more important than for example the Ca:Na ratio when assessing the suitability of future groundwater compositions. The selection of the Äspö “brine” end-member in this model was necessary due to the lack of information on most other sites (and to make easier comparisons) but this approximation does not affect the main conclusions from the model.

5.2 MODELLED CHANGES IN GROUNDWATER COMPOSITIONS

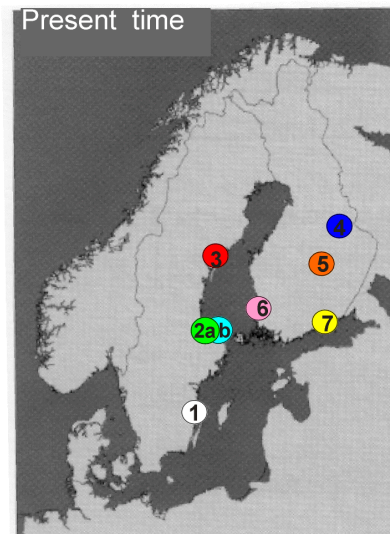
The results from modelling the effects of future climate changes on groundwater compositions for representative samples at repository depth

(500±100 m) for Swedish and Finnish sites are shown in Figure 25 to Figure 30. The modelling was based on *mixing* calculations and based on the assumptions and scenarios indicated above. The effects on the hydrochemical stability are shown by means of areas of hydrochemical stability in the PC-plots where the SKB hydrochemical *suitability criteria* are met. The initial and modelled compositions for the selected samples at repository depth are listed in Table 3.

The modelling results shown, where the initial groundwater compositions were altered in steps to simulate possible future climate changes, indicate that the SKB criteria concerning the hydrochemical stability are generally met. Under special circumstances such as injection of large amounts of glacial meltwater many of the criteria are not met. In such cases the flow rate will determine the length of time the more conductive fracture zones at repository depth will not meet the various criteria (e.g. for pH or Eh). When modelling the situation where the sites are covered and affected by the seawater, only some sites did not meet the criteria for the organic content and colloids.

An important observation is that all the modelled compositions resembled samples collected in Sweden and Finland, that is, the modelling predicted a compositional variability within the same range as observed in present-day groundwaters. The properties and compositions are therefore well known except that some of the modelled compositions may have been sampled at different depths rather than at 500 m depth, or the difference might be in some other property not used in the PC-analysis. It should also be noted that perhaps some other groundwater properties not loaded at present on the two main principal components should be checked separately. As mentioned above when discussing the limitations of the model (previous section), the 3rd principal component summarises only 10% of the information in the whole data set.

A more detailed modelling concerning the appropriate mixing portions to be added/removed can be performed by coupling the above modelling with a hydrodynamic model. In addition chemical calculations should be performed with a thermodynamic code in order to examine gradual changes and the buffering capacity of hydrogeochemical systems against expected disturbances caused by climatic changes. The aim here was to present a possible methodology and give an example of how such a calculation could be performed.



Site:	Condition:
1 Äspö	Land
2 Finnsjön	Land
3 Gideå	Land
4 Romuvaara	Land
5 Kivetty	Land
6 Olkiluoto	Land
7 Hästholmen	Land

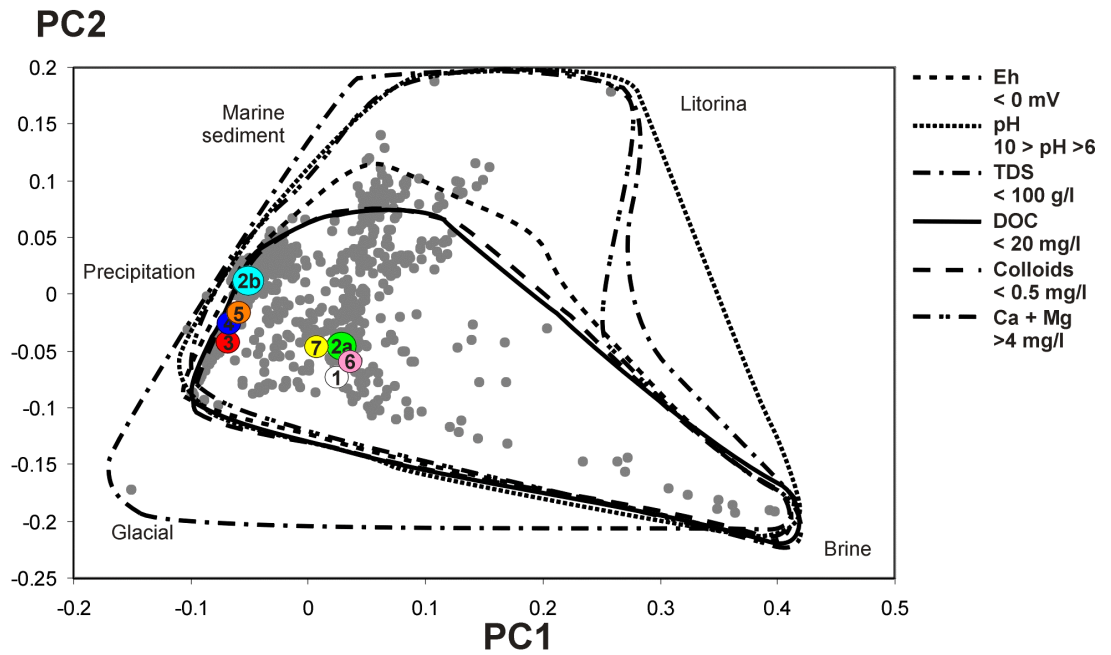
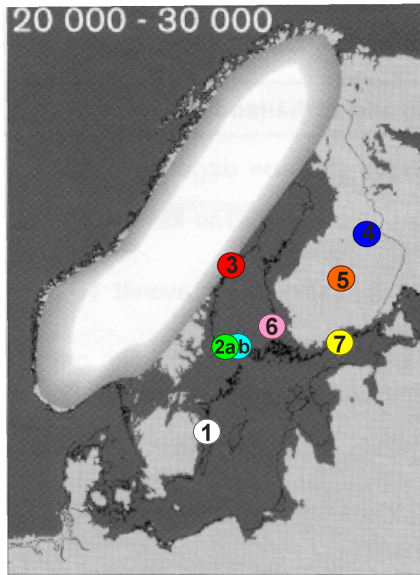


Figure 25. The results of the modelling showing the present-day conditions at the sites are listed in the legend (above figure). The PC-plot (lower figure) presents chemical compositions of selected samples at the repository depth (500 ± 100 m) in relation to all the samples (grey dots) collected at the Swedish and Finnish sites. Samples meeting the SKB criteria and regarded as hydrochemically stable plot inside the areas limited by the solid/dotted lines representing the various criteria listed in the legend. All initial samples meet all the criteria at present-day climatic conditions.



