SKI Report 2006:12

Research

Geochemical Investigations of Groundwater Stability

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SKI Perspective

Background

A reasonable understanding of groundwater flow and the expected evolution of groundwater conditions is an important component of a safety assessment for the final disposal of spent nuclear fuel. This is needed both for the evaluation of engineered barrier performance and the analysis of radionuclide transport. The groundwater flow is coupled with the climate change, so the understanding of this coupling is also relevant in the formulation of scenarios. The main tool to gain sufficient insight regarding these aspects is perhaps groundwater flow simulations. Nonetheless, it is essential that the reasonableness of simulation results is evaluated with all types of supplemental information such as composition of groundwater constituents, stable isotopes and characterisation of secondary minerals. This report focuses on the geoscientific understanding that can be obtained through analysis of geochemical data from site investigations.

Purpose of the project

The purpose of this project is to provide an overview of how geochemical information has contributed to the understanding of deep groundwater systems in the context final disposal of spent nuclear fuel. This is expected to provide a basis for addressing the use of geochemical information from the ongoing site investigations in Sweden (Forsmark and Laxemar).

Results

This report describes the concept of groundwater stability, its application in safety assessment and the associated geochemical indicators. Attention is also given to interpretation methods of geochemical information and the uncertainties that must be considered. The main result is a description of groundwater stability and previous evolution of groundwater conditions at several different sites in Sweden (e.g. Äspö, Stripa mine, Finnsjön, Forsmark), in Finland (e.g. Olkiluoto) and elsewhere (Sellafield, Whiteshell area, Tono mine)

Future work

There will be a need for a detailed review and independent evaluation of the emerging database with geochemical information from the site investigations at Forsmark and Laxemar.

Project Information

SKI Project Manager: Bo Strömberg
Project Identification Number: 200509040

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Research

Geochemical Investigations of Groundwater Stability

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Executive Summary

The report describes geochemical parameters and methods that provide information about the hydrodynamic stability of groundwaters in low permeability fractured rocks that are potential hosts for radioactive waste repositories. Hydrodynamic stability is, by implication in the Swedish regulations, a property of a prospective site that needs to be examined in the assessment of its suitability for a repository. It describes the propensity for changes in groundwater flows over long timescales, in terms of flow rates and flow directions. Hydrodynamic changes may also cause changes in water compositions, but the related issue of geochemical stability of a potential repository host rock system is outside the scope of this report.

The main approaches to assessing groundwater stability are numerical modelling, measurement and interpretation of geochemical indicators in groundwater compositions, and analyses and interpretations of secondary minerals and fluid inclusions in these minerals. This report covers the latter two topics, with emphasis on geochemical indicators.

The extent to which palaeohydrogeology and geochemical stability indicators have been used in past safety cases is reviewed. It has been very variable, both in terms of the scenarios considered, the stability indicators considered and the extent to which the information was explicitly or implicitly used in assessing FEPs and scenarios in the safety cases.

Geochemical indicators of hydrodynamic stability provide various categories of information that are of hydrogeological relevance. Information about groundwater mixing, flows and water sources is potentially provided by the total salinity of groundwaters, their contents of specific non-reactive solutes (principally chloride) and possibly of other solutes, the stable isotopic ratio of water, and certain characteristics of secondary minerals and fluid inclusions. Information pertaining directly to groundwater ages and the timing of water and solute movements is provided by isotopic systems including tritium, carbon-14, chlorine-36, stable oxygen and hydrogen isotopes, uranium isotopes and dissolved mobile gases in groundwaters, and also by stable isotopes and uranium isotopes in secondary minerals. Information on timing of water and solute movements is important because it indicates any correlation with the timing of external events that might have perturbed and destabilised the groundwater system in the past, and allows a timescale to be estimated for the persistence of stable conditions. There are many sources of uncertainties in deploying these methods, originating from problems or constraints in sampling, analysis and interpretation.

Data from a number of published site investigation projects and research programmes are reviewed to illustrate the patterns of geochemical data and the relationships between them, and how these are interpreted in terms of hydrodynamic stability. Data from Äspö and Stripa and from exploratory boreholes at Finnsjön and other sites in Sweden are compiled and discussed. Preliminary data from SKB's ongoing site investigations at Simpevarp/Laxemar and Forsmark are not considered in detail but

their general similarities with Äspö and Finnsjön/SFR respectively are introduced into the discussion of geochemical evidence for groundwater stability in inland and coastal areas. Relevant data from Finnish sites including Olkiluoto, from the Whiteshell URL area in Canada, from Sellafield in the UK, and from the Tono area and URL in Japan are also summarised in appendices and discussed because they add further insights into the interpretation of geochemical indicators for a range of geological environments.

The compiled data provide only limited scope for comparison of groundwater evolution and stability between inland and coastal areas in Sweden, because of the patchiness of representative data especially from early site studies. The external changes that might have perturbed stable groundwater conditions in the past are glaciation (i.e. melt water, mechanical loading/unloading and permafrost) and varying sea water infiltration at coastal sites due to changes in palaeo-Baltic and isostatic conditions. The present distributions of palaeo-Baltic sea water in groundwaters at coastal sites vary, reflecting local palaeohydrogeological conditions. It is likely that inland areas have had longer durations of post-glacial fresh water infiltration than coastal areas, possibly causing greater degrees of dilution and dispersion of pre-existing groundwaters and thus overprinting their hydrochemical and isotopic ‘fingerprints’. Lower post-glacial hydraulic gradients relative to inland sites may account for the occurrence of more relict cold-climate water at coastal sites.

Some general observations are based on rather thin evidence and therefore speculative. Firstly, it seems that glacial melt water penetrated many hundreds of metres and in some places to at least 1,000 m depth. However the low remaining proportions of melt water and of much older saline Shield water suggest that melt water flux did not fully displace pre-existing groundwaters at these depths. Secondly, where there has been post-glacial infiltration of palaeo-Baltic sea water, the density stratification or compartmentalisation effect coupled with low hydraulic gradient has reduced rates of subsequent fresh water circulation after shoreline recession.

There are many uncertainties in interpreting these geochemical indicators in terms of the penetration depths of glacial melt waters and the degree to which they replace pre-existing groundwaters, of other aspects of groundwater stability, and of comparisons between inland and coastal groundwater systems. Uncertainties derive partly from the reliability of groundwater samples as being representative of *in situ* conditions, and partly from the non-uniqueness of interpretative models. Future investigations using these approaches need to improve sampling, to make conjunctive use of geochemical and isotopic indicators which have varying timescales and sensitivities, and to integrate these indicators with palaeohydrogeological modelling to support the development of reliable groundwater flow and solute transport models for Performance Assessment.

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1. Introduction

1.1. Objective and Scope of Review

This report is the result of a contract (Ref. 14.9-010482/01097) from SKI (Project Manager: Dr Bo Strömberg) for a Review of Geochemical Indicators of Groundwater Stability.

The general objective is to inform SKI about the geochemical methods that provide information about the hydrodynamic stability of groundwater systems. Such methods should contribute to sound and adequately comprehensive characterisations of candidate sites for a radioactive waste repository in Sweden.

One of the main ways of assessing scenarios for hydrodynamic stability in a safety assessment is by understanding groundwater movements in the past, i.e. 'palaeohydrogeology'. Geochemical methods are the key approach to understanding those movements. Geochemical data have to be interpreted to understand their palaeohydrogeological significance, so this report also considers methods for interpretation and the assumptions and uncertainties that are associated with data and interpretations.

In summary, this report describes:

- Geochemical data that are evidence of groundwater travel times and/or solute residence times ('groundwater ages') and of past episodes in which groundwater flow and mixing conditions were different from those at present;
- Sources of uncertainties in raw data, and the extent to which those uncertainties might be minimised;
- Interpretation concepts, methods and tools that transform raw geochemical data into knowledge about the groundwater system and specifically about palaeohydrogeology, and the main areas of uncertainties and potential contention;
- Background illustrative data from Sweden and elsewhere that illustrate these methods and exemplify the 'state of the science'.

Numerical modelling of groundwater movements is the other principal approach to assessing hydrogeological stability and whether groundwater movements might have changed over time between past and present and might change in future scenarios. Numerical modelling is outside the scope of this report, but it is important to remember that it is complementary to the use of geochemical indicators which are qualitative or semi-quantitative tests of the concepts and predictions of numerical models.

Geochemical stability, i.e. the maintenance of the chemical environment in terms of pH, redox and compositions of groundwaters by geochemical water-rock interactions, is also outside the scope of this report but is considered briefly in Section 3.3. Issues of geochemical stability are strongly connected with hydrodynamic stability because, in an isothermal system, they usually concern movements of water masses with different compositions. For example, such movements are directly implicated in changes of groundwater salinity over time. The issue of redox stability concerns both groundwater movements and the ability of water-rock reactions to buffer the water composition against externally-driven change.

1.2. Background

A safety case for a radioactive waste repository in Sweden must extend for hundreds of thousands of years. Over that length of time, conditions at the land surface will inevitably change due to climatic changes and geomorphologic processes.

One of the attributes of the multi-barrier concept for radioactive waste containment in a geological repository is that the geosphere has long-term stability that allows the engineered barrier system to perform as designed for a very long time. The basic principle is that geosphere stability increases with increasing depth, due to attenuation of the impacts of climate-driven processes at the land surface. Stability ensures a continuity of known physical (including tectonic, rock mechanical and hydrodynamic) and chemical conditions in which the engineered containment provided by the waste canisters and backfill materials can operate as designed in a predictable way for a very long period. Geosphere stability at a particular site and the degree to which a site-specific safety case depends on it need to be tested to build confidence in the models and scenarios on which a safety case is based.

Hydrodynamic stability implies unchanging water flow, in terms of rate and direction. The most likely driving forces that would change water flow rates and/or directions are groundwater pressures at the system boundaries. Chemical stability implies unchanging water compositions which, as discussed in the previous section, are dependent on hydrodynamic stability and the buffering capacity of water-rock interactions. Hydrodynamic and chemical stability are also directly coupled through the effect of chemical composition on the density of groundwater and thus on the pressure (‘head’) that a column of water exerts.

In discussion of how the concept of stability might be assessed for safety assessments, a workshop of the EC-funded PADAMOT palaeohydrogeology project proposed that stability is *‘the capacity of a site to respond to external influences with minimal impact to the environment of a deep repository’* or *‘the capacity to maintain favourable conditions in the environment of a deep repository’* (Bath et al., 2003, 2005). However it was also suggested that stability is not a simple concept because a low permeability groundwater system is unlikely to be at steady state.

The Swedish regulations for safety in connection with disposal of nuclear waste stipulate that:

> ‘The repository site and repository depth should be chosen so that the geological formation provides adequately stable and favourable conditions to ensure that the repository barriers perform as intended over an adequate period of time. The conditions intended primarily concern temperature-related, hydrological, mechanical, and chemical factors’ (SKI, 2002).

Groundwater stability is not referred to explicitly in SKB's compilation of 'geoscientific suitability indicators and criteria for siting and site evaluation' (Andersson et al., 2000) but is implicit in the discussion of important parameters to be determined during site investigations, specifically in 'water chemistry for geoscientific understanding' (Section 6.5 in Andersson et al., 1998). Variations in groundwater compositions need to be understood because they indicate possible future variations in compositions and properties in both short (e.g. changes due to construction and operation) and long (e.g. ice age) timescales. Evidence of long-term stability of groundwaters is also not in the suitability indicators and criteria for site evaluation (Andersson et al., 2000). Potential impacts of changes will be taken into account in the main and variant scenarios in performance assessment. Nevertheless, it is clear that investigation and interpretation of evidence for groundwater stability should contribute to site evaluation and performance assessment.

SKI's SITE-94 assessment states that 'geochemical modelling for prediction of possible future changes at a given site and the consistent description of the variability in geochemical parameters….. must be based on an understanding of how observed geochemical phenomena have developed due to past and present processes'. In SITE-94, a scenario was proposed whereby oxygenated glacial meltwater might be to penetrate to repository depth (SKI, 1996; Glynn and Voss, 1999; Glynn et al., 1999). This was based on a hypothesis that dissolved oxygen might be preserved in infiltrating glacial meltwater. There is palaeohydrogeological evidence in the observation of relict water with cold-climate isotopic composition that glacial meltwater penetrated to more than 1000 m depth beneath the Pleistocene ice sheets. Though the geochemical indicator of a component of glacial water is agreed, the possibility of water remaining oxidising to that depth and thereby causing redox instability is contested by SKB.

SKB carried out modelling of mass transport and geochemical reactions to examine reductive buffering of chemical conditions by rock minerals. Modelling of the oxygenated glacial meltwater scenario assumed that the greatest downwards hydraulic pressure and potential flux of fresh oxygenated melt water will occur while the margin of the ice sheet is passing over the repository location. Modelling results – that there is adequate redox buffering capacity in the rock, specifically in fracture minerals – were supported by the spatial distribution of secondary mineralisation by iron oxides suggesting that dissolved oxygen is attenuated at shallow depths by reaction with ferrous minerals (Guimera et al., 1999; Gascoyne, 1999; Tullborg, 1999; Puigdomenech, 2001).

1.3. Groundwater Stability in Safety Cases

Many performance assessment (PA) models in the past have simulated the long-term behaviour of a repository with a numerical model that is parameterised for present conditions, i.e. assuming steady state groundwater flow with stable hydrodynamic boundary conditions and chemical conditions. In some PA exercises, the impacts on safety of variant scenarios representing future non-steady evolution and potential sources of instability have also been considered.

Three main approaches to assessing long-term groundwater stability have been used in support of PA:

- Numerical modelling of hydrodynamics with parameters and boundary conditions that have been set according to expert judgement of past climate impacts;

- Deductive interpretation and geochemical modelling of present-day groundwater chemical and isotopic compositions to deconvolute the 'signatures' of past infiltration conditions and the mixing of water masses that characterises past hydrodynamics;

- Characterisation and geochemical/isotopic analyses of secondary minerals and their fluid inclusions to obtain information about the groundwaters from which they were precipitated.

The main aspects of how these have been used in major PA exercises for crystalline rock sites are discussed further in Section 2.

1.4. Content of this Report

One way to assess the stability of a groundwater system is to investigate evidence for change in the past. 'Proxy' indications of past change are investigated, whereby past hydrodynamic or chemical conditions have been recorded in some sort of secondary evidence. Most of such evidence is geochemical (Bath et al., 2000; Bath and Strömberg, 2004; Bath, in press):

- groundwater masses with different compositions whose spatial distribution can be interpreted as evidence of past flow and boundary conditions;
- groundwater compositions that can be interpreted as mixtures of originally-distinct water sources;
- isotopic compositions of groundwaters that can be interpreted to provide absolute or relative ages and thus evidence of the timescales of change and heterogeneity;
- assemblages of secondary minerals that indicate geochemical reactions ('water-rock reactions) in the past;
- geochemical and isotopic compositions or other mineralogical characteristics of secondary minerals, or of specific growth zones in such minerals, that can be interpreted to give compositions of co-existing groundwaters at the time of formation.

This review describes how these geochemical indicators might be used, gives examples, and evaluates the various sources of uncertainty. Interpretation of measured geochemical parameters is exemplified by reference to data for various groundwater systems and specific formations or sites. Existing data for various Swedish sites, including those at Äspö/Laxemar and Finnsjön which are adjacent to the Simpevarp and Forsmark candidate siting areas respectively, are compiled and evaluated to illustrate potential application of the approach and associated constraints, uncertainties and alternative models. Some observations are made about the comparison of palaeohydrogeological behaviour of inland and coastal sites, although these are rather speculative because data are sparse In addition, a conceptual background is supplied by data and interpretative models from other studies worldwide in hard rock terrains in Finland, Canada, Britain and Japan. The findings of the review have implications for data requirements and interpretative approaches and models that might be valuable in the safety assessments of Swedish repository sites. The discussion of issues and feasible site investigation methods also has implications for how the concept of 'stable groundwater conditions' should be considered in the context of a safety case.

2. Palaeohydrogeology and Stability Indicators in Safety Cases

In high latitude countries, the scenario generally regarded to have the greatest potential impact on groundwater stability is glaciation. Thus evidence, including geochemical indicators, of the past impacts of glaciation and of periglacial conditions (i.e. continuous or discontinuous permafrost and meltwater runoff) has been investigated to varying extents in the northern and central European programmes (Sweden, Finland, UK, Switzerland) and Canada.

The extents to which the base case or normal evolution scenarios and variant scenarios have been tested or calibrated by palaeohydrogeological interpretation of geochemical indicators of stability are summarised in Table 1.

SKB's safety case exercise SR97 was based on three generic sites (Aberg, Beberg and Ceberg) that were parameterised by data sets from three SKB research sites: Äspö, Finnsjön and Gideå respectively (SKB, 1999). Land uplift is a known trend and was included in the base scenario, whilst climate change and its potential impact on groundwaters were considered variant scenarios. Therefore hydraulic and hydrochemical evolution of the geosphere due to land uplift only is included in the base scenario and potential instability due to other time-dependent changes was comprehensively included in the variant climate scenario. The climate scenario particularly hypothesises on the transient groundwater flows associated with glaciation and permafrost.

Evolution of hydrodynamic and geochemical conditions in the glacial climate scenario of SR97 were based on palaeohydrogeological interpretation of hydrochemical, isotopic and mineral data, though this is not explicitly acknowledged and explained. Conceptual models for future evolution of the geosphere at the three sites were constructed to resemble past evolution as inferred from these interpretations, differing considerably in the expected durations of ice cover and submergence beneath the sea. The magnitude, spatial extent and timing of these changes were studied by modelling that was validated by simulating past changes and comparison with present conditions (Svensson, 1999a, 1999b, Laaksoharju et al, 1998). Modelling of the permafrost scenario was based on the hypothesis that groundwater flow will be forced to greater depths by the reduction of permeability due to freezing at shallow depths with a consequent reduction in recharge, and also on the suggestion that saline groundwater may be generated by freeze-out as a by-product of pore water freezing. So far, palaeohydrogeology has not produced firm evidence to confirm these hypotheses, although field and laboratory studies at the Lupin Mine (northern Canada) have produced various bits of evidence (Ruskeeniemi et al., 2002, 2004). The overall conclusion in SR97 was that, for the majority of situations considered, even extreme climate change would not substantially affect the safety of a repository at the planned depth.

Table 1. Summary of scenarios considered in PAs for crystalline rock repository sites and of how palaeohydrogeology was interpreted and used in support of PA.

PA	**Scenarios**	**Evidence for Groundwater Stability**			
		Modelling[1]	**Geochemistry**[2]	**Mineralogy**[3]	**How was it used in PA?**
SR97	Land uplift in base scenario; climate scenario has effects of glaciation and permafrost on groundwaters	✓	✓	✓	Supporting research and interpretation of site data but not explicit in PA
SITE-94	Central scenario has EFEPs for permafrost, glaciation and sea level change	✗	✓	✗	Comprehensive review of palaeoclimate effects on geosphere including groundwaters
TILA-99	Various 'what if' scenarios incl. Glaciation, more fresh and more saline water, etc	✓	✓	✓	Used to constrain qualitative/semi-quant variants
AECL-94	None, 10^4y timescale	✓	✓	✓	Supporting research and interpretation of site data
Kristallin-1	Alpine uplift is within uncertainty range of ref scenario; periglacial etc	?	✓	✗	Interpreted site data cited in support of geosphere stability for EBS performance
Nirex 97	Steady state base case only	✗	✓	✓	Comprehensive interpretation and modelling of site data in associated reports
H-12	Seismicity, volcanism, uplift, erosion. No climate scenario	✗	✗	✗	Palaeohydrogeology research into climate effects but not used in H-12

Notes: [1] Modelling = Palaeohydrogeological numerical modelling; [2] Geochemistry = Interpretation of groundwater chemistry and isotope hydrology; [3] Mineralogy = Interpretation of secondary minerals and fluid inclusions.

Scenario identification in SKI's SITE-94 was done in terms of EFEPs (external Features, Events and Processes) (SKI, 1996). The Reference Case involved no changes of the EFEPs over time. A Central Scenario for 120,000 years into the future was developed incorporating changes over time in the EFEPs that concern climate, i.e. permafrost, glaciation and sea-level changes. Assessing the impact of the Central Scenario was aided by quantitative or qualitative information on how past climate events were interpreted as having perturbed the stability of the geosphere, including data for geochemical indicators such as salinities and isotopic compositions of groundwaters (King-Clayton et al., 1995, 1997). Oxygenated glacial meltwater was hypothesised to have penetrated to more than 1000m depth beneath the Pleistocene ice sheets, as mentioned in the previous section.

Posiva's safety assessment for four candidate repository sites started out with conceptual descriptions of 'normal evolution' of the natural and repository systems (Vieno and Nordman, 1999). The normal evolution safety model in TILA-99 is equivalent to the base scenario in SKB's SR97. The normal evolution description is divided into five timeframes: up to 100 years, 100 to 10^4, 10^4 to 10^5 years, 10^5 to 10^6 years and beyond a million years. These descriptions of normal evolution and the potential effects on the repository system and on geosphere conditions are constrained by palaeohydrogeological interpretations of hydrochemical, isotopic and mineral data. Lines of palaeohydrogeological evidence were (i) the observed distributions of salinity at the four sites (two of which are coastal and two are inland), (ii) the groundwater ages interpreted from stable isotopic and ^{14}C data, and (iii) the distribution of oxidised iron-containing fracture-fill minerals (Pitkänen et al, 1996, 1998a, 1998b, 1999). These indicated that post-glacial land rise and eustatic sea level change have had significant impacts on the evolution of groundwater flow over time at the two coastal sites. The groundwater flow model used in the assessment assumed steady state, but then scenarios were explored by qualitative or semi-quantitative 'what if' variants. The hydraulic and hydrochemical conditions and boundaries of these variant models were strongly constrained by palaeohydrogeology for glacial meltwater, fresh-water flow, and saline groundwater scenarios. Since TILA-99, there has been growing interest in the past evolution of the saline-fresh water transition at Olkiluoto in the context of potential upconing of saline groundwater towards an excavated repository.