Site:	Condition:
1 Äspö	Sea
2 Finnsjön	Sea
3 Gideå	Ice
4 Romuvaara	Land
5 Kivetty	Land
6 Olkiluoto	Sea
7 Hästholmen	Sea

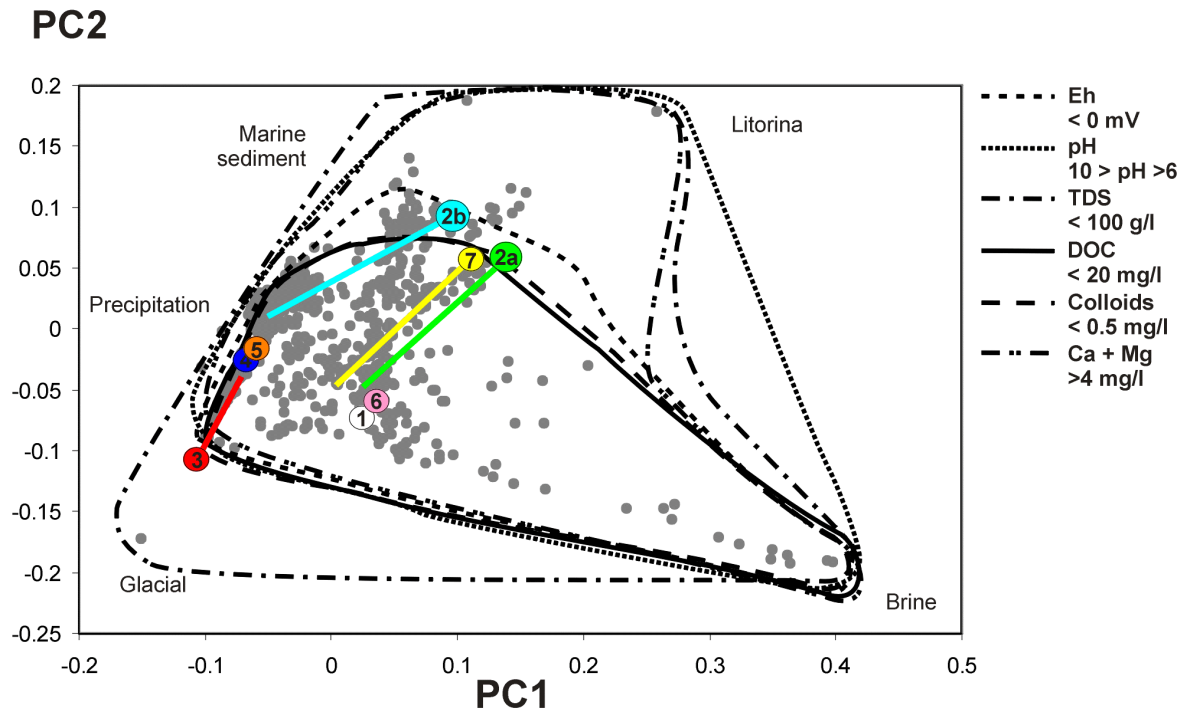
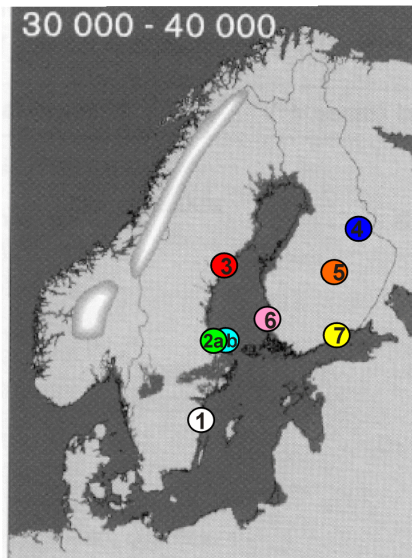


Figure 26. The results of modelling future climate changes 20 000-30 000 years from now. The conditions at the sites are listed in the legend (above figure). The PC-plot (lower figure) presents chemical compositions of modelled samples at repository depths 1 (500±100 m) in relation to all the samples (grey dots) collected at the Swedish and Finnish sites. The colour lines indicate the compositional changes of the samples in relation to the initial compositions. Samples meeting the SKB criteria and regarded as hydrochemically stable plots inside the areas limited by the solid/dotted lines representing the various criteria listed in the legend. The modelling indicates that some of the criteria are not met for the samples from Finnsjön and Gideå; the other samples meet all the criteria at these climate conditions.



Site:	Condition:
1 Äspö	Sea
2 Finnsjön	Sea
3 Gideå	Sea
4 Romuvaara	Land
5 Kivetty	Land
6 Olkiluoto	Sea
7 Hästholmen	Sea

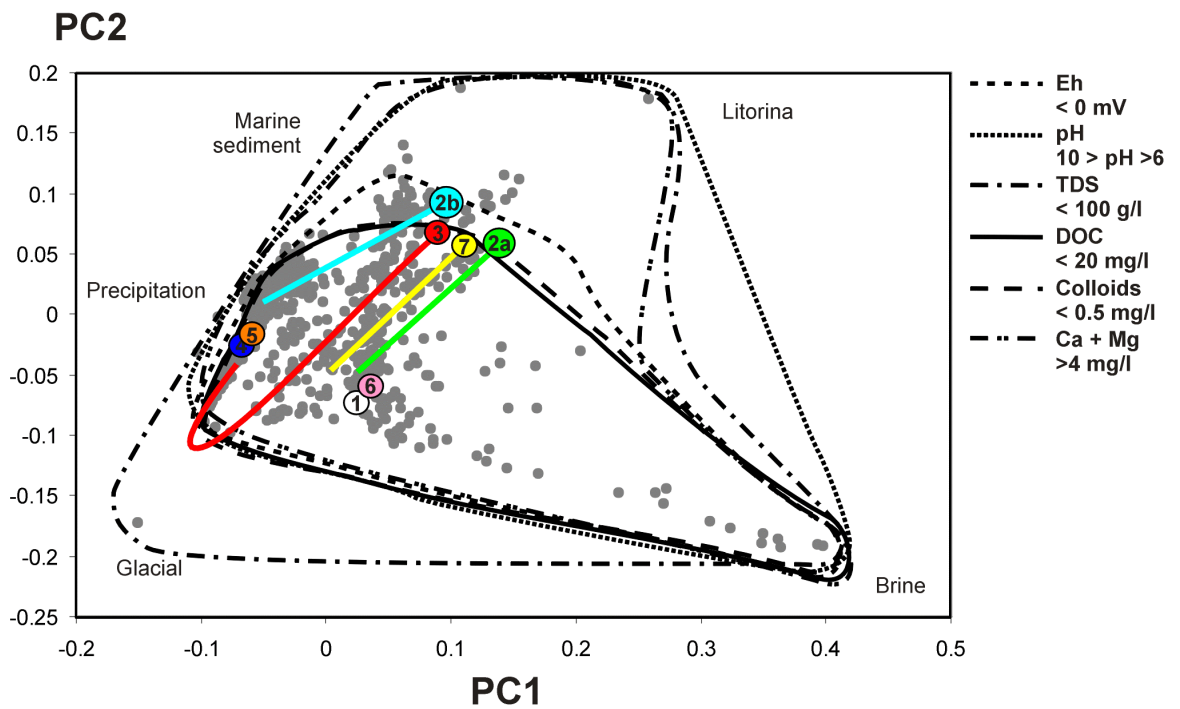
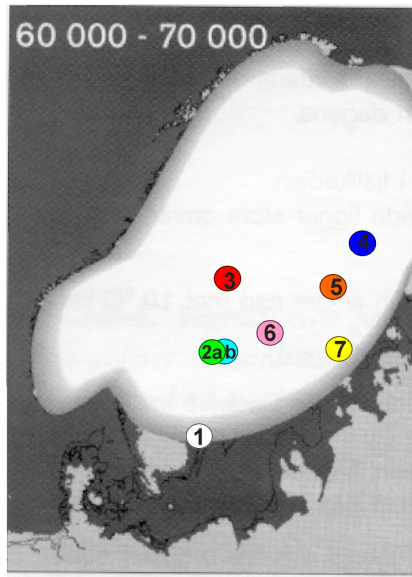


Figure 27. The results of modelling future climate changes 30 000-40 000 years from now. The conditions at the sites are listed in the legend (above figure). The PC-plot (lower figure) presents chemical compositions of modelled samples at repository depths (500 ± 100 m) in relation to all the samples (grey dots) collected at the Swedish and Finnish sites. The colour lines indicate the compositional changes of the selected samples in relation to the initial compositions. Samples meeting the SKB criteria and regarded as hydrochemically stable plot inside the areas limited by the solid/dotted lines representing the various criteria listed in the legend. The modelling indicates that some of the criteria are not met for the samples from Finnsjön; the other samples meet all the criteria at these climatic conditions.



Site:	Condition:
1 Äspö	Ice
2 Finnsjön	Ice
3 Gideå	Ice
4 Romuvaara	Ice
5 Kivetty	Ice
6 Olkiluoto	Ice
7 Hästholmen	Ice

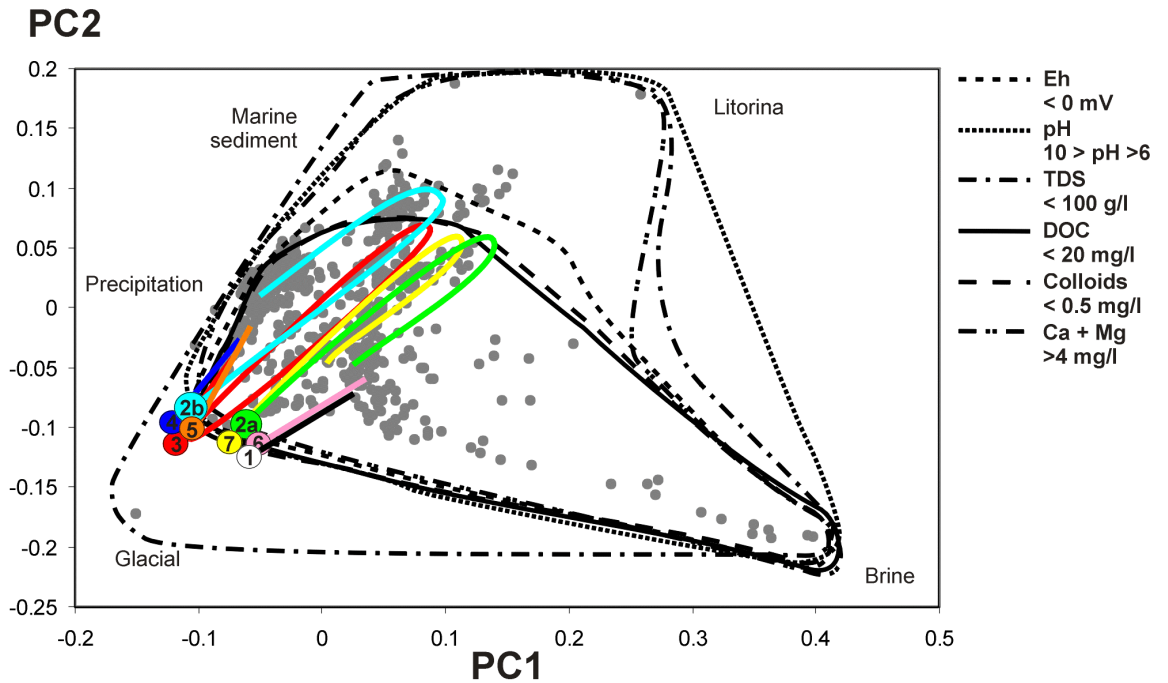
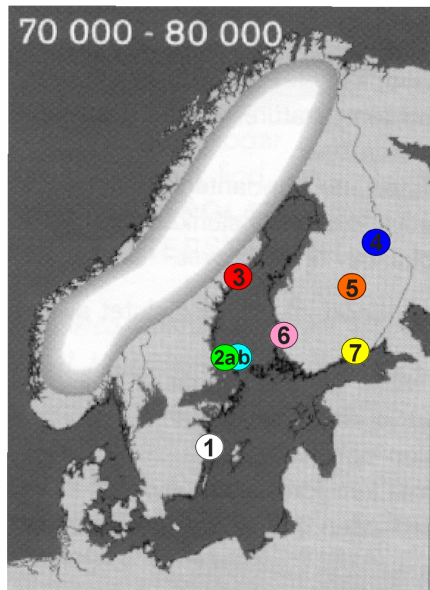


Figure 28. The results of modelling future climate changes 60 000-70 000 years from now. The conditions at the sites are listed in the legend (above figure). The modelling reflects injection of 50% glacial meltwater when the ice sheet is melting. The PC-plot (lower figure) presents chemical compositions of modelled samples at repository depths (500 ± 100 m) in relation to all the samples (grey dots) collected at the Swedish and Finnish sites. The colour lines indicate the compositional changes of the samples in relation to the initial compositions. Samples meeting the SKB criteria and regarded as hydrochemically stable plot inside the areas limited by the solid/dotted lines representing the various criteria listed in the legend. The modelling indicates that only some of the criteria are met for the samples at these climatic conditions.