Canadian regulations at the time of AECL's safety assessment of the Whiteshell area only required an evaluation of radiological safety up to 10,000 years (Davison et al., 1994). Palaeohydrogeological interpretations were based on ages and compositional mixing of groundwaters and on evidence from secondary minerals that infill fractures. Stable isotope ($^{18}O/^{16}O$, $^{2}H/^{1}H$) and ^{14}C data identified brackish waters in fracture zones at several hundred metres depth corresponding to recharge during the last glaciation, below which there are older saline groundwaters of probable pre-glacial origins (Gascoyne and Chan, 1993; Gascoyne et al, 1999, Laaksoharju et al., 2000; Gascoyne, 2004). Salinity changes and other indications of groundwater mixing indicated that present-day recharge does not penetrate much below 200 m depth and cold-climate waters in the past have not circulated deeper than about 500 m corresponding to a sharp diminution of fracture density (Gascoyne, 2004). Secondary minerals in fractures at various Shield locations were studied by isotopic and geochemical methods from which data were interpreted as indicating episodes of dissolution and precipitation with timing from early hydrothermal conditions to recent groundwater circulation (Bottomley, 1987; Bottomley and Veizer, 1992; Bottomley, 1993; Gascoyne et al., 2003).

The Swiss Kristallin-1 safety assessment considered alternative scenarios for geological and climatic changes versus the reference scenario which assumed that conditions continue as at present and that any changes are negligible (Nagra, 1993).

Potential geological changes associated with continued Alpine uplift were evaluated and were found to have ranges within uncertainty bounds already applied to reference scenario modelling. Changing groundwater fluxes and decreased groundwater travel times were considered by varying parameters in the reference scenario. Geochemical indicators were not used to provide limits to the alternative scenarios. However geochemical indicators were amongst the evidence cited by Thury et al. (1994) in support of hydrodynamic and chemical stability of the geosphere at 400 m depth for reliable operation of the engineered barriers over a long timescale.

The Nirex 97 assessment of post-closure performance of a repository at Sellafield in northwest England was carried out with a groundwater model that assumed steady state conditions, i.e. it used the present-day hydrogeological setting, boundary conditions and measured parameters (Nirex, 1997a). Palaeohydrogeological interpretations of hydrochemical, isotopic and mineralogical data were covered in a supporting report (Nirex, 1997b; Bath et al., 2005). Isotopic data indicated contrasting turnover times in different parts of the groundwater system at Sellafield. Geochemical and mineralogical information from secondary calcite suggested a large degree of long-term stability in the overall distribution of groundwaters although it also indicates varying degrees of relatively minor fluctuations of salinity and redox conditions, the potential effect of which on the stability of near field and EBS (engineered barrier system) environments would need to be considered (Nirex, 1997a, c; Milodowski et al., 1997).

A significant scenario in repository safety assessments in some regions is seismic activity and its potential effect on groundwater movements, especially the transient activation of fast flow pathways from repository depth to surface. The Japanese preliminary safety assessment H-12 focused on the perturbation scenarios of seismicity, volcanism, uplift and erosion (JNC, 1999). These scenarios were assessed qualitatively or semi-quantitatively as variants on a base scenario which assumed uniform steady state groundwater conditions. Palaeohydrogeological studies at two research sites at Tono and Kamaishi have provided geochemical data for the effects of repeated seismic events on groundwater systems in faulted rock areas. In a separate study of the Nojima fault zone, responsible for the 1995 Kobe earthquake, it was found that fracture-fill calcite down to 1800 m depth has formed from infiltration of meteoric and sea waters within the last 60,000 years (Lin et al., 2003).

3. Evolution and Stability of Groundwaters

3.1. Hydrodynamic Stability

Some physical hydrogeological principles and concepts need to be considered when making interpretations about the hydrodynamic stability of groundwater.

Movement of water through a system of low permeability rocks is driven by the pressure gradients due to heads at the boundaries of the system and due to density variations of water within the system. Density variations may be caused by water compositions and/or by thermal effects, and in an isothermal system are coupled directly to variations of water salinity. Heads at the boundaries of a groundwater system usually are influenced by the topography of the water table above the system. In short timescales, topography of the water table changes with recharge amounts. However in longer timescales, other factors may have affected (or will affect) heads at the boundaries of, and within, a groundwater system. These factors include erosion, uplift and other tectonic forces and climatic impacts such as glacial loading.

The timing of past head changes, the rate of change, and the hydraulic properties will have determined whether a groundwater system is presently in a *steady state* or *transient state*.

'Steady state' and 'stable' have similar but slightly different meanings in the context of groundwater conditions. Steady state is an important hydrodynamic concept indicating that groundwater movement is occurring at equilibrium with the hydraulic driving forces and constraints. A stable groundwater system (which may or may not be at steady state) is not readily perturbed from its present state i.e. present flux and flow direction are relatively less responsive to potential changes in driving forces within the system and at the system boundaries.

Stability is a rather imprecisely-defined concept concept - it does not mean that a groundwater system is completely inert or that water does not move. Greater groundwater stability is not necessarily correlated with lower permeability, since aquifers can also have inherently stable groundwater conditions. Another way of describing stability is that the system is in a low energy state with respect to driving forces and the potential for change. Responses to perturbations occur slowly and have relatively low magnitudes of change.

Steady state is achieved by a groundwater system when the distribution of heads throughout the system is in equilibrium internally and with heads at the boundaries. During a time step, if there are no head changes at the boundaries then there should be no head changes within the system at steady state. Low permeability groundwater systems are less likely than aquifers to be at steady state hydrodynamically because they respond to pressure changes at boundaries more slowly. A groundwater system in low permeability rocks is in a transient state if heads within the system continue to change when the heads at the boundaries remain constant. The effect is like a 'delayed response'. The time for which the transient state might persist depends on the pressure diffusivity and the distance scale. However if the system has responded to the external changes by mass transport of water masses with different densities, then the persistence of the transient state may be controlled by the diffusivity for mass transfer. Pressure, or hydraulic, diffusivity for a low permeability crystalline rock is around 10^{-5} to 10^{-4} m^2/s, whereas the large scale mass diffusivity is likely to be around 10^{-10} to 10^{-11} m^2/s.

Consideration of the stability of a low permeability groundwater system needs to understand how the potential for change varies spatially and temporally. Spatial variation is significant primarily because, in general, groundwater stability is expected to increase with depth, i.e. with increasing distance from climate changes and other energy perturbations at the surface, especially in a low permeability system.

Temporal variation is considered in terms of the timeframes (short term or long term, i.e. operational versus post-closure safety timescales) for a perturbation of driving forces and for the consequent response of the groundwater system. In a low permeability groundwater system, transient conditions are likely to prevail because mass movement of groundwater in response to pressure changes at the boundaries is much slower than it is in a system with higher permeability. Putting past groundwater changes into an absolute or relative timeframe is one of the aims of geochemical (specifically isotopic) investigations in palaeohydrogeology.

3.2. Timescales

It is clearly important to establish the timescale over which the evolution of a groundwater system is being interpreted and its stability or otherwise is considered to be significant. For this discussion, it is proposed that three divisions of timescale in the past should be considered:

0 to 1000 years
10^3 to 10^5 years
$>10^5$ years

These timescale divisions are useful for present purposes because they are compatible with the age ranges and mixing timescales for groundwaters that can be quantified with presently-available isotopic and geochemical methods. For example, the 0-1000 years timescale includes groundwaters that were recharged relatively recently and therefore are likely to have a detectable content of thermonuclear tritium (^3H) which indicates ‘modern’ water, i.e. less than 50 years old. 10^3-10^5 years corresponds roughly to the timescale that can be resolved with carbon-14 (^{14}C) dating which is up to about 35,000 years for groundwater ages. The 10^3-10^5 years timescale includes the Holocene post-glacial and the late-Pleistocene glacial periods, so groundwaters with those ages may or may not have depleted stable isotope ratios ($^{18}O/^{16}O$ and $^2H/^1H$) that are characteristic of cold-climate recharge. Groundwaters with ages $>10^5$ years can be categorised as ‘very old’ and can be characterised by the content of the long-lived cosmogenic isotope chlorine-36 (^{36}Cl) relative to the bulk of dissolved chloride.

They are also sensible divisions in the context of a repository safety assessment (NEA, 2002; Dverstorp and Strömberg, 2005). The first 10^3 years into the future is critical in terms of repository performance and the high radiotoxicity of the inventory. It also corresponds to the timescale of ‘human experience’ within which biosphere fluctuations have been minor relative to the glacial and interglacial fluctuations of longer periods. The 10^5 year timescale corresponds roughly to that of a glaciation cycle, for which repository performance should be robust. As already discussed, geosphere stability is an important contributor to that robustness. The most recent of several ice age episodes in northern Europe that must have had some influence on groundwater evolution occurred 10^3 to 5 x 10^4 years ago.. In addition to the tectonic (i.e. crustal depression) and hydrological (i.e. melt water) effects of the ice sheet at the peak of glaciation, there was also a considerably longer period when permafrost might have affected groundwater evolution.

>10^5 years is the upper end of the timescale for which safety analysis has any meaning and is also the timescale in which the radiotoxicity of a spent fuel inventory will have diminished to having the same hazard as the uranium ore from which the nuclear fuel was originally derived.

SKB evaluates the roles and performance of engineered and geosphere barriers in 'nested' timescales of 0 to 1000 years (the thermal phase), 0 to ca.10^4 years (the isolation phase) and to >10^4 years (the geologic phase) (A. Hedin in NEA, 2002).

3.3. Hydrochemical Evolution and Stability

The major aspects of hydrochemical evolution that are of interest with respect to a repository safety case are:

- salinity and density,
- redox (especially dissolved oxygen content),
- pH conditions.

Other geochemical properties of a groundwater system that are of interest in understanding its evolution and stability are:

- concentrations of specific solutes,
- equilibria between groundwaters and minerals, and precipitation/dissolution,
- diffusive exchange with matrix in a dual porosity or fractured rock medium,
- sorption and exchange of solutes by mineral/colloidal/microbial material.

SKB focuses its hydrochemical strategy on a number of 'suitability indicators', primarily salinity, redox as a proxy for dissolved oxygen, and pH, and secondarily a number of other parameters. The suitability indicators represent the main variants in the chemical environment of the repository that might influence its performance, particularly in terms of corrosion of the spent fuel canisters, and swelling and mechanical integrity of the bentonite buffer and backfill mixture. The long-term stability of these parameters is therefore an essential consideration in safety assessment.

Salinity (total mineralisation or TDS) is controlled by movement and mixing of groundwaters from different sources. Salinity for most groundwaters that have dominantly Na-Cl compositions is linearly related to chloride concentrations. Interpreting variations in chloride or salinity and using these variations to calibrate models are important aims in a site investigation. Moreover, because density is linearly related to salinity, interpreting salinity variations and sources is a key aspect of interpreting changes in forces that drive movement and thus physical stability of groundwaters.

Redox conditions in groundwaters surrounding a repository should be stable regardless of temporal fluctuations of redox at the outer boundaries of the host groundwater system. In the KBS-3 disposal concept, the use of copper canisters has a more specific requirement that dissolved oxygen should be excluded. Recharging groundwaters contain dissolved oxygen and therefore are oxidising. Under normal conditions of groundwater evolution, dissolved oxygen and other solutes that support oxidising conditions are consumed by geochemical reactions that 'buffer' deeper groundwaters to be reducing. Geochemical equilibria and 'buffering' mineral phases need to be sufficiently well-understood and characterised for a particular site that this aspect of hydrochemical evolution can be predicted with confidence (Guimerá et al., 1999).

Geochemical equilibria that control groundwater pH within the acceptable range need to be similarly understood. Evolution of pH from the point of recharge through flow to depth in a groundwater system is most likely to be controlled by combinations of partial pressure of CO_2 (pCO_2) at recharge and reactions with carbonate and aluminosilicate minerals.

Concentrations of specific solutes in groundwaters, and how they evolve over time, may be directly relevant to specific aspects of repository safety or they may be useful tracers or indicators of geochemical change and stability. Various trace elements are included, for example redox-sensitive solutes such as Fe, Mn, SO_4 and U. However they can only be useful as indicators of evolution over time if an 'archive' of past concentrations can be analysed; such an archive may be provided by secondary minerals which have grown over the timescale of interest (Degnan and Bath, 2005).

Evolution over time of the state of geochemical equilibria between minerals and groundwater determines the direction of water-rock reactions, i.e. the propensity for precipitation or dissolution of minerals. Such equilibria are essentially a measure of the chemical stability of a groundwater. The inventory of minerals that is available in the secondary mineral assemblage within fractures of a crystalline rock controls the extent of buffering of water compositions to externally-imposed changes (e.g. in redox). Minerals in the rock matrix may also provide some buffering capacity, and they also may provide sorption capacity. However the role of matrix minerals and matrix pore water in influencing the hydrochemical evolution and stability of groundwater in a fracture network is dependent on the relative timescales for diffusion into and out of matrix and for externally-driven changes to groundwater in fractures (e.g. mixing). Potentially, fracture-matrix interaction could be a major effect on hydrochemical evolution and stability.

In summary, the stability of acceptable values for the primary hydrogeochemical suitability indicators (salinity, redox, pH) and secondary indicators (dissolved organic carbon DOC, colloids, NH_4^+, Ca^{2+} & Mg^{2+}, Rn) is determined by both the stability of groundwater flow and mixing and the continuation of water-rock buffering reactions, as described above for the primary indicators.

Of the secondary indicators, increases of NH_4^+ and DOC would depend on inputs from the surface boundary, i.e. climate/soil/surface water conditions that stimulated additional production and infiltration of these from organic sources. However the concentrations of these in groundwaters at depth would remain controlled by water-rock reactions, primarily redox. Colloid abundances are dependent on both water-rock reactions and salinity, and also possibly on external inputs as with DOC. Ca^{2+} and Mg^{2+} are controlled by water-rock reaction and also depend on external inputs, primarily increase due to a Ca-rich brine (thus not itself a challenge to the requirement of >4 mg/L) or decrease due to rapid injection to depth of very dilute groundwater (e.g. unmixed, unreacted glacial meltwater).

Rn is controlled by local release from mineral hosts of U and Ra. The level of Rn is a safety issue during a construction and operational phase of a repository. Thus the stability concern is how Rn will change from the undisturbed condition, as measured during site investigation, to the highly perturbed groundwater drainage and 'degassing' regime caused by the hydraulic gradient towards an excavation.

4. Geochemical Indicators of Hydrodynamic Stability

Geochemical indicators provide two basic types of information about hydrodynamic stability: (i) the physical processes of chemical mixing that are linked with water movements, and (ii) the timing and rates of water movements (NEA, 1992, 1999). Investigations of groundwater stability should ideally analyse for geochemical indicators in both groundwaters and secondary minerals:

- Chemical and isotopic compositions of groundwaters which are mixtures of waters from distinct sources whose spatial distributions indicate flow and boundary conditions in the past, and whose absolute or relative ages indicate the timescales of water movement and mixing;
- Mineralogy and compositions of secondary minerals, and the characteristics of fluid inclusions contained in them, which indicate the geochemical conditions and water-rock reactions that prevailed at the times of formation.

The hydrochemical and mineralogical parameters that are required for palaeohydrogeological interpretations about the physical process of chemical mixing that is linked with water movements, and the timing and rates of water movements, are discussed in Sections 4.1 and 4.2 respectively.

4.1. Indicators of Groundwater Mixing, Flows and Water Sources

Data from groundwaters and secondary minerals that are most likely to provide information about mixing and past movements of water masses from different sources are summarised in Table 2.

Palaeohydrogeological information about groundwater mixing, flows and water sources in the past has to be compared with the present-day hydrodynamic and hydrochemical state of the system to make inferences about groundwater stability. The following questions can be addressed:

- Do hydrochemical and isotopic analyses indicate that past patterns of mixing of groundwater components were different from that at the present day, e.g. different sources or degrees of mixing?

- Do secondary mineral assemblages and mineral characteristics (e.g. crystal morphologies) and compositions indicate that past groundwater compositions were different from present compositions, and can the ages of the minerals be estimated?
- Are compositions of fluid inclusions, matrix waters or compartmentalised 'pockets' of groundwater inconsistent with present-day groundwater compositions?

Table 2. Data for groundwaters and secondary minerals that provide information about hydrochemical mixing, water movements and boundary conditions in the past.

Data	**Information**
TDS (Total Dissolved Solutes) in groundwaters	Total mineralisation (= salinity) is correlated with density which affects hydrodynamic stability via the effect on groundwater pressures.
Non-reactive solutes and isotopes in groundwaters: Cl^-, Br^-, $^{18}O/^{16}O$, $^{2}H/^{1}H$	Non-reactive (i.e. conservative) solutes and isotopes are tracers of water components in groundwater mixtures. Component compositions may be identified by data analysis using linear mixing graphs or statistical analysis using Principal Components Analysis (PCA). Component compositions may be 'signatures' of water sources, e.g. Br/Cl and $^{18}O/^{16}O$ signatures for sea water.
Other groundwater solutes: Na, K, Ca, Mg, SO_4, Sr, I, Li, B, etc.	Solutes that may have varying degrees of reactivity; expert judgement is required to assess possible alteration by water-rock reaction.
Paragenesis[1] of secondary minerals	Assemblage and paragenesis (sequence and relative timing of formation) of the most recently formed secondary minerals (e.g. calcite, pyrite, Fe-oxide, clays, anhydrite/gypsum) indicate variations of geochemical conditions during the timescale of deposition.
Mineralogical and geochemical character of growth zones in secondary calcite	Variations of crystal form and of chemical and isotopic compositions indicate variations of groundwater compositions during period of mineral precipitation.
Salinity and chemical compositions of low-temperature fluid inclusions trapped in late stage secondary minerals	Additional data for salinity and approximate composition of an old groundwater that may predate the components of present groundwater mixture or may correspond to the oldest component.

Notes: [1] 'Paragenesis' refers to the suite of secondary mineral reactions (i.e. precipitations and dissolutions) that have occurred in the groundwater-rock system of interest. For the present purpose, the paragenesis over the relevant palaeohydrogeological timescale is of interest.

4.2. Indicators of Groundwater Ages and Timing of Water and Solute Movements

Data from groundwaters and secondary minerals that may provide information about the ages of groundwaters and about the timing of water and solute movements are summarised in Table 3.

Information from these data about the distribution of water ages through a groundwater system can address the following questions relating to the timescale over which palaeohydrogeological evidence of groundwater stability is available and how the chronology of processes in a groundwater system can be interpreted:

- What overall timescale is represented by the groundwater system, i.e. is a maximum ‘turnover time’ indicated, and what is the age of the oldest water component in mixed groundwaters?
- Does the pattern and continuity of groundwater ages suggest steady-state conditions over a period of time up to the present, or are there peaks or gaps that indicate deviations from present-day or steady-state conditions?
- Are groundwater ages consistent with the hydrodynamic model using present-day boundary conditions or are different boundary conditions required to explain the observed pattern of water ages?
- Does the pattern of groundwater ages and inferred boundary conditions correspond with known episodicity of palaeoclimate?

Table 3. Data for groundwaters and secondary minerals that provide information about the timing and rates of water and solute movements and mixing (Clark and Fritz, 1997, provides further background).

Data	**Information**
^{14}C (carbon-14) of DIC and DOC in groundwaters	Indicator of age of water since recharge or travel time along flow paths, showing the hydrodynamic structure of groundwater system
^{3}H (tritium), ^{85}Kr and CFCs in groundwaters	Indicator of post-1950 recharge in water; identifies if modern water penetrates to depth in natural system or in system perturbed by excavation or pumping
$^{18}O/^{16}O$, $^{2}H/^{1}H$ of groundwaters	Qualitative indicators of distinct water sources that are also ‘signals’ of climate at the time of recharge
$^{36}Cl/Cl$ of dissolved chloride	Ratio approaching that for secular equilibrium with respect to in situ production suggests hydrodynamic stability over timescale of ca. 1 Ma
$^{234}U/^{238}U$ in groundwaters	Values that are >1 indicate radioactive decay series disequilibrium which can be related to uranium contents of fracture minerals, the geometry of fractures, and the groundwater age
^{4}He contents of groundwaters	Cumulative indicator of groundwater residence in contact with rock source of He. High contents are a qualitative indication of stability and a semi-quantitative estimate of water age
Ne, Ar, Kr, Xe contents of groundwaters	Semi-quantitative ‘signals’ of temperature (i.e. climate) at the time of recharge
$^{18}O/^{16}O$ in secondary calcite growth zones	Assumed to be in isotopic equilibrium with groundwater from which calcite precipitated, and thus an indicator of water source and also a signal of palaeoclimate
$^{234}U/^{230}Th$ decay-ingrowth age of secondary mineral	Age of secondary mineral (calcite, Fe-oxide) precipitation and of related hydrochemical process (e.g. groundwater mixing)
$^{40}K/^{39}Ar$ decay-ingrowth age of secondary clay	Age of K-rich clay (illite) and of related hydrogeochemical process (e.g. feldspar alteration) causing clay formation

A stable low-permeability system will tend to contain old groundwaters, though the tendency to mix by diffusion and advective dispersion means that old groundwater masses may no longer be distinguishable in terms of discrete sources and ages. In a low-permeability system, there is usually a pattern of vertical stratification of groundwater masses with the possibility of steep increases in water age with increasing depth. This vertical segregation of water masses may be controlled by changes in permeability and by the decay with increasing depth of topographic head as the driving force for lateral water movement. The pattern of vertical stratification is reinforced by density stratification at sites where groundwaters have varying salinity.

4.3. Sources of Uncertainties

In using and interpreting the indicators of hydrodynamic stability to support a safety assessment of a potential repository site, uncertainties in data and interpretations need to be considered. In general, the uncertainties in geochemical and mineralogical analyses are likely to be less significant than the interpretative uncertainties. Regarding the types of data that are listed in Tables 2 and 3, the potential sources of data uncertainty and their magnitude and significance are:

- In hydrochemical and isotopic data for interpretation of movements and mixing of water and changing boundary conditions:

    - Uncertainties in analyses of concentrations of the major hydrochemical solutes and of Total Dissolved Solids (TDS) are likely to be of low significance except in dilute groundwaters (see below);
    - Uncertainties in concentrations of non-reactive (‘conservative’) solutes in dilute groundwaters may be significant for interpretations of mixing in cases where reliable detection and quantification of small proportions of exotic components (e.g. sea water, deep saline groundwater) are required;
    - Uncertainties in analyses of conservative natural tracers, e.g. $^{18}O/^{16}O$, $^{2}H/^{1}H$, Br-, may be significant for interpretations of mixing; analytical uncertainty in stable isotope ratios especially may typically be 10% or more of the contrast between components and also compositions of end-members may have relatively large uncertainties, so resolution of mixing proportions may have substantial uncertainty;
    - Degrees of alteration of some major solutes (i.e. Na, Mg, K, Ca, SO_4, HCO_3) and many minor solutes (e.g. Fe, Mn, I) due to water-rock interactions may have large variations, so that using these parameters in mixing analyses introduces large uncertainties.

- In mineralogical data for assemblages, properties and compositions of secondary minerals, and also fluid inclusion analyses:

    - Identifications of parageneses is a matter of expert judgement and should be based on a representative number of microscopic petrographic analyses; a large number of measurements are needed to interpolate observations through a rock volume typical of a repository site and to identify spatial patterns with reasonable reliability;
    - Uncertainties in the descriptions of secondary mineral assemblages and parageneses become most significant if trace accessory minerals are missed or wrongly identified;
    - Relative ages of secondary minerals are open to quite large uncertainties without absolute mineral ages by U-Th dating; late-stage mineral parageneses have relative ages attributed according to their growth characteristics;

  - Mineralogical data should be obtained for minerals that are volumetrically significant and representative for the whole rock mass and groundwater system, or part of it, being investigated;
  - Analyses and interpretation of chemical and isotopic compositions of growth zones in secondary minerals (e.g. calcite) depend on the assumption that there has not been recrystallisation or other alteration of the compositional zoning subsequent to precipitation; there is considerable evidence, for example the distinct boundaries between growth zones, that support this assumption; bulk re-equilibration is discounted by the existence of compositionally-distinct growth zones;
  - Another source of uncertainty in analyses of secondary minerals is the variability of compositions within and between growth zones;
  - Calibrations of mineral compositions, especially for trace elements in analyses by electron microprobe (EPMA) or energy-dispersive X-ray analysis in scanning electron microscopy (SEM) may be difficult for variable matrices and microscopic minerals, introducing uncertainties of 20% upwards;
  - Calibrations and precision of stable isotopic analyses, e.g. $^{18}O/^{16}O$ and $^{13}C/^{12}C$ in calcite, in secondary minerals may introduce further substantial data uncertainties to the interpretation of co-existing groundwater compositions and mixtures, because of ‘small sample’ effects and also due to use of novel techniques such as laser ablation analyses of individual mineral growth zones;
  - Uncertainties in the age and therefore in the relationship of inclusion fluids to groundwaters presently in the system are substantial unless the enclosing secondary mineral can be dated reliably;
  - Data from microthermometry for temperatures of formation and for salinities of fluid inclusions are likely to have large uncertainties and apparent variability that are significant when comparing with present groundwater compositions, especially for dilute inclusion fluids because the lower limit of quantification is brackish/saline; there is a lower limit on temperature estimation because low temperature inclusions, i.e. those of direct interest for palaeohydrogeology, tend to be monophase and not amenable to the homogenisation temperature method;
  - Data from fluid inclusions are obtained either by microscopic analyses of individual inclusions, in which case a statistically-significant number of replicate analyses are required to reduce uncertainty, or by macroanalysis of crush-leach solutions in which case the compositional data are averages and do not identify the ranges of compositions in a specific generation of inclusions.

- In isotopic data for interpreting groundwater and secondary mineral ages and the timing of water and solute movements:

  - Contamination of water samples taken for tritium (^{3}H) and carbon-14 (^{14}C) analyses usually introduces errors that make water ages too young;
  - Analytical uncertainties at low ^{3}H and ^{14}C abundances, near to detection limits, are relatively high and become very significant because whether or not there is evidence of small proportions of a young ^{3}H-bearing component or detectable ^{14}C may have great significance to interpretations about the timescales of stability;
  - Uncertainties in anthropogenic ^{3}H inputs to groundwater systems during the last 50 years and also the ambiguity between ^{3}H levels in present-day inputs and

decay-adjusted values for less recent, plus the added effect of dispersion and mixing, make quantitative interpretation of sparse ^{3}H data unreliable and effectively mean that ^{3}H is a qualitative indicator of the presence of a smaller or greater component of water which has recharged within 50 years;

- Uncertainties in initial ^{14}C activities at time of recharge are significant for ^{14}C ages of groundwaters and may introduce uncertainty of 5000 years, i.e. around one half life, which is especially significant for reliable dating of groundwaters with ages <10,000 years, i.e. Holocene recharge;
- Analytical uncertainties in ^{36}Cl data may be significant for interpretation, especially in cases where residence times of very old (>10^{6} years) groundwaters are being investigated by comparison with ^{36}Cl/Cl ratios estimated for secular equilibrium from data for in situ production of ^{36}Cl.

4.4. Interpretation Methods for Palaeohydrogeology

Some of the specific interpretation methods for palaeohydrogeological data and stability indicators have already been mentioned in the previous section in the context of uncertainties. This section summarises the main approaches to interpreting hydrochemical, isotopic and mineralogical data to get information about palaeohydrogeology, relationship to palaeoclimate episodes, and groundwater stability. The types of models are:

- Geochemical equilibrium models of water-rock reaction;
- Hydrochemical mixing models;
- Groundwater flow and mass transport-reaction models to simulate effects of changing hydrogeological and/or geochemical initial and boundary conditions;
- Isotopic fractionation factors;
- Calculation of groundwater ages from isotopic data.

Interpretations of geochemical indicators contribute to a geoscientific approach to palaeohydrogeology which includes consideration of indications of physical and mechanical effects on groundwater stability as well as the geochemical indicators (Figure 1). The approach involves models for hydrological impacts of climate changes, which are assumed to be the primary causes of potential instability, and models for the response of the groundwater system. Conceptual models are constructed to represent potential variations in surface boundary and initial conditions correlated with palaeoclimate changes over time. Numerical transport modelling is carried out to simulate distributions of non-reactive solutes and stable isotopes, and then these simulations are compared with observed distributions of these geochemical indicators in the present groundwater system.

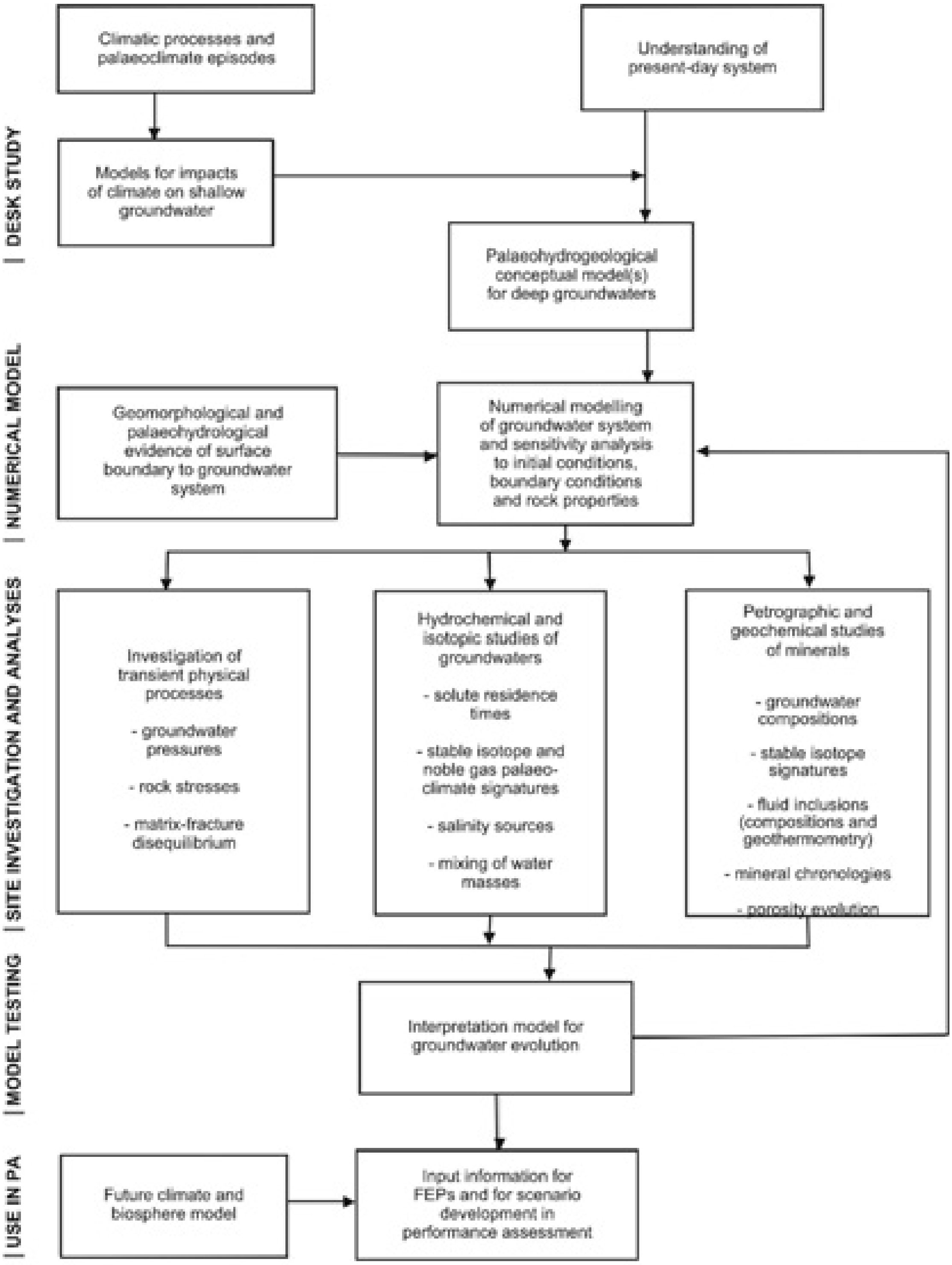

Figure 1. Scheme for interpreting palaeohydrogeology from geochemical and mineralogical indicators, plus indications of transient hydrogeological processes (from Bath et al., 2000).

Mixing models, which range from simple crossplots resolving 2-component mixing of conservative solute tracers (e.g. Cl^-, Br^-) and stable isotope ratios ($\delta^{18}O$, δ^2H), to multivariate analysis (e.g. with SKB's M3 Principal Components Analysis tool) resolving multi-component mixing in large data sets, are used to identify end-member components and mixing proportions in water samples representing spatial variability through different parts of the system. Spatial distributions of water mixtures and of component waters of different ages and from different sources give a qualitative indication of how stable the groundwater system has been over the relevant timescale. A more quantitative approach, and one that allows alternative models to be evaluated, is possible by using transport modelling to simulate the distributions of groundwater components for various assumptions about time-dependent initial and boundary conditions.

Mineralogical evidence for palaeohydrogeology and for assessing groundwater stability requires a larger degree of expert judgement and analogue evidence in its interpretation. Secondary minerals that are thought to have formed in the timescale of interest, i.e. the last million years or so, are typically calcite, clays and iron oxides. The presence or absence of these minerals, and their abundances, distributions and relationships, characterise groundwater compositions, water sources and water-rock reactions when they were precipitated. The morphology, or crystal shape, of a secondary mineral, e.g. calcite, may indicate the hydrochemical environment in which the crystal grew. Changing morphologies of successive growth layers indicate that hydrochemical and hydrodynamic conditions changed over the period of growth. For example, a morphological transition was found in secondary calcite in fractured rock at Sellafield, UK, that corresponds to a groundwater salinity transition from brackish to saline (Milodowski et al., 1997).

Stable isotope ratios, $^{18}O/^{16}O$ and $^{13}C/^{12}C$, in secondary calcites can be measured at various scales of resolution. $^{18}O/^{16}O$ of calcite is controlled primarily by the $^{18}O/^{16}O$ and the temperature of co-existing water from which calcite precipitation occurred. $^{18}O/^{16}O$ in calcite, specifically in discrete growth zones, is therefore potentially an important palaeohydrogeological indicator. By making reasonable assumptions about the probable maximum deviations of past geotemperatures in deep groundwaters from present conditions, $^{18}O/^{16}O$ data can be interpreted as an indication of the proportions of glacial melt water to have penetrated to repository depth in past glaciation episodes. Oxygen isotopic fractionation between water and secondary calcite is a function of temperature, and this dependence introduces significant uncertainty into interpretation of the isotope ratio in terms of groundwater origin and age. $^{13}C/^{12}C$ in calcite reflects the $^{13}C/^{12}C$ of dissolved inorganic carbon (DIC) in co-existing groundwater which is controlled by the sources of carbon. $^{13}C/^{12}C$ variations in secondary calcite therefore indicate fluctuations in sources of carbon that may relate to changing climate impacts at the surface or to changing microbial activity or carbon sources in deep groundwaters.

Qualitative and semi-quantitative interpretation models that are specific to the isotope system are used to derive information about groundwater ages from isotopic data in groundwaters. The range of age information that can be obtained, and the associated uncertainties, is also specific to each isotope system, depending on the decay half life of the natural or anthropogenic radioactive isotope and on other aspects such as how the isotope enters the groundwater system, in situ production, accumulation and transport of a daughter product.

Uncertainties in the model interpretation of groundwater ages from isotopic data (^{14}C, ^{36}Cl, etc) derive from a number of assumptions that have to made about initial isotope abundances and subsequent geochemical and physical processes that might have reduced (or enhanced) the isotope concentration in parallel with radioactive decay. Except in special circumstances in which the parameterisation of the interpretative model is particularly reliable, these uncertainties could make the range of overall uncertainty in an interpreted groundwater age between 0.5 times lower to 2 times higher than the best estimate value. Greater uncertainty in higher ages derives from the sampling, analytical and interpretative errors associated with low isotope abundances. For example, a measured ^{14}C content of 5 pmC (percent modern carbon) could typically be interpreted as a groundwater age of 17,000 years with an uncertainty range of 10,000-30,000 years. The complexity of dispersive groundwater mixing as age increases means that interpreted isotopic 'ages' have more complex hydrodynamic significance in terms of alternative hydrogeological models.

Anthropogenic influences and perturbations on groundwaters within the past decades and centuries can be detected with anthropogenic geochemical tracers, such as atmospheric tritium and krypton-85 (^{3}H and ^{85}Kr) from thermonuclear bomb-testing and nuclear reactor discharges respectively, and industrial chlorofluorocarbons (CFCs), can be used to detect the presence of recent (<50 years) recharge in groundwaters in fractured hard rock (e.g. Plummer et al., 2001). Carbon-14 (^{14}C) dating of groundwaters gives useful information for ages up to about 3.5×10^4 years, and is the most prominent geochemical method for dating groundwater evolution through the last glacial period.

Stable oxygen ($^{18}O/^{16}O$) and hydrogen ($^{2}H/^{1}H$) isotopic ratios vary in rainfall or snowfall in relation to the water sources and temperatures at which precipitation occurs, and therefore they 'fingerprint' cold-climate recharge in contrast to Holocene and other interglacial waters that rcharged in warmer climates. The term 'cold-climate recharge' describes water originating from any of the glacial periods during the Quaternary (i.e. more than ten episodes in the last 1.7 My), not just the most recent late Pleistocene (Weichselian) glaciation. Dissolved atmospheric noble gas concentrations, being dependent on the temperature at recharge, are geochemical tools for similarly relating groundwaters to climatic conditions at time of recharge.

The longest timeframe of relevance that was identified in Section 3.2 is $>10^5$ years. The main geochemical tools that could put dates on evolution and stability of groundwaters in that timescale are chlorine-36 (^{36}Cl) and the uranium-thorium (U-Th) isotopic decay series. However various complexities in interpretation of these isotopic data often decrease their quantitative reliability or make them inapplicable in very old groundwaters.

5. Geochemical Data from Swedish Sites

Geochemical indicators of groundwater stability from past investigations at Äspö HRL, Finnsjön, SFR Forsmark, the Stripa mine and at a few other sites in Sweden are introduced and discussed here to illustrate some of the issues of sampling, analyses and interpretation that influence their overall significance. Data are tabulated in Appendix 1 and are shown graphically in Figures 2 to 7. Preliminary data from SKB's ongoing site investigations at Simpevarp/Laxemar and Forsmark are not considered in detail but their general similarities with, and proximity to, Äspö and Finnsjön/SFR respectively mean that there is potentially renewed significance for the data from those areas depending on their validity and comparability with new data. Additionally, data from Stripa which is the most intensively-studied inland site are relevant to the discussion of geochemical evidence for groundwater stability in inland and coastal areas (Section 7). Relevant data from Finnish sites including Olkiluoto, from the Whiteshell URL area in Canada, from Sellafield in the UK, and from the Tono area and URL in Japan are also compiled in appendices because they add further insights into the interpretation of geochemical information in terms of groundwater stability for a range of hydrogeological and palaeohydrogeological environments.

5.1. Äspö Hard Rock Laboratory

Groundwaters at the site of the Äspö HRL were studied geochemically prior to excavation (Smellie and Laaksoharju, 1992; Smellie et al., 1995; Laaksoharju et al., 1999). Hydrodynamic stability of groundwaters in the Äspö area has been affected in the past by its proximity to the Baltic shoreline. Variations in the relative elevations of the rock surface and of water level in the Baltic (and its Quaternary precursors such as the Eemian Sea and the Yoldia and Littorina stages of the 'palaeo-Baltic' and the Ancylus fresh water lake) affected hydrodynamics in three ways: (i) changing hydraulic gradients between recharge zones and discharge zones, (ii) changing locations of meteoric water recharge and discharge as the shoreline moved, and (iii) changing pressure gradients due to density variation where Baltic sea water intrusion has varied spatially and compositionally over time.

Selected hydrochemical and isotopic data for pre-excavation groundwater samples are listed in Table A1.

When realistic analytical uncertainties are taken into account, all ^{3}H analyses on water samples from below 50 m depth in boreholes in the undisturbed system are negligible. Reported ^{3}H values in water samples from boreholes from the surface or from the HRL tunnel at depths to at least 70 m were up to 60 TU at shallow depths and therefore indicate significant drawdown of young recharge. Water samples from the Laxemar boreholes had reported tritium analyses up to 40 TU but these data have subsequently been reported to be unreliable so are discounted from further consideration (Nilsson, 1999a,b). However the presence of lower but still positive levels of tritium appears to have been supported by repeat analyses of duplicate samples. It appears to be almost certain that these data can be attributed to mixing of young waters within the borehole prior to sampling or to subsequent contamination of samples. The uncertainty that arises from the tritium data in Table A1 highlight the importance of obtaining reliable samples and low detection limit analyses.