Site:

Condition:

1 Äspö	Sea
2 Finnsjön	Sea
3 Gideå	Sea
4 Romuvaara	Land
5 Kivetty	Land
6 Olkiluoto	Sea
7 Hästholmen	Sea

PC2

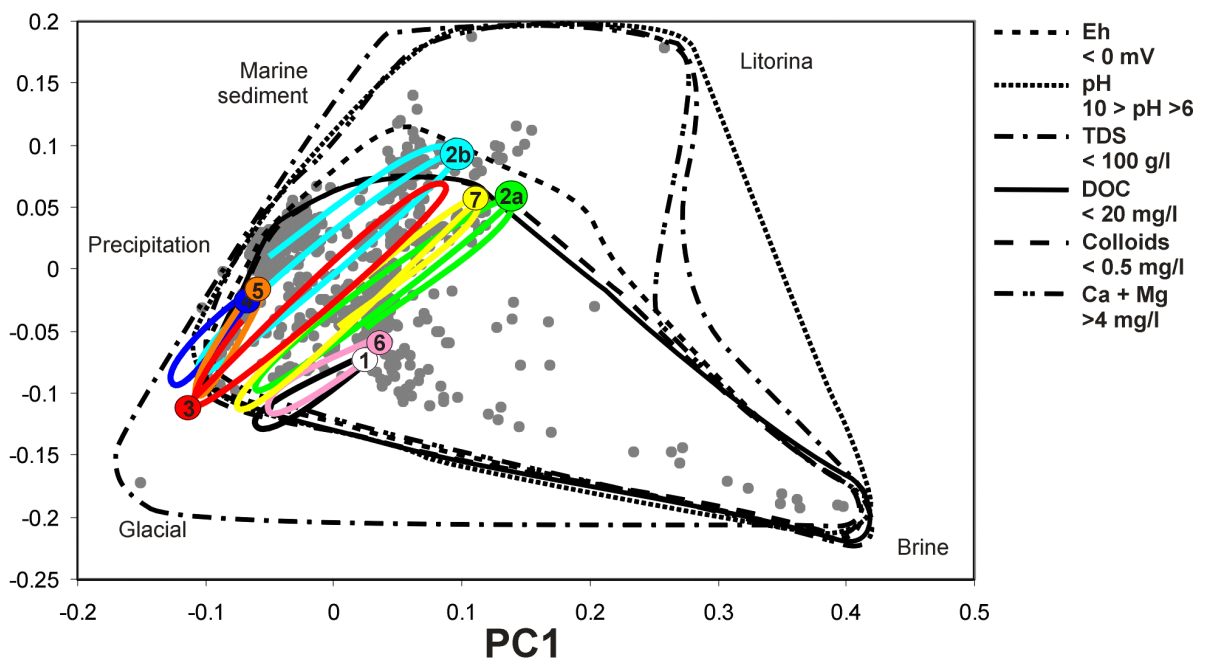
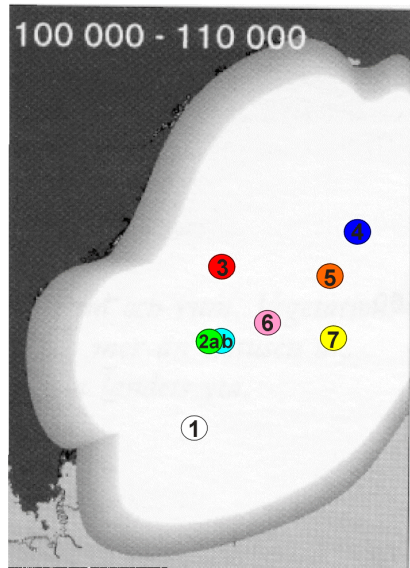


Figure 29. The results of modelling future climate changes 70 000-80 000 years from now. The conditions at the sites are listed in the legend (above figure). The PC-plot (lower figure) presents chemical compositions of modelled samples at repository depths (500 ± 100 m) in relation to all the samples (grey dots) collected at the Swedish and Finnish sites. The colour lines indicate the compositional changes of the selected samples in relation to the initial compositions. Samples meeting the SKB criteria and regarded as hydrochemically stable plot inside the areas limited by the solid/dotted lines representing the various criteria listed in the legend. The modelling indicates that the samples at Äspö, Romuvaara, Kivetty, Olkiluoto and Hästholmen meet the criteria at these climatic conditions.



Site:	Condition:
1 Äspö	Ice
2 Finnsjön	Ice
3 Gideå	Ice
4 Romuvaara	Ice
5 Kivetty	Ice
6 Olkiluoto	Ice
7 Hästholmen	Ice

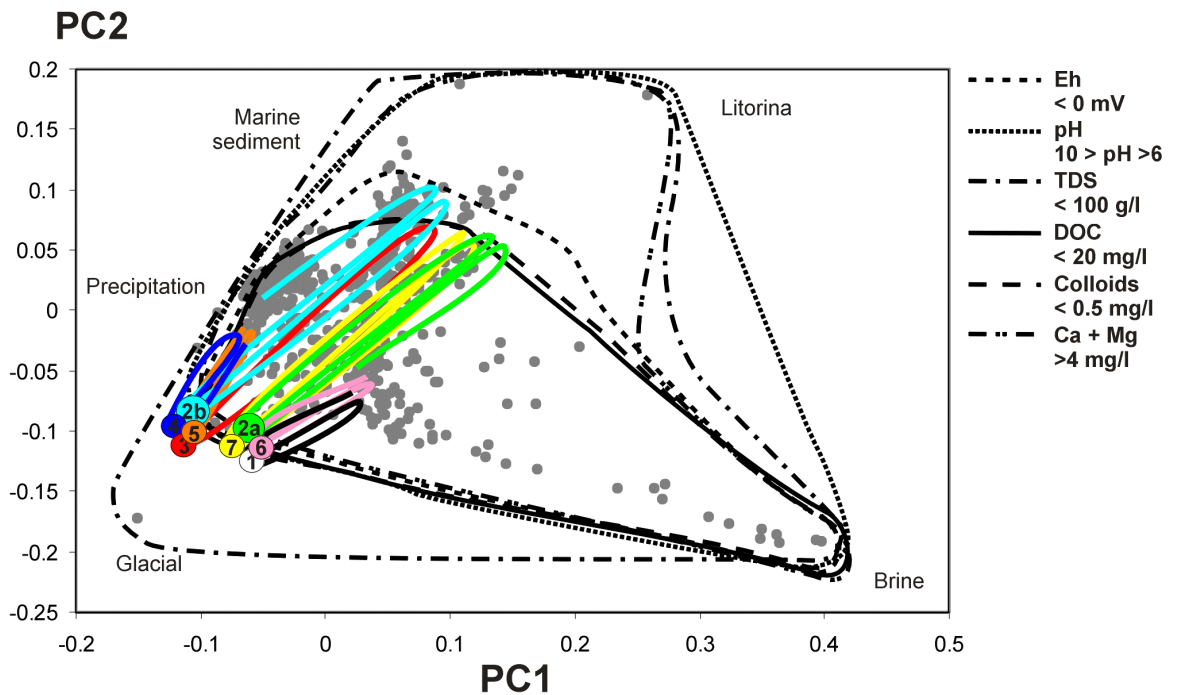


Figure 30. The results of modelling future climate changes 100 000-110 000 years from now. The conditions at the sites are listed in the legend (above figure). The modelling reflects injection of 50% glacial melt-water when the ice sheet is melting. The PC-plot (lower figure) presents chemical compositions of modelled samples at repository depths (500±100 m) in relation to all the samples (grey dots) collected at the Swedish and Finnish sites. The colour lines indicate the compositional changes of the samples in relation to the initial compositions. Samples meeting the SKB criteria and regarded as hydrochemically stable plot inside the areas limited by the solid/dotted lines representing the various criteria listed in the legend. The modelling indicates that only some of the criteria are met for the samples at these climatic conditions.