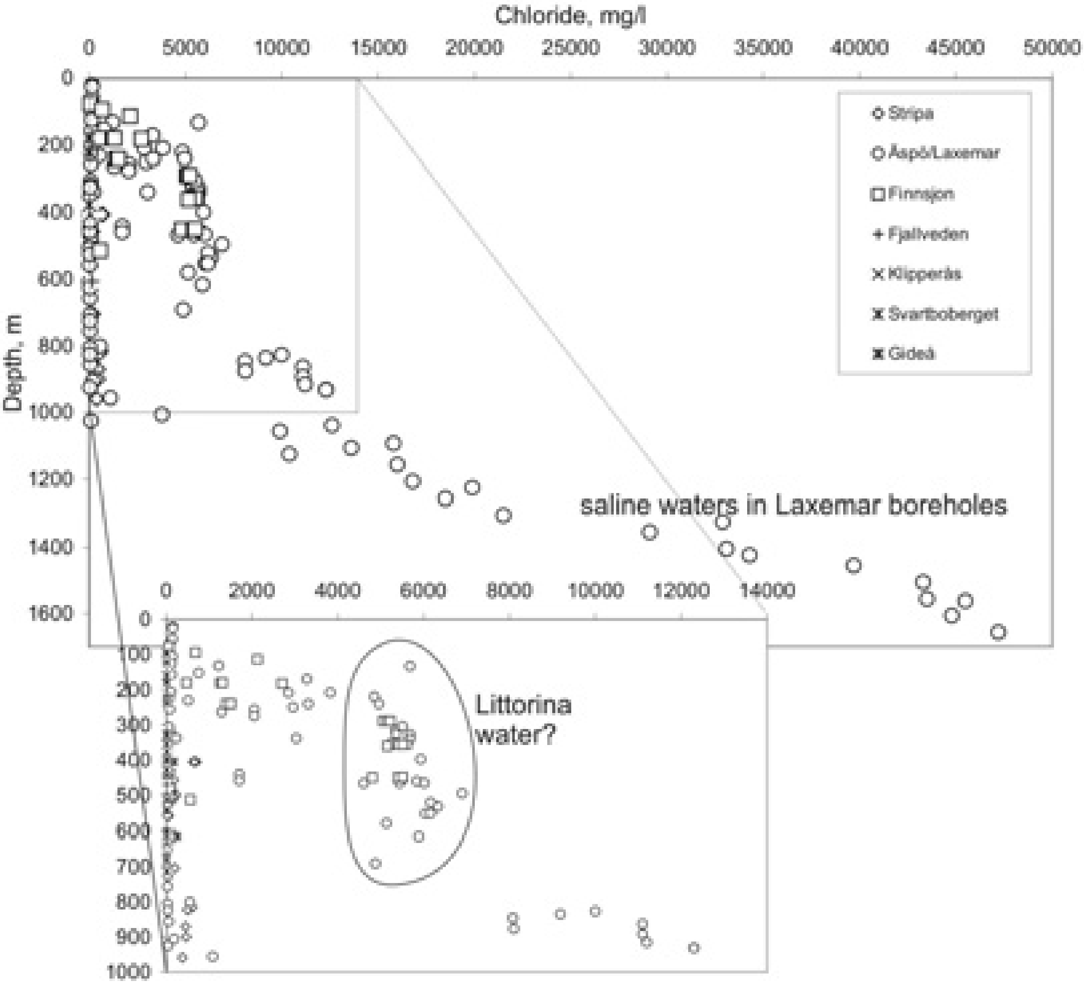

Figure 2. Salinities, as chloride concentrations, versus depth for groundwaters from sites in Sweden (the lower plot shows more detail for samples from <1000 m depth, all of which have chloride concentrations less than 12,000 mg/L).

$\delta^{18}O$ and $\delta^{2}H$ of groundwaters were found to have a wide range (e.g. -7 to -16 ‰ $\delta^{18}O$), indicating the presence of meteoric water from modern and cold-climate recharge, Baltic sea water and 'palaeo-Baltic' precursors, and ancient water from uncertain sources (Figure 3). Present-day Baltic Sea has around 3550-3800 mg/L Cl and -5.9 ‰ $\delta^{18}O$. The highest $\delta^{18}O$ values were found in fresh/brackish water at 0-200 m depth, and the lowest values at 200-500 m depth in brackish/saline waters (Laaksoharju et al., 1999).

The increasing chloride with depth in boreholes at Äspö is not associated with simple linear mixing of $\delta^{18}O$, indicating that these are complex mixtures of several end-members with varying Cl and $\delta^{18}O$ (Figure 4). However there is a good correlation of $\delta^{18}O$ with Cl in the highly saline waters at depth at Laxemar, indicating that these are dominated by mixing of two components – glacial meteoric water and deep saline 'Shield' water.

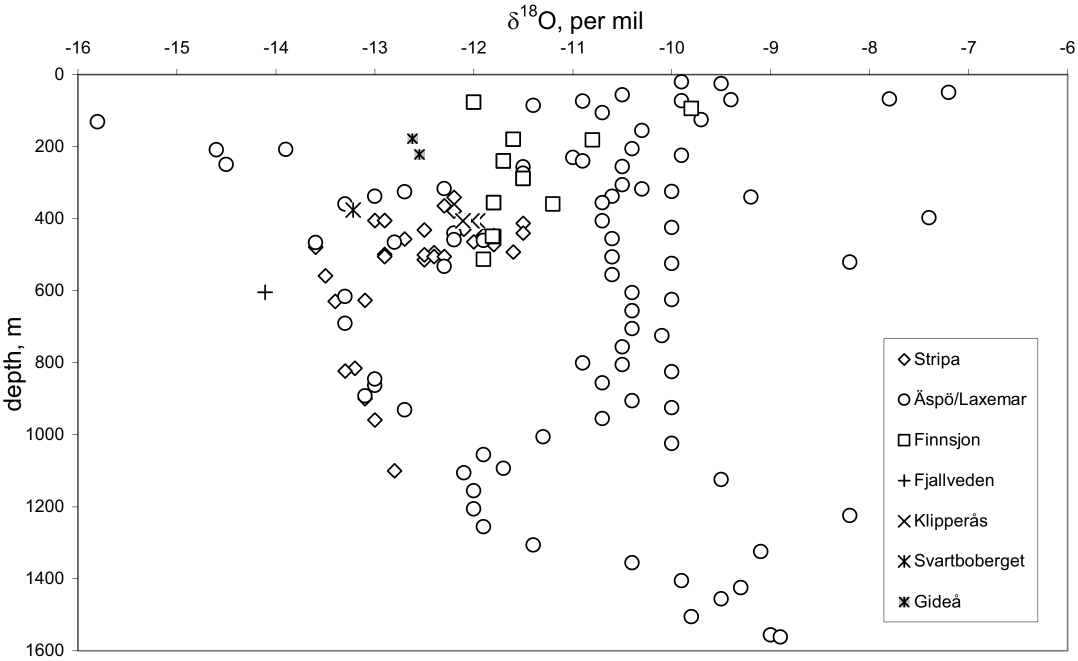

Figure 3. $^{18}O/^{16}O$ *versus depth for groundwaters from Swedish sites.*

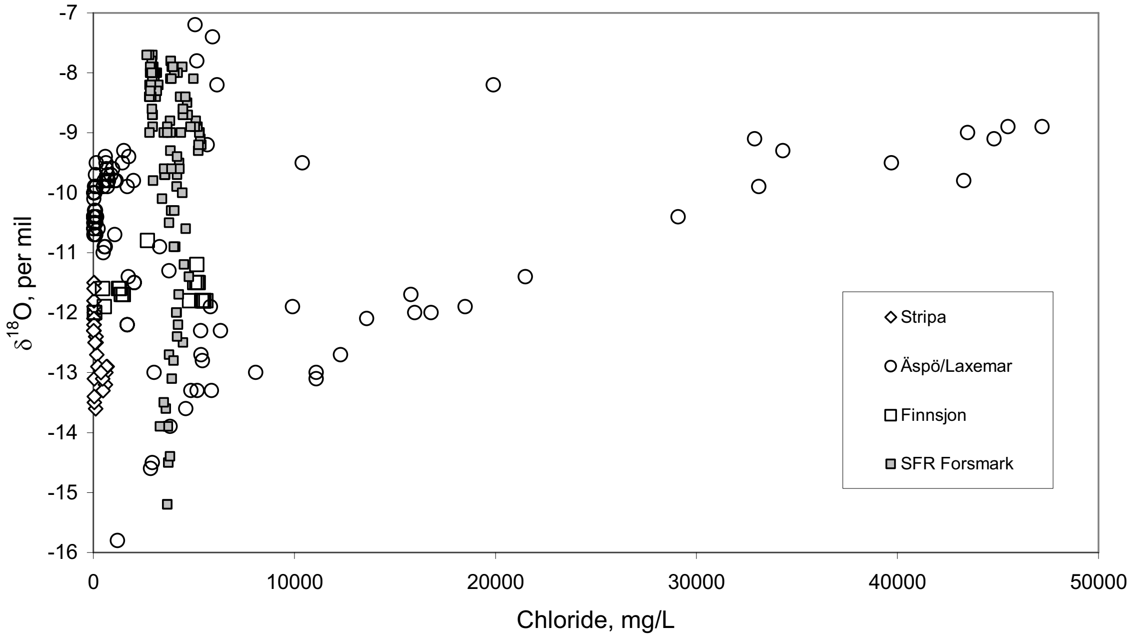

Figure 4. $^{18}O/^{16}O$ *versus chloride concentrations for groundwaters from Swedish sites.*

The depth range over which old meteoric water, specifically that with a cold-climate isotopic signature, occurs is of interest for considering the hydrodynamic stability of the groundwater system. $\delta^{18}O$ values were between -13.3 and -11.5 ‰ (some missing $\delta^{18}O$ values are estimated from measured $\delta^{2}H$ values) in saline waters to ~1000 m depth in borehole KLX01 at Laxemar. The range of $\delta^{18}O$ in fresh waters to ~1000 m in KLX02 was -11.3 to -10 ‰, going to a minimum around -12 ‰ in saline waters at about 1100-1200 m and then rising to about -9 ‰ in highly saline waters at greater depths. These data suggest that cold-climate water had not replaced (or mixed with in large proportions) pre-existing saline 'Shield' water below 1200 m or that saline Shield water has rebounded to 1200 m after being displaced deeper during glacial periods. The hypothesis that cold-climate water never penetrated below around 1200 m is supported by $\delta^{18}O$, $\delta^{13}C$ and $^{87}Sr/^{86}Sr$ data for fracture calcites (Tullborg, 1997; Wallin and Peterman, 1999; Bath et al., 2000). Moreover the stable isotopic compositions of these deep saline waters deviate from the Meteoric Water Line in a $\delta^{2}H$ versus $\delta^{18}O$ plot, suggesting that their residence times have been long enough for water-rock reaction to shift the isotopic compositions (Laaksoharju et al., 1999).

Samples from boreholes KAS02 and KAS03 show that isotopically-light water (i.e. with relatively low $\delta^{18}O$ values, less than -11 ‰ $\delta^{18}O$ which is the composition of present-day recharge) occurs at all depths below about 100 m. The lowest $\delta^{18}O$ values were found at 200 m in KAS02 (-13.9 ‰ and 3820 mg/L Cl^-) and at 122 m in KAS03 (-15.8 ‰ and 1220 mg/L Cl^-). These clearly have a large component of cold-climate recharge, mixed with brackish water. The groundwaters at these depths appear to be compartmentalised with some pockets of old water not having been replaced by more recent meteoric recharge.

The ages of the older meteoric water components are of interest because they place a timescale on the duration of these conditions and identify the origin of the isotopically-light waters. Pre-tunnelling Äspö data suggest that ^{14}C values in groundwaters deeper than 100 m are variably low (<40 pmC) and sometimes very low (<10 pmC) (Figure 5). Borehole KAS03 between 120 and 250 m has water with <8 pmC ^{14}C. The isotopically light brackish water (-15.8 to -14.5 ‰ $\delta^{18}O$) is strong evidence that the groundwater system is hydrodynamically compartmentalised, with pockets of water with ages corresponding to the period of glaciation. Interpreting ^{14}C data from boreholes KAS02, 03, 04 and 06 as approximate water ages has quite large uncertainties because the groundwaters are clearly mixtures between old meteoric recharge and a saline water that is assumed to be predominantly of palaeo-Baltic origin (this is supported by the M3 principal components analysis of groundwater mixing; Laaksoharju et al, 1999). Baltic and palaeo-Baltic (Littorina) components in groundwaters at Olkiluoto (Finland) have been assumed to have ^{14}C between 120 and 40 pmC (Pitkänen et al., 2004).

After the start of construction of the Hard Rock Laboratory, shallow boreholes drilled from the surface into fracture zones at 15 and 30 m depth in 'redox zone' studies gave water samples with 66 and 86 pmC ^{14}C, -15 and -17‰ $\delta^{13}C$, and 100 and 550 mg/L Cl^-. Other boreholes (KR0012, 13, 15) were drilled upwards from the HRL access ramp at about 69 m depth. Water samples from these have 61-97 pmC ^{14}C, -18 to -12‰ $\delta^{13}C$, and 330-2780 mg/L Cl^-. They show that fresh water was being drawn down towards the tunnel, diluting the existing brackish water (Mahara et al., 2001).

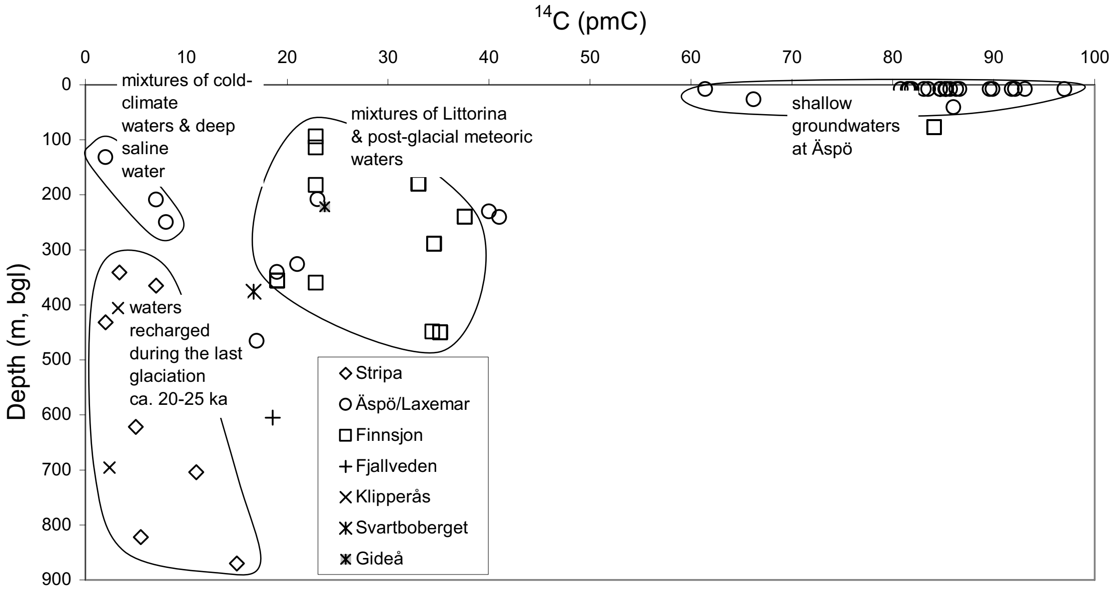

Figure 5. Carbon-14 data versus depth for groundwaters from Swedish sites.

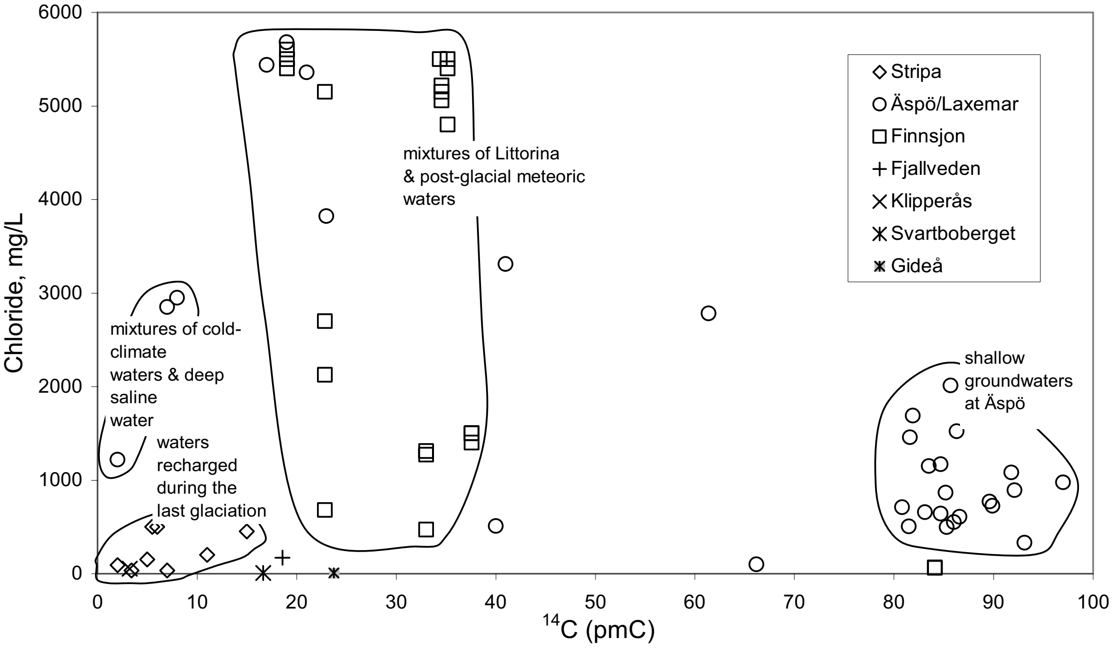

Figure 6. Carbon-14 versus chloride concentrations for groundwaters from Swedish sites.

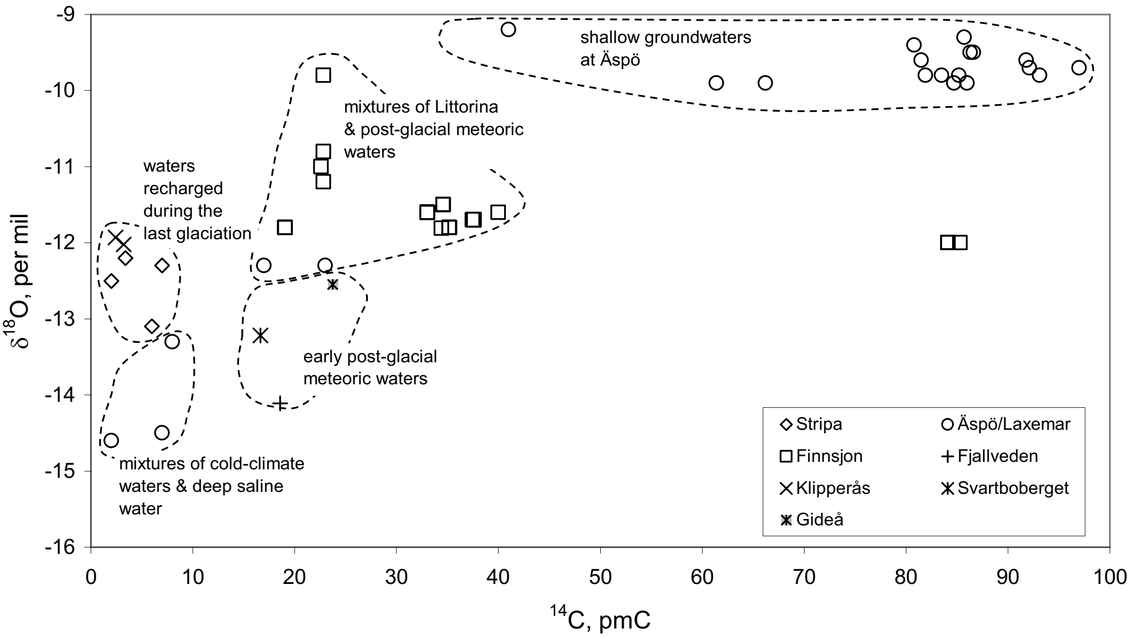

Figure 7. Carbon-14 data versus $\delta^{18}O$ for groundwaters from Swedish sites.

$^{36}Cl/Cl$ values for fresh/brackish water at 226-314 m depth in KAS03 were 20-24 x 10^{-15} and were 40-43 x 10^{-15} in saline waters at 860 and 1420 m depths in boreholes KAS03 and KLX02 (Louvat et al., 1999). The estimated $^{36}Cl/Cl$ ratio at secular equilibrium with Äspö diorite was ~49 x 10^{-15} (±15%), whilst the ratios in Baltic Sea water and local meteoric water were 4 x 10^{-15} and 45 x 10^{-15} respectively (Andrews et al., 1989b). The proximity of the ratio in deep saline waters to that for secular equilibrium suggests that the saline Shield water has been stable for at least 1.5 Ma (Louvat et al., 1999).

The morphology-salinity relationships observed in ten secondary calcites from Äspö resemble those found at Sellafield (see Appendix A3.2), with c-axis flattened calcite in the upper part of the bedrock co-existing presently with groundwater salinities up to 5 g/L chloride and c-axis elongated calcite in the deeper part with salinities up to 16 g/L (Bath et al., 2000). However there is no clear evidence here of morphological changes during growth, although they would be expected because of the known history of groundwater evolution by mixing during the late Quaternary. The small samples from Äspö made petrographic analysis difficult.

Stable oxygen and carbon isotope compositions of calcites from Äspö vary greatly, from -20 to 0 ‰ $\delta^{18}O$ (PDB) and -74 to -2 ‰ $\delta^{13}C$, reflecting repeated hydrothermal activity and complex past and present hydrological situations (Tullborg, 1997; Bath et al., 2000).

The following observations have been made based on interpretation of stable isotope analyses conjunctively with microscopy:

- In the upper 50 m all $\delta^{18}O$ values are within the range -11.5 to -6 ‰ (corresponding to $\delta^{13}C$ between -13 to -3.5 ‰) which may suggest an interaction with meteoric water and brackish Baltic Sea water at ambient temperatures.
- Between 50 and 300 m a very wide span of $\delta^{18}O$ values are found (-22 to +2 ‰). Of these the highest values (close to 0 ‰) are most probably calcite precipitated from oceanic marine water. These calcites are only found down to 300 m depth. Since the Baltic Sea is not likely to have had water of oceanic signature during the post-glacial phase, these calcites should be older than the Eemian (117,000 to 130,000 years ago).
- Values with extremely low $\delta^{18}O$ values (ca. -20 to -25 ‰) and high $\delta^{18}O$ values (-2 to -5 ‰) are found at all depth below 50 m. Observations of hydrothermal mineral paragenesis in some of these fractures favour a hydrothermal origin for these calcites. From 300 m and deeper there is a tendency towards lower $\delta^{18}O$ values in the fractures.
- For the calcites with $\delta^{18}O$ values in the range -5 to -20 ‰, various origins such as precipitation from brackish Baltic sea water, temperate and cold climate recharge and warm hydrothermal fluids can be proposed on the basis of oxygen isotopes only. However, one of the challenges for the study at Äspö has been to combine results from different methods to sort out the actual origins of these calcites.

As discussed above, the interpretation of stable isotope data has been used in support of a hypothesis that glacial meltwater or other isotopically-light cold-climate waters did not penetrate below about 1200 m depth at Äspö.

In general, high $\delta^{13}C$ values (-2 to -7 ‰) have been interpreted as due to interaction with atmospheric or hydrothermal carbon dioxide. Extreme low values of $\delta^{13}C$ (-25 to -74 ‰) were interpreted as the result of *in situ* microbial activity. Such activity has also been supported by the findings of bacteria-like fossils on calcite surfaces (Pedersen et al., 1997). This indicates a low-temperature origin of such calcites, and precipitation from brackish and temperate meteoric water was suggested based on $\delta^{18}O$ values. Moderately low $\delta^{13}C$ values (in the range -10 to -20 ‰) were found to be more frequent in the uppermost 500 m, whereas they were found to be absent in the fractures sampled below 950 m.

It has not been possible to identify fluid inclusions with sufficient size and abundance in young calcites from Äspö to permit characterisation. Fluid inclusions in older fracture calcites are two-phase saline (Na-Ca-Cl type) inclusions with homogenisation temperatures from 70 to 150 ºC. Such inclusions have been found elsewhere in the Fennoscandian Shield and may represent an ancient allocthonous source of moderately hydrothermal fluids (e.g. intrusion of a sedimentary brine); they have no significance for salinity variations in groundwaters or hydrodynamic stability over the timescale of interest.

5.2. Finnsjön and SFR Forsmark

Groundwater samples from Finnsjön boreholes had salinities up to ~5,600 mg/L Cl^- between 350-450 m depth (Table A2; Smellie and Wikberg, 1991). ^{14}C values were

19-35 pmC in the deepest samples, corresponding to uncorrected ages of 8,000-14,000 y and suggesting that these are mixtures of Littorina sea water and post-glacial meteoric water (Figure 2). Other samples at shallower depths had up to 85 pmC ^{14}C. δ^{18}O values were fairly constant, -11.5 to -12 ‰, indicating that none of the groundwaters is dominated by glacial water or cold-climate recharge (Figure 3).

Monitoring boreholes at SFR Forsmark have Cl^- from 1,840-5,380 mg/L. Groundwaters in the boreholes with higher Cl^- concentrations have mostly tended to become more dilute over time (1992-2000). Although the range of Cl^- encompasses the value for present-day Baltic water (around 3,550-3,800 mg/L), δ^{18}O values (mostly -8 to -15 ‰) are lower than the Baltic value (around -5.9 ‰ δ^{18}O), indicating that these waters are probably dominated by mixing of glacial meltwater or cold-climate waters with Baltic or Littorina sea water and/or deep saline Shield water.

It is noteworthy that the range of δ^{18}O at SFR Forsmark is so much greater than that reported for Finnsjön, emphasising the important influence on groundwater stability of a long period of cover by Littorina and Baltic brackish sea waters. The variability of δ^{18}O whilst Cl^- values remain relatively uniform in SFR Forsmark waters suggests that mixing to homogenise salinity and density may be an important process. It can be speculated that homogenisation caused by dispersion would have become more significant as other processes that have impacts on hydrodynamic stability, e.g. glaciation and uplift, have become less important.

^{3}H values are mostly positive, up to 33 TU, suggesting that the sea water component may be from the recent Baltic (within 50 years). Some caution is necessary in case these were poor tritium analyses or contaminated samples. On the other hand, ^{14}C contents are 14-27 pmC (ca. -8 ‰ δ^{13}C) indicating uncorrected ages of ca. 5,000 to 10,000 y. Interpretations of these ^{14}C data in terms of ages are, however, uncertain, because they have to take account of the different initial isotope compositions of the end-member components: between 120 and 40 pmC ^{14}C for Baltic and Littorina waters (Pitkänen et al., 2004).

5.3. Stripa Mine

Groundwaters in a granitic intrusion at Stripa in central Sweden were investigated in an international cooperation project, coordinated by NEA/OECD and managed by SKB, through 1980-90. Iron ore had been mined at Stripa for centuries, so the groundwater system around the mine was already disturbed by drawdown towards the pumped mine workings which are at about 300-400 m depth (Nordstrom et al., 1989). The spatial extent of hydraulic disturbance was estimated to extend to at least 3000 m depth and several km laterally (Nordstrom et al., 1989). The maximum sampled depth was 1232 m.

The Stripa Mine study provided an opportunity to evaluate a number of geochemical indicators of hydrodynamic stability. Indications of stability are considered in two contexts: (a) the natural system, prior to excavation of the mine, and (b) the system that is disturbed by mining. Geochemical indicators are potentially useful in both cases – the first for assessing evidence for response to past perturbations of the natural system (palaeohydrogeology), for example due to glaciation, and the second for investigating present-day disturbance by the mine.

One of the tasks that were tackled by the hydrogeochemical group in the Stripa Project was to distinguish the extent of disturbance of the groundwater system due to mining from the natural evolution of water-rock reactions and mixing. It is interesting to assess the evidence from geochemical indicators for the perturbation of the groundwater system by mining, i.e. what are the sources, mixing and salinities in water inflows to the mine and how do these change over time.

Travel time from recharge to inflow to the mine was calculated to be around 600 years. This relatively short travel time contrasts with much longer travel time estimates for water to flow from recharge to depth in the undisturbed regional system. Travel time along the longer regional flow paths from recharge on higher ground north-west of Stripa may be around 10,000 years according to hydrodynamic modelling (Nordstrom et al., 1989).

Data for the main hydrochemical indicators of water movement and mixing, Cl^-, ^3H, ^{14}C, $^{18}O/^{16}O$ and $^2H/^1H$, are listed in Table A3. The variations of Cl^-, $^{18}O/^{16}O$ and ^{14}C are illustrated in Figures 2, 3, 4, 5 and 6.

Flow from ground surface to the mine appears to have been faster than the modelled 600 year travel time based on the evidence of tritium analyses of inflowing water. Tritium concentrations up to 42 TU were reported for some borehole samples from 300 m depth – suggesting transit time of water from the surface is no greater than 20 years with remarkably little dispersion or dilution by mixing (Moser et al, 1989). There was a possibility of small amounts of tritium at 850m depth though *in situ* production could account for that, and there is also some doubt about the reliability of low but positive tritium analyses. Equally, other borehole samples contained insignificant tritium, which is the first indication of heterogeneity in the 'connectivity' of the fracture network.

Samples from boreholes drilled from the mine galleries showed that groundwater is generally dilute (maximum 200 mg/L chloride) down to about 700 m depth (Figure 2). Ca-HCO_3 type water occurs at <300 m, below which it evolves towards Na-Ca-Cl type water. Chloride concentrations were found to be rather heterogeneous, within the range 0-200 mg/L, over short distances, showing that different flowpaths have been activated by the drawdown to the excavations.

Dilution of saline groundwaters due to progressive drawdown of fresher shallow groundwater is another indication of the perturbation caused by excavation, though the effect is not consistent spatially and temporally (e.g. trends in V2 boreholes at Stripa; Nordstrom et al., 1989). Fairly complex variations in salinity (e.g. in Cl^- concentrations) are evident in the deep borehole monitoring records at both Stripa and Äspö – one reason for this is the effect of 'draw-up' of more saline groundwaters from greater depth, superimposed on the 'draw-down' of more dilute groundwaters.

The highest salinity was only brackish and was found at 810-910 m where water had ~700 mg/L Cl^- (Figure 2). Monitoring of discrete packered intervals in one of the deeper boreholes showed that Cl^- was increasing slightly with time, suggesting a continuing upconing of saline water. In contrast, Cl^- decreased slightly in a short borehole from the mine workings, possibly coupled with a rise of ^3H, indicating flushing by drawn-down fresh water.

$\delta^{18}O$ values of ^3H-containing groundwaters that had penetrated to at least 300-400 m depth at Stripa were -10.5 to -12 ‰ (Moser et al., 1989) which is typical of modern recharge (-11.5 ‰; Burgman et al., 1981). $\delta^{18}O$ values were found to be -12 to -13.4 ‰ in tunnel inflows at >400 m depth, i.e. lower than overlying groundwater by ~1-2 ‰; these corresponded to near-zero values of ^3H. The pattern of $\delta^{18}O$ versus Cl^- (Figure 4) excludes simple two-component mixing, supporting further the concept that the perturbation caused by the mine has caused complex flow patterns that differ between individual fractures, especially in the vicinity of the greatest hydraulic instability, i.e. close to the mine workings. A three-component mixture was inferred, comprising meteoric waters with different recharge ages and saline 'basement' groundwater.

It is therefore interesting to distinguish, if possible, whether deep flow and mixing took place during specific episodes or whether they have been a continual process. The distinction might be based on recharge age distribution of the meteoric water component, the heterogeneity and residence times of the mixtures, and the compositions of secondary minerals (especially calcite) deposited during the mixing process.

^{14}C and $\delta^{13}C$ in shallow boreholes from the ground surface suggested that the initial ^{14}C activity, A_i, was ~50-80 pmC with -13 to -23 ‰ $\delta^{13}C$. ^{14}C contents of mixed groundwaters from deep boreholes below the mined levels were measured at 2.5 to 19 pmC, with corresponding $^{13}C/^{12}C$ ratios mostly -19 to -15 ‰ (Fritz et al, 1989) (Figure 5). Within this group of samples, there are some discrete groups in terms of ^{14}C and $\delta^{13}C$, apparently related to depth (Figure 5 in Fritz et al., 1989). ^3H values of 10-15 TU in borehole M3 suggested at least two components – one old and one young, which could only result from hydraulic instability due to the hydraulic drawdown.

Apparent ^{14}C ages of deep groundwaters below 400-500 m depth are 20,000-25,000 yrs, predating the end of the last glaciation, though the 'dilution' corrections using $\delta^{13}C$ to obtain these ages have large uncertainties (Figure 5; Fritz et al., 1989). The ages, if correct and not much older, suggest that the meteoric water component to at least 800 m depth was mostly renewed during the last glacial cycle and that the system has since been sufficiently stable to preserve these deep groundwaters. There are insufficient data and too much uncertainty in the calculation of ^{14}C ages to interpret further the apparent depth-dependent variations of ^{14}C which change from 2-10 pmC at 300-450 m depth to 10-15 pmC at 770-790 m depth.

The evidence from Stripa data concerning the depth to which glacial melt water penetrated at this location during the last ice age is rather sparse and uncertain. The deepest groundwater samples from Stripa are from just below 1000 m and this water has low salinity (Figure 2), low ^{14}C (Figure 5) and intermediate $\delta^{18}O$ (Figure 3). Although the interpreted ^{14}C ages correspond to the last ice age, the water does not have a very distinctive (i.e. ^{18}O-depleted) stable isotope composition. There are alternative interpretations for the low salinity and the isotope data for groundwater at 800-1000 m depth: (i) that they characterise water that has circulated slowly to depth under non-glacial hydrodynamic conditions that are normal for this inland location, or (ii) that they characterise a mixture of waters with different recharge and hydrodynamic histories including 'cold-climate' recharge (which includes glacial melt water) and much older saline basement water.

The first interpretation suggests that the deeper groundwater is a mixture of waters that recharged throughout the Quaternary period, i.e. during the last 2 Ma, mixing in small proportions with pre-existing groundwaters at these depths and now being dominated by water components that give an average ^{14}C age of around 20-25 ka. Driving forces that caused water to flow to these depths and might have disrupted stability could have been:

- normal gradient developed due to the regional topography (around 240 m at present-day);
- additional head developed by melt water in an ice sheet;
- depression of the rock mass due to the loading by the ice sheet and uplift due to unloading, occurring in several glacial cycles through the Quaternary.

^{36}Cl contents in groundwaters at Stripa are derived mainly from in situ radiogenic production from ^{35}Cl due to irradiation by the natural neutron flux. The ^{36}Cl/Cl equilibrium ratios are distinct between the granite itself and surrounding metasediments because of their different U contents and in situ neutron fluxes. Secular equilibrium for ^{36}Cl would be established when in situ production of it is balanced by the rate of radioactive decay, for which the half life is about $3x10^5$ years. The ^{36}Cl data indicate that the Cl^- has not been in the granite for long enough for secular equilibrium to be established, which would take about 1.5 Ma (i.e. five half lives; Andrews et al., 1989a). By implication, flow times for movement of water into the granite formation are <1.5 Ma.

Very low δ^{13}C values around -30 ‰ for groundwaters at ~900m depth are probably bacteriogenic because they are associated with reduction of sulphate. It could be suggested that microbial activity was initiated by the glaciation-induced 'turnover' of the groundwaters and relatively rapid ingress of cold climate recharge

Fracture-filling calcites that are platy or finely-crystalline were reported to have δ^{18}O values suggesting equilibrium with recent groundwaters, but also having δ^{13}C over a wide range of -40 to +10 ‰ indicating that reactions affecting carbon (inorganic and organic) varied over the time during which fracture calcites were forming (Fritz et al., 1989). That timescale is at least 350,000 years according to U-Th dating of three samples, this timescale (Milton, 1987 in Fritz et al., 1989).

The extent of the hydraulic and geochemical perturbation due to the mine excavations at Stripa is an indication of the potential scale of impact due to future natural perturbations of hydraulic gradients and/or in situ geochemical conditions. However this analogy probably has only qualitative validity because the mine is a localised perturbation that 'developed' over a relatively short timescale.

5.4. Other Swedish Sites

Fjällveden and Gideå are fairly close to the present shoreline and would probably have been seaward of the shoreline of the palaeo-Baltic at some time during the Holocene. None of these sites has brackish water at shallow depths (Figure 2), so either the palaeo-Baltic water did not enter the groundwater systems, or intruded seawater has since been flushed out by fresh water recharge. The latter seems most likely, giving a broad indication of the turnover time for the postglacial freshwater system. Increasing chloride concentrations (>100 mg/L) were reported only in samples below 600 m depth at Fjällveden and 400 m at Gideå.

Only three samples from Fjällveden and Gideå are reported to be reasonably representative of *in situ* groundwaters (Table A4). A sample from 605 m at Fjällveden has 170 mg/L Cl^- and a ^{14}C content of 18 pmC (Figures 5 and 6). .Cl^- is very low at around 200 m at Gideå and ^{14}C is 23 pmC. ^{14}C can only be interpreted in terms of minimum ages which are probably around 12,000-14,000 y, i.e. late-glacial. This approximate age is supported by $\delta^{18}O$ data (Figure 7). Therefore it can be tentatively concluded that cold-climate water, probably glacial melt water, has penetrated to 600 m depth at Fjällveden.

Svartboberget is inland and therefore has not been affected by modern or past intrusion of Baltic or palaeo-Baltic waters (Table A4). It might therefore be easier to detect the effects of glacial meltwater intrusion on groundwater stability. The one representative water sample from 376 m depth at Svartboberget is similar, with low Cl^- and 17 pmC ^{14}C (Table A4 and Figures 5, 6 and 7).

^{14}C was measured in two samples from Klipperås which also have low tritium (Table A4). These gave 3.2 pmC at 406 m depth (55 mg/L Cl^-) and 2.4 pmC at 696 m (Figure 5). These correspond to ages that are probably ~30,000y although low $\delta^{13}C$ values (-16 to -17‰) suggest that some biogenic carbon has been added to the TIC which would dilute ^{14}C. Therefore uncertainty in estimation of age from ^{14}C is quite large; it seems probable that the deep groundwaters below at least 400 m were recharged during the last glaciation. The stable isotope compositions of these waters are around -12 ‰ $\delta^{18}O$ and are only slightly lighter than recently-recharged groundwater which is probably about -11.3 ‰ (Figure 3). This contrasts with the negative isotopic shifts of 2 to 3 ‰ in $\delta^{18}O$ that are seen at the more northerly sites and suggests that Klipperås may not contain melt water despite the apparently 'glacial age' of the water. Thus there might be a difference in the impacts of sub-glacial hydraulics between northern and southern Swedish sites, though this suggestion is based on data from only one site and is therefore speculative.

6. Summary of Stability Indications from Illustrative Data

6.1. Äspö Hard Rock Laboratory

- Deeper penetration of marine water in fault zone EW-1 indicates the local effect of density-driven flow in a transmissive fault zone. It is not certain whether this is stable or transient. Lateral salinity gradients between Laxemar boreholes KLX01 and KLX02 have been interpreted by modelling as representing a steady state distribution of variable salinity/density groundwaters.

- Cold-climate water penetrated to depths probably between 500 m and 900 m at Äspö and to 1200 m at Laxemar, though the corresponding degree of turnover of the system is uncertain because subsequent fresh water circulation has dispersed the isotopic signal. The apparent contrast between Äspö and Laxemar suggests that the more ‘inland’ location may have been affected by glacial meltwater recharge to greater depths than Äspö. It is not clear whether this is due to the varying depths of meteoric water penetration depending on the lateral position in a regional flow system or due to the effect of different pre-existing vertical salinity gradients on meteoric water penetration. These two palaeohydrogeological hypotheses anyway involve similar processes.

- The preservation of cold-climate recharge at shallow depths is noteworthy, indicating that mixing with saline Baltic water has stabilised this part of the system through the post-glacial period of land uplift.

- ^{14}C data support the possibility that pockets of cold-climate saline water correspond to the timing of the last glaciation and deglaciation, i.e. possibly >10,000 years.

- ^{36}Cl content of chloride in saline water confirms a very long residence time for salinity in the deep formations, i.e. the salinity is very unlikely to be derived from cryogenic ‘salting-out’ from permafrost formation which has been proposed as a hypothesis for the origin of deep saline waters and brines in Shield rocks.

6.2. Finnsjön and SFR Forsmark

- Finnsjön stable isotopic compositions are uniform and apparently do not show a significant trend towards cold-climate water, i.e. glacial meltwater recharge, with increasing depth. This, and high reported ^{14}C data, suggest that the water to 500 m in post-Holocene meteoric water mixed with saline basement water.

- The salinity gradient is more gradual, increasing gradually from below weathering cove to 300 m. This may typify the mixing process with a source of deep salinity, as opposed to the pattern at coastal sites where the source of salinity is intruding Baltic.

- Forsmark SFR groundwaters are more complex mixtures, including present-day Baltic, Littorina and glacial meteoric. The presentation of glacial water mixtures suggests that this system has been more stable than Finnsjön, possible due to the low hydraulic gradients and stability effect of saline water.

6.3. Stripa Mine

- Tritium is a good indicator of rapid drawdown from shallow groundwaters towards excavations, but needs very careful analysis to distinguish non-zero from zero or ‘baseline’ values

- Heterogeneity of water compositions, i.e. salinities, in the fracture network is a natural feature at a scale that is characteristic of each system. The degree of heterogeneity may be an indication of susceptibility to further hydrochemical changes and greater heterogeneity caused by excavation, though this is not clear from Stripa data. Both increasing salinity (‘draw-up’ from deeper groundwaters) and decreasing salinity (‘draw-down’ of shallow fresh groundwaters) were observed in different places, indicting the sensitivity of the system to perturbation by excavation.

- Cold-climate water (?glacial meltwater) has reached 1000 m depth, but is always mixed with saline basement water, so either the system was never flushed at that depth or the saline basement water has rebounded to give the present-day mixed groundwaters. At these depths, diffusion-control in microfractures and matrix may effectively be the process that controls the rate of change (i.e. stability) and mass transfer in the groundwater system (as also suggested by Gascoyne for Canadian Shield deep groundwaters).

- Groundwaters below the mined depth have ^{14}C which are >20-25 ka, i.e. late glacial/or late Pleistocene, but none have zero ^{14}C so there is a component of water from the last glacial period in all of them. Variations of ^{14}C data and water compositions suggest that these groundwaters do not represent a single recharge episode.

- ^{36}Cl data confirm that deep groundwater and solutes have moved site-scale distances with a 10^6 y timescale.

6.4. Other Swedish Sites

- The only trace of non-meteoric chloride is at 600 m depth at Fjällveden. ^{14}C ages are glacial, 12-30 ka, so it is likely that present groundwater to several hundred metres depth is dominantly the result of melt water infiltration. However it is likely that the depth of melt water penetration, the extent of flushing of pre-existing water, and the extent of post-glacial displacement of glacial groundwater are all site-dependent. Differences between inland and coastal sites are not apparent from this small data set.

6.5. Olkiluoto, Finland

Data and notes are in Appendix 2.

- Modern meteoric water has flushed Baltic (Littorina) water down to at least 100-150 m in 2,400 years.

- Before then, over about 50,000 years, Littorina replaced most of the cold-climate glacial water down to 300-500 m.

- It seems that glacial meltwater penetrated to only around 300-500 m at Olkiluoto, perhaps due to the presence of highly saline basement water at fairly shallow depth. An alternative interpretation is that the 'Shield' saline water has rebounded to the present depth since glaciation. A hypothesis has been proposed that glacial meltwater penetration was limited by structural features, e.g. a sub-horizontal fracture zone that caused vertical compartmentalization.

6.6. Other Finnish Sites

Data and notes are in Appendix 2.

- There are few data and inadequate supporting information, and the reliability of data is considered variable, so only tentative comments are possible.