6 CONCLUSIONS AND IMPLICATIONS FOR REPOSITORY PERFORMANCE

Chemical conditions in a nuclear repository might be affected by climate changes. For example, O₂-rich meltwaters might penetrate to great depths under a warm-based continental ice-sheet; upconing might induce saline waters to move upwards at the glacier limits; saline waters may also be formed as residual fluids resulting from the rejection of salts during ice formation under aggradation of permafrost; and the movement of shorelines might cause water infiltration.

These phenomena have been reviewed in this report, both by discussing evidence of effects from past climatic changes, and by focussed modelling exercises. Of all chemical parameters that affect the performance of a repository, salinity and O₂ are deemed the most dependent on climatic conditions. The results of the modelling performed here show that although there will certainly be changes in groundwater compositions at repository depths due to future climate variations, the groundwaters will have compositional ranges similar to those found now at other depths. The model results indicate that on the average the new groundwaters will fulfil the suitability criteria set to ensure the long-term safety and stability of a HLNW repository.

The first period from 100 to 1000 years is most important for the performance of a HLRW repository. During this period, the amount and toxicity of radionuclides is substantially greater than during later periods. The hydrochemical stability of a repository site is therefore most important over this initial period.

During the initial disturbed state of the repository, i.e. the most complex evolutionary period up to 100 years, several processes simultaneously occur within the repository involving thermal, mechanical, hydraulic, chemical and biological effects. Following this period, hydrogeochemical conditions during the next 100-1000 years should reflect, relatively stable groundwater flow conditions resulting in steady state mixing and reaction processes. At coastal sites the movement of the shoreline is the only significant hydrological and chemical event. In summary, the main geochemical reaction processes that control the hydrochemistry are:

- Fast precipitation/dissolution reactions (equilibrium) for several fracture filling minerals: calcite, iron oxyhydroxides and sulphides, gypsum, fluorite, etc. These reactions control the chemistry of HCO₃⁻, Ca²⁺, Fe^{II} and Fe^{III}, SO₄²⁻, F⁻.
- Ion exchange reactions: Na⁺, Ca²⁺ and Mg²⁺ ratios.
- Weathering reactions of silicates: control of silica and aluminium groundwater concentrations.

- Redox reactions (microbial): control of organic material, Fe^{III}/Fe^{II} ratio, S^{VI}/S^{II}, O₂, CH₄ and H₂, etc.
- pH controlled, mainly by carbonate equilibria but also to some extent by the most rapid weathering reactions

The expected concentration ranges for groundwater constituents at repository level for the Swedish sites are shown in Table 4. Similar concentrations are found at the Finnish sites with the exception of higher salinity levels (Cl, Na, Ca) at the Olkiluoto site.

What could change this picture during a 1000 or 10 000 year period? Anthropogenic climate changes could change local precipitation regimes, thus slightly affecting groundwater flow conditions. Also, in the long run, slow global cooling/heating will change gradually the hydrological regimes. Isostatic recovery of the Fennoscandian Shield will also affect the groundwater paths and groundwaters at repository levels may become dominated by meteoric recharge waters to the detriment of more saline types.

After a period of 10 000 years the total amount of radioactivity in the repository will have decreased to less than 1% of the initial inventory and some radionuclides will have disappeared completely. Intact canisters will have kept safely the remaining radionuclides.

Table 4. The concentration intervals expected for fresh and saline groundwaters at repository level for the Swedish sites (SKB, 1999 , Vol II).

Component	At repository closure		After 1000 years		Glacial period:	
					saline upconing	meltwater
pH	6 to 9		7 to 10		6 to 8	8 to 10
Eh (mV)	0 to -400		-250 ± 100		-200 ± 100	-100 ± 100
Major components (mg/L):						
Na ⁺	10	to 3000	50	to 2000	4500	4.5
K ⁺	1	to 20	0	to 10	37	4
Ca ²⁺	1	to 3000	10	to 2000	9900	7
Mg ²⁺	1	to 200	1	to 100	41	1
HCO ₃ ⁻	10	to 1000	10	to 40	71	25
Cl ⁻	20	to 10000	100	to 5000	25000	< 1
SO ₄ ²⁻	0.1	to 600	0.1	to 400	511	5
HS ⁻	0.01	to 10	< 1		< 1	< 0.1
TOC	0	to 30	< 2		< 2	< 2

During 10 000 to 100 000 years, the hydrochemical conditions will be influenced by the local climatic conditions which will probably have large variations during this period. The main process that affects hydrochemical stability is: varying groundwater flow conditions. These variations will introduce large changes in mixing groundwater patterns. Possible scenarios, and main effects are:

Scenario	Effects
1. Colder climate, which eventually will lead to permafrost	Changes in precipitation amounts and recharge. Permafrost will probably change groundwater flow paths. This might affect salinity at repository levels. Permafrost may also lead to an increase in salinity due to rejection of salts.
2. Ice sheet: glaciation and deglaciation.	Infiltration of glacial meltwater. A minimum amount of cations is quickly achieved by fast water-mineral interactions. Perhaps high O ₂ contents. Oxidising conditions might reach repository level depending on the ratio between groundwater flow and chemical and microbial reactions.
3. Marine conditions: either freshwater or saline water regimes (lake/sea coverage).	Under saline marine conditions, differences in water densities might cause a "turnover" facilitated by relatively fast groundwater flows in vertical fracture zones.
4. Interglacial periods (land)	Climate conditions similar to present, or perhaps colder. Hydrochemistry probably similar to the first 10 000 year period.

The main conclusions from the work are that the present hydrochemistry is and has been affected by present and past hydrodynamic conditions. The past groundwater changes are still traceable in the bedrock. The groundwater at repository depth has and will be affected by extreme waters such as brine, seawater and glacial and precipitation waters in various proportions. The changes are cyclic and are determined by the changing climate. Modelling has predicted a compositional variability similar to what is observed in the samples collected at various depths today. However, despite these hydrodynamic changes the buffer capacity of the rock is such that hydrochemical stability and favourable chemical conditions can be sustained in the perspective of thousands of years. Radical climatic changes causing high flow (such as quick glacial meltdown) can cause short-term hydrochemical instability in the more conductive parts of the rock. The low conductive parts will probably be less affected during such conditions.

7 ACKNOWLEDGEMENTS

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8 REFERENCES

- Ahlbom K., Andersson J.-E., Nordqvist R., Ljunggren C., Tirén S., and Voss C. (1991) Gideå study site. Scope of activities and main results, SKB-TR-91-51, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.
- Ahlbom K. and Tirén S. (1991) Overview of geologic and geohydrologic conditions at the Finnsjön site and its surroundings, SKB-TR-91-08, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.
- Ahonen L. and Vieno T. (1994) Effects of glacial meltwater on corrosion of copper canisters, YJT-94-13, Nuclear Waste Commission of Finnish Power Companies, Finland.
- Andersson J., Ström A., Svemar C., Almén K.-E., and Ericsson L. O. (2000) Vilka krav ställer djupförvaret på berget? Geovetenskapliga lämplighetsindikatorer och kriterier för lokalisering och platsvutvärdering, SKB-R-00-15, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden. In Swedish.
- Anttila P., Ahokas H., Front K., Heikkinen E., Hinkkanen H., Johansson E., Paulamäki S., Riekkola R., Saari J., Saksa P., Snellman M., Wikström L., and Öhberg A. (1999a) Final disposal of spent nuclear fuel in Finnish bedrock - Kivetty site report, POSIVA-99-09, Posiva Oy, Helsinki, Finland.
- Anttila P., Ahokas H., Front K., Hinkkanen H., Johansson E., Paulamäki S., Riekkola R., Saari J., Saksa P., Snellman M., Wikström L., and Öhberg A. (1999b) Final disposal of spent nuclear fuel in Finnish bedrock - Hästholmen site report, POSIVA-99-08, Posiva Oy, Helsinki, Finland.
- Anttila P., Ahokas H., Front K., Hinkkanen H., Johansson E., Paulamäki S., Riekkola R., Saari J., Saksa P., Snellman M., Wikström L., and Öhberg A. (1999c) Final disposal of spent nuclear fuel in Finnish bedrock - Olkiluoto site report, POSIVA-99-10, Posiva Oy, Helsinki, Finland.
- Anttila P., Ahokas H., Front K., Hinkkanen H., Johansson E., Paulamäki S., Riekkola R., Saari J., Saksa P., Snellman M., Wikström L., and Öhberg A. (1999d) Final disposal of spent nuclear fuel in Finnish bedrock - Romuvaara site report, POSIVA-99-11, Posiva Oy, Helsinki, Finland.

- Bath A., Milodowski A., Ruotsalainen P., Tullborg E.-L., Cortés Ruiz A., and Aranyosy J.-F. (2000) Evidence from mineralogy and geochemistry for the evolution of groundwater systems during the quaternary for use in radioactive waste repository safety assessment (EQUIP project), EUR 19613 EN, European Commission, Nuclear Science and Technology.
- Blomqvist R. (1999) Hydrogeochemistry of deep groundwaters in the central part of the Fennoscandian Shield, YST-101, Geological Survey of Finland, Espoo, Finland.
- Blomqvist R., Ruskeeniemi T., Kaija J., Ahonen L., Paananen M., Smellie J., Grundfelt B., Bruno J., Péres del Villar L., Rasilainen K., Pitkänen P., Suksi J., Casanova J., Read D., and Frapé S. (2000) The Palmottu natural analogue project. Phase II: Transport of radionuclides in a natural flow system at Palmottu, EUR 19611 EN, European Commission.
- Blyth A., Frapé S., Blomqvist R., and Nissinen P. (2000) Assessing the past thermal and chemical history of fluids in crystalline rock by combining fluid inclusion and isotopic investigations of fracture calcite. *Appl. Geochem.* **15**, 1417-1437.
- Boulton G. S., Kautsky U., Morén L., and Wallroth T. (2001) Impact of long-term climate change on a deep geological repository for spent nuclear fuel, SKB-TR-97-05, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.
- Donner J., Kankainen T., and Karhu J. A. (1999) Radiocarbon ages and stable isotope composition of Holocene shells in Finland. In *Proceedings of the Conference: The Baltic - past, present and future, Stockholm, March 14-16th, 1994*. Quaternaria, Vol. A:7 (ed. T. Andrén), pp. 31-38. Stockholm University, Stockholm, Sweden.
- Eronen M. and Olander H. (1990) On the world's ice ages and changing environments, YJT-90-13, Nuclear Waste Commission of Finnish Power Companies, Finland.
- Fontes J.-C., Fritz P., Louvat D., and Michelot J.-L. (1989) Aqueous sulphates from the Stripa groundwater system. *Geochim. Cosmochim. Acta* **53**, 1783-1789.
- Gascoyne M. (1999) Long-term maintenance of reducing conditions in a spent nuclear fuel repository, SKB-R-99-41, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.
- Gascoyne M. (2000) A review of published literature on the effects of permafrost on the hydrogeochemistry of bedrock, POSIVA 2000-09, Posiva Oy, Helsinki, Finland.
- Gascoyne M. (2001) ^{36}Cl in Olkiluoto groundwaters: Evidence for intrusion of Litorina seawater, Working Report 2001-20, Posiva Oy, Helsinki, Finland.
- Gascoyne M. and Cramer J. J. (1987) History of actinide and minor element mobility in an Archean granitic batholith in Manitoba, Canada. *Appl. Geochem.* **2**, 37-54.