- Existence of deep basement brine, at least at Miikhali, is confirmed and it is similar to those sampled fairly widely in the Canadian Shield. Its existence, and the depth of occurrence and salinity gradient above it, may be indicative of long-term hydrodynamic stability at these depths, e.g. around 1000 m. The brine is an indication that regional lateral flow of groundwater has not occurred at this depth.

- It is unclear whether glacial meltwater is present in some or all of the deep freshwater profiles at inland sites. Its absence would indicate that lateral fresh water flows are sufficiently rapid that any cold-climate waters had been flushed in the last 10^4 years. Alternatively, absence of any meltwater component could indicate that its infiltration was prevented by permanently frozen ground beneath ice sheets.

- At Palmottu, ^3H data show that young meteoric water penetrates to 100-200 m depth and thus relatively rapid water movements occur over this depth interval. Underlying brackish water has Holocene ages up to 10,000 years and is therefore a distinct flow system from the more mobile shallow fresh water mass. Correlation of water flows and water compositional changes with information on geological structures indicates that this partial isolation and stabilisation of the deeper part of the groundwater system is due to a sub-horizontal fracture zone acting as a hydraulic boundary.

- Isotopically-light groundwaters at Palmottu are identified as cold-climate waters but have been considered to originate as deglaciation surface water rather than from sub-glacial recharge.

- Indications of the effects of long periods of permafrost on groundwater stability are essentially absent. This could mean that permafrost had no substantial effect or that these effects have since been removed or overprinted. It is unlikely that saline groundwaters or bring (as at Miikhali) have cryogenic origins from permafrost – all indicators suggest that deep brine has an ancient geological origin.

6.7. Whiteshell URL and Other Canadian Shield Areas

Data and notes are in Appendix 3.1.

- Interpretation of hydrochemical, isotopic and hydrogeological data from Whiteshell suggested that the groundwater system is compartmentalised vertically into an advective flow system at steady state above 400-500 m and a diffusive system at greater depths. Hydrogeological properties, i.e. decreasing permeability with increasing depth, and sub-horizontal transmissive structures, primarily determine this and salinity stratification is a secondary factor.

- The significance of transmissive fracture zones in controlling the hydrodynamic stability of the stratified groundwater system is exemplified by the occasional occurrences of saline discharges to the surface. The role of these fracture zones in propagating perturbation by excavation is the drawdown of fresh/brackish waters containing ^{3}H towards underground discharges in deep wines.

- Stable isotopic evidence for a glacial meltwater component of groundwaters in the lower part of the advective part of the system suggests that steady state advection has a maximum flushing time in the order of 10^4 years.

- In the diffusive ‘stagnant’ part of the investigated system, 500 m, saline fracture waters are not in equilibrium with matrix waters which have significantly greater salinity and density. The effect of this on the long-term hydrodynamic and geochemical stability of the deep system is not clear. It suggests that a diluting water component has entered the deep system at some tie in the past.

6.8. Sellafield, UK

Data and notes are in Appendix 3.2.

- The groundwater system at Sellafield comprises three chemically and isotopically-distinct groundwater masses or ‘regimes’. The distribution of these groundwater regimes is controlled by the location with respect to the sedimentary basin to the west of the site and the inland topography to the east, by depth, and by the hydrogeological properties of the different sedimentary and basement formations. The fresh water regime is more active hydrogeologically than the two saline water and brine regions.

- Stability of these groundwaters can be considered in terms of the interfaces or 'transition zones' between the distinct water masses. Age and history of movement of the water masses is another factor to be considered. Hydrochemical, stale isotopic and mineralogical indicators show that the interfaces and, by implication, the deeper water masses have been stable. The inferred timescales of stability are at least 10^4 y in the case of the basement saline water regime in which cold-climate water is detected by stable isotopes and at least 10^6 y in the case of the basinal brine regime in which ^{36}Cl and ^{4}He are useful indicators of stability. However, ^{36}Cl evidence equally shows that brine has moved between the sedimentary and basement formations in the basinal regime in a timescale of less than 10^6 y, which is consistent with a density-dependent hydrodynamic model of basin-edge processes. ^{4}He data suggest that anomalously low concentrations might be associated with a major sub-vertical fault zone. This would mean that the fault zone is a pathway for water movement across the stabilising stratification.

- ^{14}C data were almost valueless for dating groundwaters and quantifying the timescales of turnover and stability in the Sellafield groundwater system. This was the case because contamination of samples introduced large and irregular uncertainties which were particularly severe because in situ ^{14}C values were expected to be near- or at zero for the deep groundwaters. This problem was particularly serious for understanding the hydrodynamics and mixing of groundwaters in the fresh and brackish water regimes in the sedimentary formation and outcropping basement formation. A similar problem discounted ^{3}H as a diagnostic indicator of modern recharge penetration.

- Mineralogical indicators of geochemical and hydrodynamic history have been most intensively studied in Sellafield drillcore samples. Morphology of secondary calcite, chemical variability in growth zones, stable isotopes and fluid inclusions contribute evidence of qualitative or semi-quantitative fluctuations of geochemical and, by implication, hydrodynamic conditions. Interpretation of these mineralogical lines of evidence is subject to various uncertainties and assumptions regarding conceptual models for processes. Overall, the balance of evidence in this case supports an interpretation that the present organisation of the groundwater system into regimes of varying salinities has not experienced major changes over a long timescale though there have been relatively minor salinity changes indicating hydrogeological fluctuations and also relatively minor geochemical fluctuations. There is uncertainty in the timescale over which these indicators provide information because of the difficulty in dating minerals and the specific growth zones reliability.

6.9. Tono Mine and Underground Laboratory, Japan

Data and notes are in Appendix 3.3.

- Stable isotopic, ^3H and ^{14}C data in fresh groundwaters in outcropping granite near Tono indicate that the groundwater system is active and relatively responsive to changes of external boundary conditions for several hundred metres depth.

- Similar data plus ^4He for groundwaters in sedimentary rock cover and underlying granite at Tono itself indicate that groundwaters below 150-200 m depth are considerably older with slower flow rates. Data also suggest that groundwaters in the covered granite may be rather little affected by excavation of the URL, or at least that groundwaters in the sedimentary rocks act as a buffer for drawdown.

- Fracture-filling secondary calcites are mostly older than the timescale of interest and thus are not valuable directly as palaeohydrogeological indicators. However preservation of these older calcites suggests that the system has had general hydrodynamic and geochemical stability for a long time.

7. Comparison of Stability Indicators in Groundwaters at Inland and Coastal Sites

The review of geochemical data and interpretations in terms of groundwater stability allows a comparison to be made between inland and coastal sites on Fennoscandian Shield rocks. Caution is required, however, in generalising the conclusions, especially in view of the patchy basis for the comparison.

The first point to be made is that data are variable, both in terms of quantity, quality and completeness. Therefore the comparisons discussed here are sometimes speculative and are conditional on the quality of data. Data for inland sites in Sweden are sparse and are dominated by data from Stripa. There are more data from coastal sites in Sweden, of which some are from recent investigations and are thus likely to be more reliable. Data from Finnish sites, except Olkiluoto, are sparse and of variable reliability.

The presence of Littorina (palaeo-Baltic) water or Baltic water in coastal sites is suggested by a cluster of groundwaters with salinities around 5000-6000 mg/l chloride (see Figure 2). This cluster includes groundwaters from Äspö, compositions of which are broadly similar to water samples from new investigations at the adjacent Simpevarp area, and from Finnsjön, compositions of which are similar to some water samples from new investigations at Forsmark. However a recent comparison of patterns of Mg, Br and $\delta^{18}O$ versus Cl in coastal groundwaters from Simpevarp and Forsmark suggests that the influence of Littorina water in groundwaters at Simpevarp/Äspö is very localised (Laaksoharju et al., 2004a,b; SKB, 2004). Most of the brackish-saline groundwaters in that area are attributed to mixing of meteoric water with deeper non-marine saline groundwater that contains a cold-climate or glacial melt-water component, rather than to Littorina water (SKB, 2004). An alternative interpretation of salinity variations and $\delta^{18}O$, supported by limited ^{14}C data, suggests that brackish groundwaters at intermediate depths (300-600 m) at Äspö retain a substantial component of Littorina water (Bath and Strömberg 2004). It is more certain that groundwaters to 500 m depth at Finnsjön and SFR Forsmark, and most water samples to at least 500 m depth from the preliminary stage of the Forsmark investigation, have retained a large component of Littorina water. Brackish waters at similar depths at Olkiluoto are interpreted to have a similar predominance of Littorina water.

Components of modern Baltic and/or Littorina seawaters are, of course, absent in groundwaters at inland sites which, on the basis of available evidence, remain fresh to depths greater than 500 m and possibly to 1000 m or more in some cases. However much of the data, other than data from Stripa, is from old investigations where degrees of mixing with drill waters are uncertain, so in situ salinities may be underestimated. Compositions of water samples from borehole KLX02 at Laxemar apparently remain fresh-to-brackish to around 1000 m depth (though new drillings are Laxemar may cause a revision of this view). Below 1000 m, salinities of water samples from KLX02 rise sharply to fairly high salinities (e.g. 45,000 mg/l Cl^- at around 1550 m). These are the highest salinity values seen in Swedish boreholes. The limited data for inland Finnish sites suggest a similar condition with fresh or brackish water to at least 1000m in depth except at Miihkali and Outokumpo where saline groundwaters were reported from 500 m and 1000 m respectively (with a brine salinity reported at 1000 m at Miihkali). Thus groundwater systems at inland sites essentially have two component water types: fresh meteoric water and deep saline water or brine which has evolved over a long time (i.e. probably through a pre-Quaternary timescale and perhaps much older). The ages of the meteoric waters can be assumed to vary within each site as well as between sites. At Stripa, they varied up to 20-25 ka (i.e. corresponding to the glacial peak) at depths below 400 m. ^{14}C data for fresh groundwaters at other Swedish sites, both inland and near-coast, suggest ages that are late-glacial to glacial, 12-30 ka.

Some general questions concerning palaeohydrogeological evidence for groundwater stability can be considered in the context of the above observations:

- What was the effect of glaciation on groundwaters at inland and coastal locations?
- How much groundwater movement has occurred since the last glaciation?
- Are there general inferences concerning groundwater stability in these different hydrogeological settings?

(i) **What was the effect of glaciation on groundwaters at inland and coastal locations?**

$\delta^{18}O$ data for Stripa show that isotopically-light cold-climate water (i.e. glacial melt water) remains as a major component to around 400-600 m depth. Below that, cold-climate water is probably present to at least 1000 m depth but is increasingly mixed with deeper older water. At Laxemar (KLX02), the fresh-to-saline water transition occurs below 1000 m but $\delta^{18}O$ data indicate that the deep fresh water is not dominated by cold-climate water.

These observations suggest that groundwaters at inland sites were affected by melt water inflow to many hundreds of metres and in some places to at least 1000 m depth. It is probable that the downwards flux of glacial melt water was insufficient to displace entirely the pre-existing groundwater from these depths, since if it had done so there would be a greater proportion of relict melt water. Very old saline water/brine is assumed to underlie these fresh groundwaters, though it is not known to what depths this saline water has been mixed and diluted by small proportions of glacial water. The same mixing/dilution process would have resulted from normal circulation of topographically-driven fresh water which has occurred over a considerably longer time period than just that of melt water influxes. The process would have been enhanced by the hydrostatic adjustment of the saline water/brine due to isostatic changes. Interpretation of the isotope data including ^{14}C suggests that most of the fresh water in the top 1000 m at inland sites has originated as recharge since the end of the last glaciation.

Glaciation and melt water inflow affected groundwaters at coastal sites, e.g. Äspö, in a similar way, except that the maximum depth of influence may be rather less than that at inland sites. The impact at shallow depths is still evident in pockets of relict cold-climate water which may be preserved more at coastal sites because the post-glacial gradients have been lower than at inland sites. The most significant difference is the much lesser degree of post-glacial fresh water circulation than at inland sites (see below).

In summary, the distribution of glacial melt water has been diluted and dispersed by subsequent groundwater circulation, especially at inland sites. It is reasonable to assume that the depth of significant melt water flow was at least as great as that of post-glacial water flow.

(ii) **How much groundwater movement has occurred since the last glaciation?**

The balance of interpretation suggests that there has been a large degree of post-glacial groundwater movement down to at least 500 m and possibly to 1000 m depth at inland sites. As discussed above, there has been a substantial ‘turnover’ of fresh groundwater displacing cold-climate fresh water since the last glaciation, plus dispersive mixing of post-glacial water with deep saline water. Decreasing degrees of flushing with increasing depth accounts for the traces of salinity in deep fresh-brackish water at Stripa and Fjällveden. The apparently sharper transition from fresh-to-saline at Laxemar suggests less dispersive mixing which might be related to fresh water flow paths being more localised (‘up and down’ local circulation) at this near-coast site compared with sites that are further inland.

At coastal sites, groundwater movement at some has involved substantial Littorina water (e.g. Finnsjön/Forsmark and Olkiluoto) and perhaps less seawater and more post-glacial fresh water at others (e.g. Äspö/Simpevarp). Relict salinity above 1000 m depth at Äspö, as well as preserved pockets of cold-climate water, suggest that neither inflows of Littorina nor of post-glacial fresh water have been comparable with flows elsewhere. The balance between post-glacial sea water and fresh water circulation and the identity of the waters that are presently in place, presumably depends on the relevant hydrodynamic gradients and the durations for which the palaeohydrogeological boundary conditions persisted.

Water densities, i.e. Baltic or Littorina seawater having a slightly higher density than fresh water, may have played a role in that balance in cases where the changes and contrasts in topographic gradients were small.

(iii) **Are there general inferences concerning groundwater stability in these different hydrogeological settings?**

At inland sites, groundwater is continually moving, although the flux becomes lower with increasing depth. The topographic boundary conditions and constant rock properties are fairly constant in post-glacial conditions so that the movements of fresh water are stable. The most significant impact on stability would have been glaciation, causing mechanical effects and hydraulic changes. It can be suggested speculatively that the greatest destabilisation of a pre-existing steady state between deep saline waters or brines and overlying fresh water would have been due to crustal depression and water injection associated with the ice sheets in each glacial episode. The distribution of dense saline groundwaters may still be out of equilibrium with respect to the rate of uplift and present hydrogeology. However the dominance of post-glacial fresh waters indicates that at least the hydraulic steady state (i.e. with respect to pressures) is close to being re-established.

Groundwater stability at coastal sites is different in that it is influenced by seawater intrusion as well as by glaciation. Seawater intrusion depends on shoreline changes, which in turn are coupled indirectly with glaciation and other climatic factors (e.g. run-off into the Baltic). Therefore stability of hydrodynamic conditions and groundwater distributions at coastal sites is expected to be more transient than at inland sites and dependent on a larger variety of subtle variations. Changes of boundary conditions due to shoreline displacement and salinity of the Baltic are seen to have had substantially differing impacts on groundwater compositions and distributions at different coastal sites. However the fluctuations of stable hydrodynamic (i.e. flow) conditions would have been quite small. Varying water compositions provide a clearer ‘fingerprint’ of past changes of boundary conditions than can be obtained from uniform freshwater compositions at an inland site. As at inland sites, glaciation was probably the greatest impact on hydrodynamic stability of coastal sites. Yet evidence of the degrees of groundwater ‘turnover’ in the coastal groundwater systems due to glaciation have been mostly dispersed by subsequent Littorina influx and/or fresh water circulation.

8. Concluding Summary

Geochemical indicators of hydrodynamic stability are those parameters that respond in an interpretable way to groundwater movements and that signal changes in those movements. In addition there needs to be evidence of the timing of changes and, ideally, sufficient resolution of the interpreted age data to test for correlation with external changes such as episodes of past climate or other environmental changes. In other words, these geochemical indicators of stability provide a link, through their palaeohydrogeological interpretations, with the definitions and evaluation of external FEPs (EFEPs) in Performance Assessment.

Numerical modelling of physical hydrogeology, specifically to assess the likely response of groundwater movements to changing boundary conditions, is complementary to the measurement and interpretation of geochemical indicators. Coupling solute transport to the physical groundwater flow model allows salinity evaluation to be simulated and solute residence times to be calculated for direct comparison with interpreted geochemical and isotopic data. The synthesis of modelling and geochemical measurements results in an integrated palaeohydrogeological model of the groundwater system.

Interpretation and modelling of geochemical stability, i.e. the internal capacity of the rock-groundwater system to regulate or 'buffer' its chemical properties such as pH, redox and groundwater compositions, are not covered in this report. However hydrodynamic stability is inevitably a factor, along with water-rock reactions, that determines the evolution and stability of groundwater compositions. Geochemical stability of near-field and geosphere conditions is an important issue for long-term safety assessment that is considered in other research reports by both SKI and SKB.

The principal geochemical indicators of hydrodynamic stability are non-reactive 'conservative' solutes, mainly chloride, and isotopic parameters that label water origins and solute residence times, viz. stable oxygen and hydrogen isotopes, carbon-14, tritium, chlorine-36 and a few other less prominent isotopic systems such as uranium-thorium and dissolved helium. In addition to the specific interpretation of, for example, salinity and groundwater ages, the spatial variability of these parameters is equally important for understanding their significance with respect to groundwater stability. Heterogeneity of groundwater compositions and ages, especially if uncorrelated with inferred groundwater movements, is an indication of compartmentalization. Groundwater movements and compositions are interpreted to be compartmentalized where they are heterogeneous due to the influence of strongly variable and anisotropic rock properties, i.e. transmissivities and fracture connections, at the scale of interest.

Values and variations of salinity, i.e. of chloride concentrations, are significant in all of the areas from which data have been used to illustrate interpretations in this report. High salinities, as in the deep Shield brines and in the basinal brines originating in sedimentary strata, are an inherent cause of stability due to their density and are also an indication that turnover of groundwater is very low. However salinity variations, as the examples show, require interpretation to ascertain their significance for groundwater stability. These interpretations may be qualitative judgements and/or attempts to quantitatively model the palaeohydrogeology and long-term evolution of groundwater compositions. Palaeohydrogeological modelling invariably involves assumptions, e.g. of initial and boundary compositions, other uncertainties and non-unique 'best fit' solutions, and it is important that alternative conceptual models and boundary conditions should be considered.

Isotopic parameters are an essential tool for investigating groundwater stability because they provide indications of groundwater sources, ages and mixing. Stable oxygen and hydrogen isotope ratios are the most widely and easily available data. Interpretation of stable isotope ratios depends strongly on the general background literature that relates O and H isotope ratios to water recharge sources and, indirectly via assumptions about climate-water relationships, to water ages. Carbon-14 data, if they can be quantitatively modelled and interpreted, provide a more direct indication of groundwater ages based on the assumption that dissolved carbonate provides a meaningful proxy for water movement. However the effect of matrix diffusion on the effective rate of solute movement through a fractured rock or dual porosity formation must be considered as a possible source of uncertainty in estimations of groundwater ages. It may anyway be the case that solute residence times rather than rates of advective groundwater movements are the more valuable interpretations. These potential differences between solute movement rates and groundwater flow rates have to be considered when comparing trace isotopic indicators such as carbon-14 with advective travel times from hydrodynamic modelling.

Similar considerations apply to the interpretation of chlorine-36 as a groundwater age indicator in dilute groundwaters. However in the majority, if not all, of the possible applications of Cl-36 in crystalline rock groundwaters, atmospheric Cl-36 sources are overwhelmed in saline groundwaters by Cl-36 from *in situ* production. In these cases, interpretation of Cl-36 is in terms of overall residence times of chloride in that geochemical environment, and it can be only qualitatively related to groundwater movements and groundwater stability.

Depending on specific geochemical and hydrogeological site conditions, and on the particular question to be addressed, other geochemical indicators may provide valuable information. Amongst these parameters are dissolved helium, uranium isotope ratio and secondary minerals such as calcite.

Secondary minerals such as calcite, iron oxides, pyrite and clays are potentially useful in terms of large scale patterns of rock alteration and mineral precipitation providing information about past hydrogeochemical conditions. Discrete mineralogical characterisation methods such as micrography, microanalyses, stable isotope analysis and isotopic dating are potentially valuable but have many practical limitations such as sample availability and uncertainties in interpretations including dating the timescale for which the secondary mineral is acting as a palaeohydrogeological proxy indicator. Studies at Äspö and Olkiluoto have illustrated these difficulties due to the very small amounts of material that can be sampled. There are several possible methods for retrieving information about geochemical and hydrodynamic evolution, stability and episodicity related to external changes, but at present they are viable with a reasonable degree of confidence only in certain cases, e.g. Sellafield and Palmottu, whilst in other cases, e.g. Olkiluoto and Äspö, they have had much more limited applicability.

A significant conclusion from the case studies of geochemical indicators in groundwaters is that reliable sampling and the best possible analytical resolution, especially with respect to low values of isotopes such as tritium and carbon-14, are very important prerequisites for making the most reliable interpretations and for reducing uncertainties and non-uniqueness in interpretations. In general, all of the geochemical indicators described here are dependent on interpretative models that introduce assumptions and simplifications. It is necessary to be aware of these factors when developing a site investigation strategy so that geochemical indicators are applied to maximum benefit.