- Gascoyne M., Ross J. D., and Watson R. L. (1996) Highly saline pore fluids in the rock matrix of a granitic batholith on the Canadian Shield. In *30th Int. Geol. Congr., Aug. 1996*, Beijing, China. Report SKB-ICR-97-04.
- Glynn P. D. and Voss C. I. (1999) SITE-94: Geochemical characterization of Simpevarp ground waters near the Äspö Hard Rock Laboratory, SKI-R-96:29, Swedish Nuclear Power Inspectorate, Stockholm, Sweden.
- Glynn P. D., Voss C. I., and Provost A. M. (1999) Deep penetration of oxygenated meltwaters from warm based ice-sheets into the Fennoscandian Shield. In *Use of Hydrogeochemical Information in Testing Groundwater Flow Models, Workshop Proceedings. Borgholm, Sweden 1-3 Sept. 1997* (ed. OECD NEA), pp. 201-241. OECD, Nuclear Energy Agency, Paris, France.
- Guimerà J., Duro L., Jordana S., and Bruno J. (1999) Effects of ice melting and redox front migration in fractured rocks of low permeability, SKB-TR-99-17, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.
- Gurban I., Laaksoharju M., and Andersson C. (2001) Geodata evaluation and summary of 7 sites in Finland and Sweden, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden. (*in preparation*).
- Herut B., Starinsky A., Katz A., and Bein A. (1990) The role of seawater freezing in the formation of subsurface brines. *Geochim. Cosmochim. Acta* **54**, 13-21.
- Juhlin C., Wallroth T., Smellie J., Eliasson T., Ljunggren C., Leijon B., and Beswick J. (1998) The Very Deep Hole Concept - Geoscientific appraisal of conditions at great depth, SKB-TR-98-05, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.
- Kankainen T. (1986) Loviisa power station final disposal of reactor waste. On the age and origin of groundwater from the rapakivi granite on the island of Hästholmen, YJT-86-29, Nuclear Waste Commission of Finnish Power Companies, Finland.
- Karhu J. (2000) Carbon, oxygen and strontium isotopic characteristics of late-stage fracture calcites at Olkiluoto and Romuvaara, Working Report 2000-19, Posiva Oy, Helsinki, Finland.
- Kotelnikova S. and Pedersen K. (1999) The Microbe-REX project. Microbial O₂ consumption in the Äspö tunnel, SKB-TR-99-17, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.
- Laaksoharju M. (1999) Groundwater Characterisation and Modelling: Problems, Facts and Possibilities. Ph.D., Royal Institute of Technology, Stockholm, Sweden. TRITA-AMI-PHD 1031; ISSN 1400-1284; ISBN 993-049759-5.
- Laaksoharju M., Skårman C., and Skårman E. (1999a) Multivariate mixing and mass-balance (M3) calculations, a new tool for decoding hydrogeochemical information. *Appl. Geochem.* **14**, 861-871.
- Laaksoharju M., Tullborg E.-L., Wikberg P., Wallin B., and Smellie J. (1999b) Hydrogeochemical conditions and evolution at the Äspö HRL, Sweden. *Appl. Geochem.* **14**, 835-859.

- Laaksoharju M. and Wallin B. (1997) Evolution of the groundwater chemistry at the Äspö Hard Rock Laboratory. Proceedings of the second Äspö International Geochemistry Workshop, June 6-7, 1995, SKB-ICR-97-04, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.
- Laaksoharju M. e., Gustafson G., Pedersen K., Rhén I., Skårman C., Tullborg E.-L., Wallin B., and Wikberg P. (1995) Sulphate reduction in the Äspö HRL tunnel, SKB-TR-95-25, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.
- Lampén P. (1992) Saline groundwater in crystalline bedrock - a literature study, YJT-92-23, Nuclear Waste Commission of Finnish Power Companies.
- Landström O. and Tullborg E.-L. (1990) The influence of fracture mineral/groundwater interaction on the mobility of U, Th, REE and other trace elements, SKB-TR-90-37, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.
- Landström O., Tullborg E.-L., Eriksson G., and Sandell Y. (2001) Effects of glacial/post glacial weathering compared with hydrothermal alteration – implications for matrix diffusion. Results from drillcore studies in porphyritic quartz monzodiorite from Äspö SE, Sweden, SKB-R-01-37, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.
- Louvat D., Michelot J. L., and Aranyossy J. F. (1997) Salinity origin and residence time of the Äspö groundwater system. In *Evolution of the Groundwater Chemistry at the Äspö Hard Rock Laboratory. Proceedings of the Second Äspö International Geochemistry Workshop, June 6-7, 1995* (eds. M. Laaksoharju and B. Wallin). Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden. Report SKB-ICR-97-04.
- Luukkonen A. (2001) Groundwater mixing and geochemical reactions - An inverse-modelling approach. In *Groundwater flow, mixing and geochemical reactions at Äspö Hard Rock Laboratory. Task 5, Äspö Task Force on groundwater flow and transport of solutes* (eds. A. Luukkonen and E. Kattilakoski). Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden. Report SKB-ICR (*in print*).
- Luukkonen A., Pitkänen P., Ruotsalainen P., Leino-Forsman H., and Snellman M. (1999) Hydrogeochemical conditions at the Hästholmen site, POSIVA-99-26, Posiva Oy, Helsinki, Finland.
- Löfman J. (1999) Site Scale Groundwater Flow in Olkiluoto, POSIVA-99-03, Posiva Oy, Helsinki, Finland.
- Löfman J. (2000) Site Scale Groundwater Flow in Olkiluoto - Complementary simulations, POSIVA-2000-07, Posiva Oy, Helsinki, Finland.
- Milodowski A. E., Gillespie M. R., Pearce J. M., and Metcalfe R. (1998) Collaboration with the SKB "EQUIP" programme: Petrographic characterisation of calcites from Äspö and Laxemar deep boreholes by scanning electron microscopy, electron microprobe and cathodoluminescence petrography, WG/98/45C, British Geological Survey, Keyworth, Nottingham.

- Olkiewicz A. and Stejskal V. (1986) Geological and tectonical description of the Klipperås study site, SKB-TR-86-06, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.
- Parkhurst D. L. (1995) User's guide to PHREEQC - A computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations, USGS/WRI-95-4227, U.S. Geol. Survey, Lakewood, Colorado. 143 p.
- Parkhurst D. L., Thorstenson D. C., and Plummer L. N. (1980) PHREEQE: A computer program for geochemical calculations, USGS/WRI-80-96, U.S. Geological Survey, Reston, VA. Revised: May 1982 and Jan. 1985.
- Pearson F. J. (1987) Models of mineral controls on composition of saline groundwaters of the Canadian Shield. *Geol. Assoc. Can. Spec. Pap.* **33**, 39-52.
- Pedersen K. (2000) Microbial processes in radioactive waste disposal, SKB-TR-00-04, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.
- Pitkänen P., Luukkonen A., Ruotsalainen P., Leino-Forsman H., and Vuorinen U. (1999) Geochemical Modelling of Groundwater Evolution and Residence Time at the Olkiluoto Site, POSIVA-98-10, Posiva Oy, Helsinki, Finland.
- Pitkänen P., Luukkonen A., Ruotsalainen P., Leino-Forsman H., and Vuorinen U. (2001) Geochemical modelling of groundwater evolution and residence time at the Hästholmen site, POSIVA-2001-01, Posiva Oy, Helsinki, Finland.
- Plummer L. N., Parkhurst D. L., and Thorstenson D. C. (1983) Development of reaction models for ground-water systems. *Geochim. Cosmochim. Acta* **47**, 665-685.
- Puigdomenech I., Ambrosi J.-P., Eisenlohr L., Lartigue J.-E., Banwart S. A., Bateman K., Milodowski A. E., West J. M., Griffault L., Gustafsson E., Hama K., Yoshida H., Kotelnikova S., Pedersen K., Michaud V., Trotignon L., Rivas Perez J., and Tullborg E.-L. (2001) O₂ depletion in granitic media: The REX project, SKB-TR-01-05, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.
- Puigdomenech I., Banwart S. A., Bateman K., Milodowski A. E., West J. M., Griffault L., Gustafsson E., Hama K., Yoshida H., Kotelnikova S., Pedersen K., Lartigue J.-E., Michaud V., Trotignon L., Morosini M., Rivas Perez J., and Tullborg E.-L. (1999) Redox experiment in detailed scale (REX): First project status report, SKB-ICR-99-01, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.
- Raven K. G. and Clarck I. D. (1993) Survey of geoscientific data on deep underground mines in the Canadian Shield, Report 92-012, Atomic Energy Control Board.
- Rhén I., Bäckbom G., Gustafson G., Stanfors R., and Wikberg P. (1997a) ÄSPÖ HRL - Geoscientific evaluation 1997/2. Results from pre-investigations and detailed site characterization. Summary report, SKB-TR-97-03, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.