The compiled data provide only limited scope for comparison of groundwater evolution and stability between inland and coastal areas in Sweden, because of the patchiness of representative data especially from early site studies. The external changes that might have perturbed stable groundwater conditions in the past are glaciation (i.e. melt water, mechanical loading and permafrost) and varying sea water infiltration at coastal sites due to changes in palaeo-Baltic and isostatic conditions. The present distributions of palaeo-Baltic sea water in groundwaters at coastal sites vary, reflecting local palaeohydrogeological conditions. It is likely that inland areas have had longer durations of post-glacial fresh water infiltration than coastal areas, possibly causing greater degrees of dilution and dispersion of pre-existing groundwaters and thus overprinting their hydrochemical and isotopic 'fingerprints'. Lower post-glacial hydraulic gradients relative to inland sites may account for the occurrence of more relict cold-climate water at coastal sites.

Some concluding general observations are based on rather thin evidence and therefore are speculative. Firstly, it seems that glacial melt water penetrated many hundreds of metres and in some places to at least 1,000 m depth. However the low remaining proportions of melt water and of much older saline Shield water suggest that melt water flux did not fully displace pre-existing groundwaters at these depths. Secondly, where there has been post-glacial infiltration of palaeo-Baltic sea water, the density stratification or compartmentalisation effect coupled with low hydraulic gradient has reduced rates of subsequent fresh water circulation after shoreline recession.

There are many uncertainties in interpreting these geochemical indicators in terms of the penetration depths of glacial melt waters and the degree to which they replace pre-existing groundwaters, of other aspects of groundwater stability, and of comparisons between inland and coastal groundwater systems. Uncertainties derive partly from the reliability of groundwater samples as being representative of *in situ* conditions, and partly from the non-uniqueness of interpretative models. Future investigations using these approaches need to improve sampling, to make conjunctive use of geochemical and isotopic indicators which have varying timescales and sensitivities, and to integrate these indicators with palaeohydrogeological modelling to support the development of reliable groundwater flow and solute transport models for Performance Assessment.

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Appendix 1. Data for Swedish Crystalline Rock Groundwaters

Table A1. Parameters for groundwater samples from Äspö before and after excavation of the HRL and from Laxemar, selected to include most of the isotopic data. Data from Smellie and Laaksoharju (1992), Rhén et al. (1997), Laaksoharju et al. (1998), Tullborg and Gustafson (1999). Tritium analyses carried out by IFE in 1993-4 may be too high and those in 1997-8 are often too high and unreliable (Nilsson, 1999a,b). Tabulated data may differ from later SKB compilations with respect to which data are considered to be representative; the differences are not substantial except for some ^3H data.

Borehole	**Date**	**Depth^1, m**	**Cl^-, mg/L**	**^3H, TU^3**	**^{14}C, pmC**	**$\delta^{18}O$, ‰**	**δ^2H, ‰**
Undisturbed system, 1988-89							
HAS13	890703	50	5070	1.2		-7.2	-69.3
KAS02	890111	208	3820	$0.3^4/0.8^5$	23	-13.9	-108.9
KAS02	880411	316	5340*	8.0*		-12.3*	-100.6*
KAS02	880927	326	5360	<8.5	21	-12.7	-99.8
KAS02	880425	465	5440*	<8.5*	17*	-12.8*	-99.9*
KAS02	880505	532	6330	8.0		-12.3	-97.2
KAS02	880920	863	11100*	<8.5*		-13.0*	-96.8*
KAS02	890131	892	11100	$0.2^4/0.9^5$		-13.1	-96.8
KAS03	890221	131	1220	0.15	2	-15.8	-125.0
KAS03	880810	209	2850	<8	7	-14.6	-115.3
KAS03	880828	249	2950	<8	8	-14.5	-118.1
KAS03	880816	360	5180	<8		-13.3	-104.9
KAS03	880822	466	4600	<8		-13.6	-109.6
KAS03	880903	616	5880	<8		-13.3	-103.4
KAS03	880908	846	8080*	<8*		-13.0*	-99.7*
KAS03	890315	931	12300	0.4		-12.7	-96.4
KAS04	890417	230	508	4.3	40	-11.0	-84.8
KAS04	890427	338	3030	$0.5^4/<8^6/0.9^5$		-13.0	-99.6
KAS04	890403	460	5840	0.03		-11.9	-92.3
KAS06	890531	240	3630	3.8	41	-10.9	-94.3
KAS06	890607	340	5680	$0.3^4/1.0^5$	19	-9.2	-77.8
KAS06	890614	397	5970	0.6		-7.4	-69.2
KAS06	890621	520	6150	3.5		-8.2	-70.8
Post-excavation, 1991-1994							
KR0012B	910507	[513^{11}]	695	34		-11.4	-82.1
KR0012B	920422	[513^{11}]	1330	25		-10.2	-77.3
KR0012B	921028	[513^{11}]	970	17		-9.9	-79.9
KR0012B	930516	[513^{11}]	710	17		-9.9	-72.0
KR0012B	931108	[513^{11}]	619	34		-9.6	-69.6
KR0012B	940810	[513^{11}]	500	31.3		-9.8	-68.1
SA0813B	921202	[813^{11}]	3450	6.8		-7.5	-59.8
SA0813B	930929	[813^{11}]	3350	14		-7.3	-50.4
SA0813B	940607	[813^{11}]	3272	28.7		-7.2	-53.7
SA0958B	930623	[958^{11}]	4088	8.4		-7.5	-56.0
SA0958B	930928	[958^{11}]	4260	14		-7.4	-57.5
SA0958B	940607	[958^{11}]	3641	28.7		-7.2	-55.6
SA1420A	921015	[1420^{11}]	3930	17		-8.7	-72.0
SA1420A	930622	[1420^{11}]	3419	31		-7.5	-59.0
SA1420A	930929	[1420^{11}]	3530	22		-7.0	-52.5

Borehole	Date	Depth[1], m	Cl^-, mg/L	^{3}H, TU[3]	^{14}C, pmC	$\delta^{18}O$, ‰	$\delta^{2}H$, ‰
SA1420A	940607	[1420[11]]	3052	33.8		-7.5	-57.0
SA1614B	921119	[1614[11]]	5160	8		-13.1	-103.1
SA1614B	930622	[1614[11]]	6207	4.2		-11.5	-85.5
SA1614B	930928	[1614[11]]	5650	4.2		-10.4	-77.6
SA1614B	940606	[1614[11]]	5176	8.4		-9.7	-71.9
SA1828B	921119	[1828[11]]	5200	4.2		-10.8	-84.4
SA1828B	930621	[1828[11]]	5850	4.2		-10.3	-75.9
SA1828B	930928	[1828[11]]	6010	4.2		-10.3	-71.4
SA1828B	940606	[1828[11]]	5123	8.4		-8.9	-67.8
SA2074A	930617	[2074[11]]	5282	5.9		-8.5	-65.2
SA2074A	930928	[2074[11]]	4670	7		-8.4	-60.0
SA2074A	940607	[2074[11]]	4276	10.1		-8.5	-63.3
Laxemar boreholes							
KLX01	881208	274	2050	8.0		-11.5	-89.9
KLX01	881123	441	1700			-12.2	-94.5
KLX01	881103	691	4870	<8.4		-13.3	-102.1
KLX01	901009	835	9180				-96.9
KLX01	901030	915	11200				-92.9
KLX02	940210	318	73	5.9[7]		-10.3	-73.4
KLX02	931108	338	235	13[7]		-10.6	-75.7
KLX02	931123	801	548	8.4[7]		-10.9	-78.7
KLX02	931216	1093	15800	7.6[7]/<0.2[9]		-11.7	-78.6
KLX02	940117	1562	45500	26[7]/<0.8[9]		-8.9	-47.4
KLX02	970925	25[2]	150	38[8]/17[5]		-9.5	-76.5
KLX02	970925	125[2]	120*	24[8]*		-9.7*	-77.4*
KLX02	970925	225[2]	66*	25[8]*		-9.9*	-77.0*
KLX02	970925	325[2]	46*	30[8]/<6[5]*		-10.0*	-77.4*
KLX02	970925	425[2]	36	26[8]		-10.0	-77.7
KLX02	970925	525[2]	35	26[8]/10[5]		-10.0	-77.8
KLX02	970925	625[2]	35*	32[8]/16[5]*		-10.0*	-78.1*
KLX02	970925	725[2]	35	32[8]/10[5]		-10.1	-81.2
KLX02	970925	825[2]	35*	32[8]/14[5]*		-10.0*	-79.3*
KLX02	970925	925[2]	35*	27[8]/13[5]*		-10.0*	-82.2*
KLX02	970925	1025[2]	83*	28[8]/13[5]*		-10.0*	-79.3*
KLX02	970925	1125[2]	10400*	<4.2[7]/30[8]/5[5]*		-9.5*	-76.2*
KLX02	970925	1225[2]	19900*	<4.2[7]/25[8]/4.2[5]*		-8.2*	-66.0*
KLX02	970925	1325[2]	32900*	19[8]/<0.8[5]*		-9.1*	-63.4*
KLX02	970925	1425[2]	34300*	<4.2[7]/25[8]*		-9.3*	-62.8*

[1] Average depth of sampled interval

[2] Tube sampling in 50m sections

[3] Tritium analyses were carried out by various labs (IFE, GSF, Waterloo, CRIEPI) at various times

[4] Tritium analyses by IAEA in 1989

[5] Tritium analyses by Univ of Waterloo in 1998 of duplicate samples from same or nearby intervals

[6/7/8] Tritium analyses by IFE Norway in 1989/1993-4/1997; these analyses are considered by SKB to be erroneously high (Nilsson, 1999a,b).

[9] Tritium analyses by GSF Germany in 1993

[10] Approx magnitude of IFE analyses confirmed by analyses by CRIEPI Japan of nearby samples

[11] These values are the distances along the HRL access tunnel at which samples were collected.

* These data are not marked as ‘representative’ in subsequent SKB compilations.

Table A2. Selected parameters for groundwater samples from Finnsjön and SFR Forsmark. Data from Smellie and Laaksoharju (1992), Laaksoharju et al. (1998), Laaksoharju and Gurban (2003), Tullborg and Gustafson (1999), Smellie et al. (1985).

Borehole	**Depth[1], m**	**Cl^-, mg/L**	**^{3}H, TU**	**^{14}C, pmC**	**$\delta^{18}O$, ‰**	**$\delta^{2}H$, ‰**
Finnsjön						
Fi1	77.0	61	36±3	84.1	-12	-88
Fi1	180.0	1310	5±2	33.0	-11.6	-85.2
Fi1	240.0	1500	<3	37.6	-11.7	-85.7
Fi1	289.0	5220		34.6	-11.5	-89
Fi1	356.0	5500	<3	19.0	-11.8	-86.9
Fi1	450.0	5500	<3	35.2	-11.8	-88.7
Fi9	94.0	680	8	22.8	-9.8	-79
Fi9	114.0	2125		22.8		
Fi9	182.0	2700	<3	22.8	-10.8	-86
Fi9	360.0	5150	<3	22.8	-11.2	-89
Fi7	513.0	555	8		-11.9	-89
Fi5				40.0	-11.6	
SFR Forsmark						
KFR01	98.4	4090	16.9		-10.9	-79
KFR02	185.3	4460	8.2		-12.5	-95
KFR03	107	3720	12.7		-13.9	-103
KFR03	133	3740	12.6		-14.5	-108
KFR03	151	3820	12.1		-14.4	-107
KFR03	176	4170	10.0		-12.4	-95
KFR04	111.8	3520	13.9		-13.5	-104
KFR04	138.8	4269	9.4		-9.5	-73
KFR04	166.8	4290	9.3		-9.6	-74
KFR05	160.1	3830	12.0		-8.8	-70
KFR08	93.4	3170	16.9		-8	-59
KFR09	83.7	2980	33.4		-8	-66
KFR10	147.5	4430	8.4		-7.9	-61
KFR13	143.1	3690	12.9		-15.2	-115
KFR19	58.2	2880	17.7		-8.2	-65
KFR19	65.5	2890	17.7		-8.4	-64
KFR19	53.8	2930	17.4		-8.6	-67
KFR55	134.3	3861	11.8		-9	-71
KFR7A	134.5	5380	8.4		-9.2	-72

[1] Average depth of sampled interval

Table A3. Selected parameters for groundwater samples from the Stripa Mine investigation. Data from Wikberg et al. (1987), Nordstrom et al. (1985), Moser et al. (1989), Fritz et al. (1989).

Borehole	**Depth[1], m**	**Cl^-, mg/L**	**^{3}H, TU**	**^{14}C, pmC**	**$\delta^{18}O$, ‰**	**$\delta^{2}H$, ‰**
N2	457	170	8		-12.7	-96
N2	500	230	<8		-12.9	-94
N2	514	140	<8		-12.5	-91
N3	495	120	8		-12.4	-90
N3	501	125	<8		-12.5	-90
N3	505	145	<8		-12.4	-90
N4	379	39	<8		-12.2	-89

Borehole	**Depth^1, m**	**Cl$^-$, mg/L**	**^{3}H, TU**	**^{14}C, pmC**	**δ^{18}O, ‰**	**δ^{2}H, ‰**
N4	412	39	8		-12.1	-91
N4	447	35	17		-11.8	-88
N4	465	55	8		-12	-90
W1	408	38	<8		-12.1	-94
W1	413	49	<8		-12.1	-92
W1	446	40	8		-11.9	-90
W1	472	42	<8		-11.8	-92
W2	413	48	8		-11.5	-91
W2	430	43	8		-12.1	-92
W2	440	31	8		-11.5	-89
W2	493	35	8		-11.6	-90
R1	365	34	6	7.0	-12.3	-87
M3	341	36	10	3.4	-12.2	-91
E1	505	22	20		-12.3	-90
N1	505		0.2		-12.9	-94
N1	479	122	0.3		-13.6	-99
N1	559	58	0.2		-13.5	-98
N1	627	48	0.1		-13.1	-95
N1	630	50	0.23		-13.4	-97
V1	405	630			-13	-94
V1	405	700	0.7		-12.9	-92
V1	405	650	1		-12.9	-93
V1	627					
V1	823					
V1	823					
V2	622			5.0		
V2	432	91		2.0	-12.5	-91
V2	704			11.0		
V2	822			5.5		
V2	816	608	0		-13.2	-94
V2	823	490	0.9		-13.3	-96
V2	870			15.0		
V2	900	460	0.12		-13.1	-94
V2	959	375	0.26		-13	-93
V2	1100		0.2		-12.8	-92

[1] Average depth of sampled interval

Table A4. Selected parameters for groundwater samples from Fjällveden, Gideå, Svartboberget and Klipperås. Data from Smellie et al. (1985), Laaksoharju et al. (1998), Laurent (1983, 1986).

Borehole	**Depth^1, m**	**Cl$^-$, mg/L**	**^{3}H, TU**	**^{14}C, pmC**	**δ^{18}O, ‰**	**δ^{2}H, ‰**
Fjallveden						
Fj2	605	170	<3	18.6	-14.1	
Gideå						
Gi2	178	4.8	<3		-12.6	-90.4
Gi4	222	7.9	5	23.7	-12.5	-89.7
Svartboberget						
Sv4	376	9	<3	16.7	-13.2	-95.3
Klipperås						
Kl1	406	54	3		-11.9	-85.7
Kl1	406	55	<3	3.2	-12.0	-86.3
Kl1	406	55	<3		-12.1	-86.5

[1] Average depth of sampled interval

Appendix 2. Olkiluoto and Other Finnish Sites

Olkiluoto is a small island with an area of about 7 km^2 with a low topography (maximum elevation 18 metres) on the south-western coast of Finland on the Gulf of Bothnia. It is the candidate site for construction of a deep repository for disposal of spent nuclear fuel. Boreholes were drilled to 1050 m depth. The uppermost 100-200 m of the bedrock is more transmissive than the deeper parts, in which hydraulic conductivity decrease with increasing depth. The lateral hydraulic gradient varies from 0.01 to 0.05. Hydrogeological testing has indicated that some low dipping, nearly horizontal fracture zones have a major effect on the local groundwater conditions. Olkiluoto island emerged from a long period of submergence beneath the Baltic about 2400 years ago. Continuing crustal uplift has progressively raised the hydraulic gradient at Olkiluoto, causing the fresh groundwater regime to deepen by 100-150 m with respect to ground surface since the island rose above the sea level.

As in the case for Äspö and the other coastal sites in Sweden, groundwater salinity at Olkiluoto is variable and generally increases with depth (Table A5; Pitkänen et al., 1996, 1999, 2004; Ruotsalainen et al., 2000). Relatively young meteoric water occurs down to 100-150 m depth. A distinctive SO_4-rich brackish groundwater occurs at 100-300 m depth. It has higher Cl^- than that in modern Baltic seawater and most probably infiltrated during the Littorina. ^{14}C values for these waters (20-30 pmC) also indicate a Littorina source (Figures A1 and A2). Groundwater in the lower part of the brackish layer at 300-400 m has a lighter stable isotopic composition which indicates a component of glacial meltwater. The interface between brackish and saline groundwaters is around 400-500 m depth. Below that, saline water (up to 70 g/L TDS at 1000 m) has Ca-Cl composition with a relatively heavier stable isotopic composition suggesting an ancient origin.

In summary, chemical and isotopic data at Olkiluoto indicate five end-member water types affecting the current groundwater compositions at the site: (i) meteoric water infiltrated from the surface since 2.4 ka ago, (ii) seawater from the Gulf of Bothnia (0-2.4 ka ago; about 5 g/L TDS), (iii) Littorina seawater (2.4-7.5 ka ago; about 11 g/L TDS), (iv) relict fresh water containing glacial melt water from before the Littorina stage (7.5-10 ka ago), and (v) saline water that is characteristic of deep groundwaters in Shield basement.

A palaeohydrogeological simulation for glacial meltwater penetrating to 300 m depth, which is shallower than at Äspö, has suggested that a sub-horizontal fracture zone might have had a significant role in restricting fresh water recharge to the upper part of the bedrock (Löfman, 1999). Modelling also indicated that intrusion of Littorina seawater has been relatively fast. The model suggested that groundwater in the upper part of the bedrock was brackish by 7 ka and that the variably saline groundwater system was at steady state from 6 ka. Steady state continued until postglacial land uplift raised Olkiluoto above sea level at about 2.4 ka and fresh water replaced brackish and saline water.

Table A5. Selected parameters for groundwater samples from Olkiluoto. Data from Lampén and Snellman (1993), Pitkänen et al. (1999, 2004) and SKB (2004).

Borehole	**Depth^1, m**	**Cl$^-$, mg/L**	**^{3}H, TU**	**^{14}C, pmC**	**δ^{18}O, ‰**	**δ^{2}H, ‰**
Olkiluoto						
OL-KR1	123.0		1	50.0		
OL-KR1	470.0	8800	2.1	52.8	-10.9	-75.8
OL-KR1	483.0		10	40.0		
OL-KR1	496.0	275	5.5	57.2	-10.9	-77.7
OL-KR1	605.0		10	40.0		
OL-KR2	400.0	16500				
OL-KR2	544.0	32000				
OL-KR3	342.0		10	20.0		
OL-KR3	602.0	3720	0.9	18.3	-12.4	-92.1
OL-KR5	151.0		17	40.0		
OL-KR9	630.0	11480	1.6	13.4	-11	-82.2
OL-KR10	160.0	5400	0.8	24.0		
KR1_T76_2	101	430	5.6	63.5	-11.10	-78.40
KR1_T612_2	615	14800	2.8	43.6	-10.70	-72.90
KR1_S754_2	878	22000	<8		-9.00	-70.30
KR2_T51_1	71	210	10.7		-10.80	-79.70
KR2_T91_1	121	1500	2.2		-11.90	-89.20
KR2_T196_1	214	3870	<0.8		-10.80	-80.90
KR2_T231_1	244	4600	<0.8	28.1	-9.20	-69.70
KR2_T281_1	293	4300	1.3		-11.10	-81.20
KR2_T305_1	328	4200	<0.8		-12.40	-90.80
KR3_T86_1	114	3420	0.9	45.8	-12.40	-92.10
KR3_T141_1	186	2800	<0.8		-12.10	-92.10
KR3_T231_1	246	2700	<0.8	10.5	-12.80	-94.90
KR3_243_1	248	2760	<0.8		-13.13	-96.90
KR3_T356_1	381	3400	<0.8		-12.10	-90.60
KR3_T416_1	439	3900	<0.8		-12.20	-91.50
KR3_438_1	441	2880	1.1		-12.30	-92.50
KR3_T461_1	482	5865	0.9	34.7	-11.70	-86.90
KR4_T107_1	120	1140	1.3	33.9	-10.00	-76.00
KR4_T132_2	162	4500	<0.8	22.9	-9.50	-72.40
KR4_860_1	863	43000	<0.8	3.0	-10.09	-49.75
KR5_T61_1	76	910	1.7	41.5	-10.70	-77.20
KR5_T106_1	124	3800	<0.8		-10.00	-74.00
KR5_T191_1	226	4300	1.1		-10.30	-77.30
KR5_T261_1	279	4000	1.2	27.9	-11.60	-89.10
KR5_T376_1	411	4700	0.8	59.7	-11.30	-84.40
KR5_446_6	502	9500	0.8		-11.80	-89.30
KR6_58_1	59	369	7.1	57.0	-10.50	-85.60
KR6_98_1	100	1000	5.7	49.6	-10.50	-85.30
KR6_135_1	136.0	2850	4.1	46.4	-10.79	-77.63
KR6_525_1_T01	526.5	12300	2.6		-11.27	-73.43
KR7_282_1	285.5	2630	1.6	33.9	-9.90	-75.50
KR8_302_1	306.0	4770	10.0	14.8	-9.60	-79.70
KR9_149_1_TVO	149.5	780	3.1	53.1	-10.95	-76.64
KR9_470_1	472.5	8030	0.9	40.6	-12.27	-84.50
KR9_563_1	567.0	11480	1.6		-11.00	-82.20
KR10_324_1	328.0	5400	<0.8		-11.70	-89.30
KR10_498_1	500.5	13500	<0.8		-11.81	-76.9
KR11_125_1_TVO	125.8	1850	2.4	50.8	-10.28	-74.79
KR11_952_1	954.9	41300				