- Rhén I., Gustafson G., Stanfors R., and Wikberg P. (1997b) ÄSPÖ HRL - Geoscientific evaluation 1997/5. Models based on site characterization 1986-1995, SKB-TR-97-06, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.
- Ruotsalainen P. and Snellman M. (1996) Hydrogeochemical baseline characterisation at Romuvaara, Kivetty and Olkiluoto, Finland, PATU-96-91e, Posiva Oy, Helsinki, Finland.
- Sjöberg L., Georgala D., and Rickard D. (1984) Origin of interstitial water compositions in postglacial black clays (Northeastern Sweden). *Chem. Geol.* **42**, 147-158.
- SKB. (1999) Deep repository for spent nuclear fuel. SR 97 - Post-closure safety, SKB-TR-99-06, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.
- Smellie J. (1996) Very deep hole concept: Geoscientific appraisal to conditions at large depth - Hydrochemistry, SKB-U-96-17, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.
- Smellie J., Larsson N.-Å., Wikberg P., Puigdomenech I., and Tullborg E.-L. (1987) Hydrochemical investigations in crystalline bedrock in relation to existing hydraulic conditions: Klipperås test-site, Småland, southern Sweden, SKB-TR-87-21, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden. 115 p.
- Smellie J. A. T., Bath A. H., and Karlsson F. (1999) Applications of hydrogeochemistry in performance assessment. In *Use of Hydrogeochemical Information in Testing Groundwater Flow Models, Workshop Proceedings. Borgholm, Sweden 1-3 Sept. 1997* (ed. OECD NEA), pp. 43-62. OECD, Nuclear Energy Agency, Paris, France.
- Smellie J. A. T., Laaksoharju M., and Wikberg P. (1995) Äspö, SE Sweden: a natural groundwater flow model derived from hydrogeochemical observations. *J. Hydrol.* **172**, 147-169.
- Smellie J. A. T. e. (2000) Matrix Fluid Experiment: Status report (June 1998 - June 2000), SKB-ICR-00-35, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.
- Suksi J. and Rasilainen K. (2001) Isotopic fractionation of U in rocks reflecting redox conditions around a groundwater flow route. In *Scientific Basis for Nuclear Waste Management XXIV*. Mat. Res. Soc. Symp. Proc. Mater. Res. Soc., Pittsburgh, Penn. (*in print*).
- Suksi U. J., Juntunen P., Pitkänen P., Rasilainen K., Ruskeeniemi T., and Casanova J. (2001) Application of uranium-series disequilibrium data to interpretation of oxygen intrusion in rocks. In *Water-Rock Interaction (WRI-10)* (ed. R. Cidu), pp. 1395-1398. A.A. Balkema, Rotherdam, The Netherlands.
- Svensson U. (1997) A regional analysis of groundwater flow and salinity distribution in the Äspö area, SKB-TR-97-09, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.

- Svensson U. (1999a) Subglacial groundwater flow at Äspö as governed by basal melting and ice tunnels, SKB-R-99-38, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.
- Svensson U. (1999b) A numerical simulation of the origin and composition of the groundwater below Äspö, SKB-R-99-39, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.
- Svensson U. (2001) Representation of porosity and conductivity in a continuum model - Basic concepts, test cases and applications to the Äspö Hard Rock Laboratory, SKB-TS-01-02, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.
- Svensson U., Laaksoharju M., and Gurban I. (2001) Impact of the tunnel construction on the groundwater system at Äspö, SKB-TR-xx-xx, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden. (*in preparation*).
- Tullborg E.-L. (1988) Fracture fillings in the drillcores from Äspö and Laxemar. In *Detailed Investigation of the Drillcores KAS02, KAS03 and KAS04 on Äspö Island and KLX01 at Laxemar* (eds. H. Wikman, K.-A. Kornfält, L. Riad, R. Munier, and E.-L. Tullborg). Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden. SKB-HRL-PR-25-88-11.
- Tullborg E.-L. (1989) The influence of recharge water on fissure-filling minerals - A study from Klipperås, southern Sweden. *Chem. Geol.* **76**, 309-320.
- Tullborg E.-L. (1997) Recognition of low-temperature processes in the Fennoscandian shield. PhD thesis, Dept. Geol., Earth Sciences Centre, Göteborg University, Göteborg, Sweden.
- Tullborg E.-L. and Larson S. Å. (1984) $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ for limestones, calcite fissure infillings and calcite precipitates from Sweden. *Geologiska föreningens i Stockholm förhandlingar* **106**(2).
- Walker D., Rhén I., and Gurban I. (1997) Summary of hydrogeologic conditions at Aberg, Beberg and Ceberg, SKB-TR-97-23, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.
- Wallin B. (2001) Hydrochemical Stability - Modeling of the isotopic ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$, $\delta^{34}\text{S}$ and $\delta^{87}\text{Sr}$) evolution of the groundwater at Äspö, Sweden, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden. (*in preparation*).
- Vieno T. (2000) Groundwater salinity at Olkiluoto and its effects on a spent fuel repository, POSIVA-2000-011, Posiva Oy, Helsinki, Finland.
- Wikberg P. (1998) Äspö Task Force on Modelling of Groundwater Flow and Transport of Solutes. Plan for modelling Task #5: Impact of the tunnel construction on the groundwater system at Äspö, a hydrological-hydrochemical model assessment exercise, SKB-PR-HRL-98-07, Swedish Nucl. Fuel Waste Manag. Co., Stockholm, Sweden.
- Wolery T. J. (1979) Calculation of chemical equilibrium between aqueous solution and minerals: the EQ3/6 software package, UCRL-52658, Lawrence Livermore Nat. Lab., Livermore, California.