Borehole	Depth[1], m	Cl^-, mg/L	^3H, TU	^{14}C, pmC	$\delta^{18}O$, ‰	δ^2H, ‰
KR12_65_1_T01	66.0	1160	1.1	43.9	-11.78	-85.37
KR12_365_1_T01	366.5	5100	2.6	29.4	-12.34	-87.14
KR12_664_1	665.0	23800	0.6		-11.07	-67.20
KR12_736_1	738.3	29200	0.2		-10.75	-64.00
KR12_741_1_T00	746.0	30600	1.0		-10.86	-64.26
KR13_112_1_TVO	114.0	2450	1.1	32.7	-13.39	-96.90
KR13_214_1_TVO	217.0	3300	<0.8	31.4	-9.80	-75.70
KR13_362_1_TVO	363.5	4940	<0.8		-11.20	-83.50

[1] Average depth of sampled interval

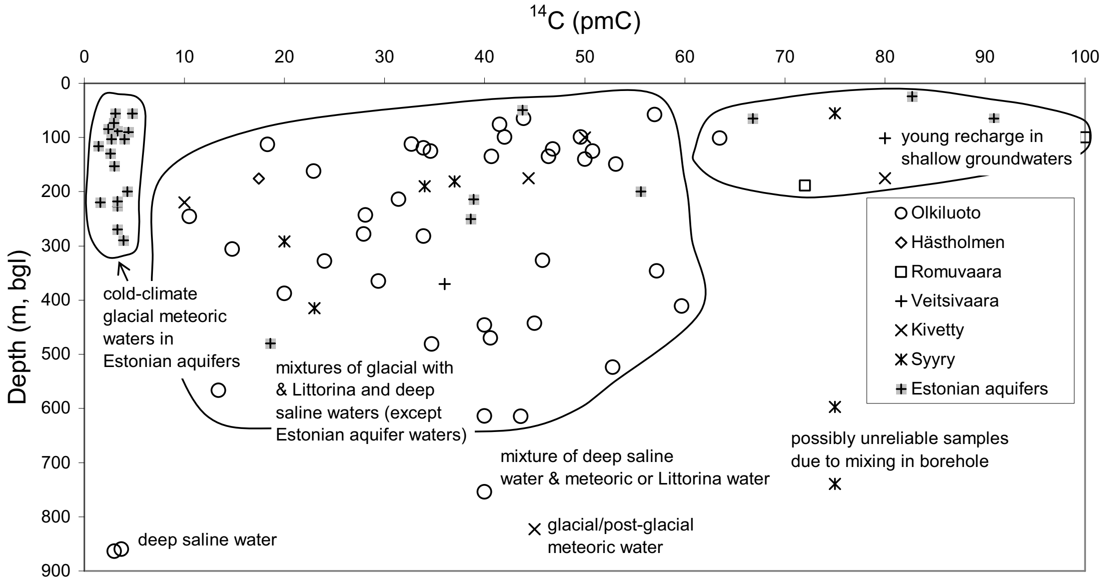

Figure A1. Carbon-14 versus depth for groundwaters from Finnish sites, plus data from Estonian multi-layered sedimentary rock aquifers (Vaikmäe et al., 2001).

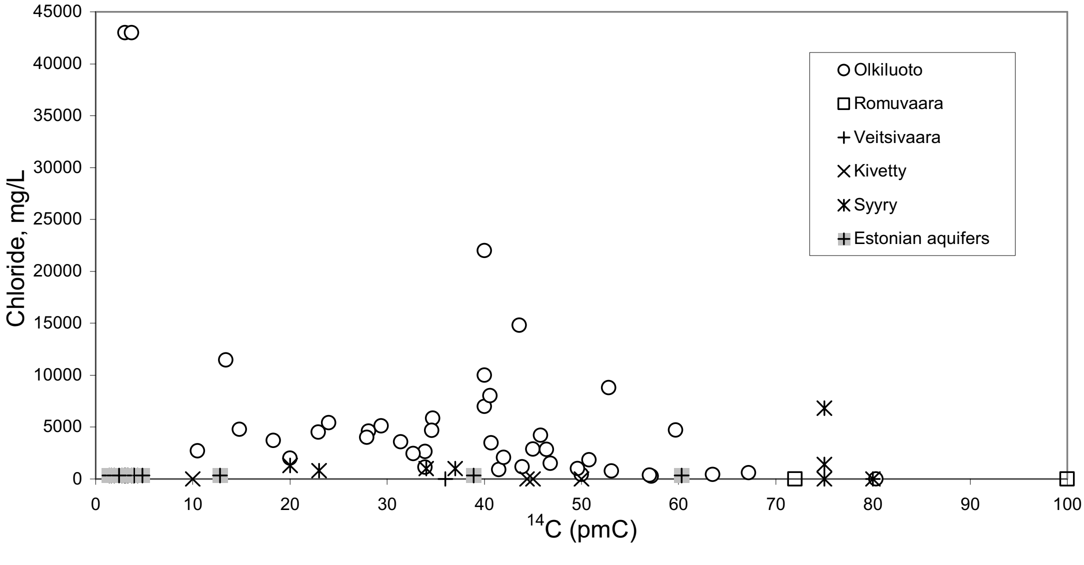

Figure A2. Carbon-14 versus chloride concentrations for groundwaters from Finnish sites, plus data from Estonian multi-layered sedimentary rock aquifers (Vaikmäe et al., 2001).

Of twenty samples of secondary fracture calcites sampled at Olkiluoto, only five samples indicated hydrologically-open crystallisation environments (Gehör et al., 2002). These calcites were subdivided into two types: (i) thin, filmy or scaly calcite that is observed on both surfaces of a possibly open fracture as small patches that are mostly less than a few cm^2 in area and 10-50 µm in thickness, and (ii) 100-500 µm layers of idiomorphic calcite crystals, occurring on earlier fracture minerals and sometimes directly on the host rock. The small quantities and occurrences with older calcites meant that it was not possible to obtain meaningful palaeohydrogeological information from them.

U-Th data from three distinct types of secondary calcite lining a deep fracture at Olkiluoto gave ages in the range of 117-285 ka (Blomqvist et al., 1993). Subsequent analyses of U and Th in acid leachates of late-stage fracture calcites found that ages grouped around 84-90 ka and 173-203 ka. This was tentatively correlated with the onset of permafrost and cessation of recharge at the start of glacial periods (McDermott et al., 1996).

δ^{18}O values of the youngest secondary calcites from Olkiluoto are in a narrow range from -11.2 to -9.1 ‰ PDB, whilst δ^{13}C values are more variable, between -10 and +12 ‰. The range of δ^{18}O is smaller than that for all types of fracture-filling calcite (-18 to -8 ‰; Blomqvist et al., 1993) and is in isotopic equilibrium with present-day groundwater. However δ^{13}C values are significantly higher than groundwater carbonate (about -20 ‰; Pitkänen et al., 1999), indicating that the calcites formed in different conditions.

A number of other locations in addition to Olkiluoto, both coastal and inland, were investigated by preliminary boreholes as parts of early reconnaissance and siting studies in Finland (Table A6). The coastal locations, i.e. within the highest shoreline of the Littorina Sea, were Hästholmen, Pori, Parainen, Liminka, Eura and Eurajoki. Coastal sites in Finland were found to have brackish groundwaters at 50-200 m depth that originate either from intrusion of modern Baltic water or from the Littorina Sea at its highest stand. Many of these brackish waters have ^{14}C contents suggesting apparent ages of 10,000-20,000 years (Lahermo and Lampén, 1985; Lampén and Snellman, 1993), though simplified interpretations for the age of the fresh water component in the mixed groundwaters are not valid.

Table A6. Selected parameters for groundwater samples from other Finnish sites. Data from Smellie et al. (1985), Lahermo and Lampén (1987), Nurmi et al. (1988), Lahermo et al. (1989), Blomqvist et al. (1988), Lampén and Snellman (1993), Ruotsalainen and Snellman (1996), SKB (2004).

Borehole	Depth[1], m	Cl$^-$, mg/L	^{3}H, TU	^{14}C, pmC	δ^{18}O, ‰	δ^2H, ‰
Hästholmen						
Y1	176			17.4	-8.6	
Y1	193	5040				
Y1		4759	<1.2			
Romuvaara						
RO-KA1	100	1	53	104		
RO-KA2	100	1	20	100		
RO-KR1	189	3	28	72		

Borehole	Depth[1], m	Cl^-, mg/L	^3H, TU	^{14}C, pmC	$\delta^{18}O$, ‰	δ^2H, ‰
2/T6	245	8.2	0.8		-12.9	-93.1
2/T5	283	1.7	1.7		-13	-94.9
2/T4	325	17.8	3.8		-12.9	-96
2/T3	360	24.1	5.4		-13.2	-94.9
2/T2	395	4.5	25.4		-13.1	-96.1
3/T6	155	0.74	8		-12.9	-96.5
3/T4	240	0.77	2		-13.1	-96.6
3/T1	458	109	1.4		-13	-99.6
4/T6	185	7.4/7.6	0.8/1.1		-13.3/-12.8	-94.2/-99.3
4/T5	275	3.3	17.6		-13.1	-99.4
4/T3	378	23	10.5		-13.2	-97.5
5/T7	150	0.75	24.5		-13.7	-100.7
5/T6	180	2	4.5		-13.1	-97.9
5/T4	318	29	2.3		-13	-97.4
5/T1	480	6	3.2		-13.4	-99.9
Veitsivaara						
VE-KR1	687	20	20-40			
VE-KR4	370	10	51	36		
VE-KA1	101	0.6	25	80		
VE-PR1	70	1				
Kivetty						
KI-KA1	100	1				
KI-KA2	100	1	<8	50		
KI-KR1	823	5.8	8	45		
KI-KR1	175	2	7	44.4		
KI-KR2	220	2	10	10		
KI-KR6B	175	2	38	80		
1/T6	322.5	3.5	0.8		-12.7	-95.3
1/T5	392.5	22.2	0.8		-13.7	-100
1/T4	535	2.05	0.8		-12.6	-90.4
1/T3	757.5	9.7	0.8		-13.2	-94.9
1/T2	835	4.5	0.8		-12.4	-93.2
2/T7	60	0.47	17		-12.7	-94.8
2/T6	115	0.54	1.8		-13.3	-96.2
2/T5	175	7.8	0.8		-13.6	-99.3
3/T7	107.5	1.21	13.5		-12.8	-93.9
3/T7	107.5	1.5	10.75		-12.8	-97.2
3/T6	160	0.88	8.5		-12.9	-96.4
3/T3	375	6.2	4.7		-13.6	-99.3
4/T7	110	1.09	0.8		-12.7	-93.3
4/T6	145	1.38	0.8		-12.8	-92.4
4/T3	285	1.14	0.8		-12.8	-95.8
4/T2	365	2.1	1.2		-13	-95
4/T1	465	1.4	4.6		-12.7	-96.5
5/T7	111	1.68	8.8		-12.8	-91.3
5/T6	235	3.53	2.4		-12.4	-92.2
5/T5	282.5	2.1	8.8		-13.1	-94.3
5/T4	325	13.8	8.1		-14.5	-108
5/T3	377.5	4.68	14		-13	-94.9
5/T2	435	4.3	11.8		-12.7	-94.4
5/T1	477.5	2.1	8.1		-12.6	-90.6
KR5	794	48	1.65		-13.9	-101.5
Syyry						
SY-KR1	739	6830	8	75		
SY-KR1	597	1400	7	75		

Borehole	Depth[1], m	Cl^-, mg/L	^3H, TU	^{14}C, pmC	$\delta^{18}O$, ‰	δ^2H, ‰
SY-KR2	415	800	8	23		
SY-KR6	190	1000	8	34		
SY-KR6	292	1300	37	20		
SY-KR6	181	1000	8	37		
SY-KA2	55	3.4	25	75		
Miihkali						
MIK-112	500					
MIK-113	500					
MIK-116	500	ca.25000				
MIK-116	1000	ca.100000				
Pori						
POR/600	600	1078	<2.3			
Eura						
EUR/232	232	3124	40			
Eurajoki						
EAJ/32	32	5390	24			
Kotalahti mine						
KOT/836	836	18000				
Outokumpu						
OKU-741	270	3	70.3		-13.9	-99
OKU-741	600	8100	12.1		-14.4	-102
OKU-741	770	8400	13.9		-14.3	-102
OKU-741	810	8900				
OKU-741	1010	16500	6.9		-13	-75
OKU-741	1070	16800	1.3		-13	-73
Kerimäki						
KER/140	140	16	4.4		-13.4	-94
KER/540	540	2400	19.3		-13.5	-94
KER/700	700	3200	14.1		-13.7	-95
Parainen						
PAR/280	280	70	53.3		-11.5	-79
PAR/410	410	410	45.4		-11.3	-76
PAR/490	490	3700	42.8		-9.8	-68
Liminka						
LIM/100	100	2700	8.2		-14.5	-106
LIM/400	400	7400	8.5		-12.7	-89
LIM/600	600	19200	15.2		-12.2	-84
LIM/720	720	22100	11.5		-12.1	-81

[1] Average depth of sampled interval

Inland sites were found to have fresh groundwater to 300-600 m depth, though penetration beyond 500m is reported in only a few cases. Below that there are brackish/saline groundwaters to drilled depths in most cases (Nurmi et al., 1988). The stable isotopic compositions of groundwaters at Kivetty and Romuvaara do not give clear indications of glacial melt waters being present. ^{14}C data from these groundwaters have a wide range from 60 to 10 pmC, indicating that water ages range from relatively young to more than 10,000 years (Figures A1 and A2). If glacial meltwater is absent or low relative to other sites, e.g. Olkiluoto, then that would be an interesting indication that some locations may have had permanently frozen ground through the glaciations that prevented meltwater infiltration, whereas others such as Olkiluoto had periods of wet-based glaciation during which infiltration of meltwater occurred.

The Palmottu research site is in an inland location, in an area previously associated with uranium mining, and is situated on a topographic high so the area is a groundwater recharge zone. Ca-HCO_3 water containing ^3H occurs over at least the upper 100 m, and penetrates to 200 m or more in some parts of the site (the 'dynamic deep flow system'). This is probably the best indication of how deep modern water can penetrate in this type of rock. Underlying brackish water has Na-SO_4 or Na-Cl compositions and has an age of up to 10,000 years (i.e. Holocene) estimated from ^{14}C (Blomqvist et al., 1997). The fresh and brackish/saline waters are regarded as distinct groundwater masses with the latter being more or less immobile. This degree of isolation and stabilisation of the deeper part of the groundwater system is associated with a sub-horizontal fracture zone which seems to act as a hydraulic boundary of the active upper part of the system. Relatively isotopically-light groundwaters have been attributed to meltwater intruded from the retreating ice sheet prior to the Yoldia Sea stage (ca. 10,000 years ago). This indicates that cold-climate isotope compositions are not necessarily indicative of sub-glacial high pressure/gradient recharge – they may originate simply from post-glacial surface water whose composition is dominated by melt water. Studies of U-bearing minerals and U contents of groundwaters in a vertical fault zone that extends to at least 400 m depth indicate that oxidising water with relatively high U contents occurs down to 130 m depth, below which reducing conditions occur.

Additional data for deep groundwaters in Finnish Shield rocks come from mineral exploration boreholes. The most noteworthy data are for deep groundwaters in mineral exploration boreholes at Miihkali. These had variable compositions in quite close proximity supporting the concept of compartmentalisation (Lahermo et al., 1986). A brine with about 100 g/L Cl^- was reported from 1000 m depth in Borehole MIK-116: this is the highest salinity reported from groundwaters in the Fennoscandian Shield.

In addition to previous mineral exploration drilling in the area, a deep borehole for research purposes has recently been drilled at Outokumpu and had reached 2187 m depth by mid-December 2004 (Geological Survey of Finland, 2005). It was predicted that saline Ca-Na-Cl groundwaters, up to 27 g/L TDS, would be encountered below about 400 m, and this has been confirmed by samples collected at about 1000 m (although samples from about 500 m were too contaminated to be useful and were not obtainable from 1500 and 2000 m because of lack of flow zones). Groundwater at 1000 m is also reported to have a 'high' content of dissolved methane.

Appendix 3. Other Fractured Rock Groundwater Systems

A3.1 Whiteshell URL and other Canadian Shield areas

Active groundwater flows with <1000 mg/L TDS are believed to be ubiquitous at depths between 0 and 200 m throughout the Canadian Shield. In general, groundwater salinity is thought to correlate inversely with rock permeability. The proposed conceptual model is of water composition above 300 m depth being controlled by advective transport and mixing, and diffusion being the dominant mechanism below that (Gascoyne et al., 1987). The argument for control by diffusion is based on a common trend of salinity versus depth seen at various sites not perturbed by mining across the Canadian Shield (Figure 5 in Gascoyne et al., 1987). Occasional departures from this pattern are found at identifiable discharge zones (e.g. saline ground or 'moose licks') or as fresh water at anomalously great depth e.g. 800 m at Atikokan). These are significant because they exemplify the possibility for saline waters to flow to the surface locally with a relatively undiluted composition, suggesting that there are localised fracture connectivity may provide sufficient transmissivity to allow mass transfer of water over large distances when the hydraulic gradient is perturbed. The possibility of flows that are transients due to relict gradients caused by long-term geological movements, e.g. crustal rebound from glaciation, are not excluded but otherwise a steady state stable groundwater system is implied by the observations.

At greater depths in the Shield, down to ~2000 m, it has been suggested that lateral homogenisation of concentrated Ca-Na-Cl brines (>250 g/L TDS) has been facilitated by horizontal transmissive fracture zones. The fact that they have not been diluted has been suggested as evidence that these deep systems are not hydrogeologically continuous with shallower groundwaters, and have been stable for a very long time (Frape and Fritz, 1987). However a fairly linear increase of TDS versus depth suggests that mixing does occur and that there may not be a distinct 'barrier' between shallow and deep systems. The diffusive model suggested by Gascoyne (see above) seems to be a better match to the hydrochemical evidence.

Table A7. Selected parameters for groundwater samples from Whiteshell and other sites in the Canadian Shield. Data from Gascoyne (2004).

Borehole/test	Depth, m	Cl^-, mg/L	^{3}H, TU	^{14}C, pmC	δ^{18}O, ‰	δ^{2}H, ‰
Boreholes at URL area						
B34-2-3	40	595	1.1	20.9	-18.4	-138
B37-1-3	22	2.2	11.9		-13.0	-93
B37-2-3	45	10.1	<0.8		-13.5	-101
B43-2-3	123	7.9	32.0		-13.2	-107
M1A-3-7	265	207	<0.8	9.1	-16.6	-120
M1B-2-3	75	1.9	10.0	32.2	-13.1	-100
M2A-3-4	310	20.0	2.5	*13.7*	-13.6	-104
M2B-2-5	150	3.6	10.0	28.0	-13.3	-101
M3A-3-4	375	3006	<0.8		-17.5	-127
M3B-2-1	120	6.6	37.0		-11.8	-93
M4A-1-15	180	28.0	21.0		-12.9	-102
M4A-2-2	215	45.7	37.0		-13.4	-107
M4A-3-7	260	64.7	<8.0		-13.8	-108
M4A-4-6	310	652	<0.8	*5.9*	-18.5	-136
M5A-3	165	281	<8.0		-18.3	-142
M5A-IN8	340	3980	<8.0	20.0	-17.4	-126
M5B-IN9	120	29.8	*19.0*	*61.7*	-15.2	-115
M6-2-5	110	1.6	10.7	36.5	-13.5	-98
M7-72-DH	72	207	<8		-13.6	-98
M7-4-11	390	8600	1.8		-15.5	-112
M8-3-7	360	21.2	7.4	*9.4*	-14.1	-109
M9-3-3	230	6.0	20		-13.7	-101

Borehole/test	**Depth, m**	**Cl^-, mg/L**	**^3H, TU**	**^{14}C, pmC**	**$\delta^{18}O$, ‰**	**δ^2H, ‰**
M10-1-7	50	35.8	9.5		-14.5	-105
M10-3-2	410	3020	1.6	*10.6*	-18.1	-137
M11-2-12	140	2.4	7.0		-13.3	-109
M11-3-4	290	590	8.8		-18.5	-141
M12-93-DH	93	5.5	*<8*		*-14.2*	*-114*
M12-159-18DH	159	6.7	18.0	*48.0*	-13.4	-105
M12-171-15DH	171	24.0	15.0	16.0	-13.9	-113
M13-2-5	250	1240	<0.8		-19.7	-149
M14-1-4	50	19.5	1.3		-13.8	-104
M14-2-13	105	86.8	32.0		-14.5	-112
M14-4-4	370	5800	<0.8		-17.4	*-124*
Boreholes at URL						
URL1-4-24	110	11.1	3.0		-12.0	-93
URL2-11-2	780	13096			-12.5	-153
URL3-5-1	120	96.6	3.0		-13.2	-104
URL3-6-9	140	11.7	3.8	19.5	-13.9	-109
URL4-5-10	65	1.0	22.7	57.1	-13.5	-102
URL5-4-43	100	84	<8		-14.5	-111
URL6-25	270	336	92.0		-15.2	-116
URL7-24	60	1.1	33.0		-13.2	-98
URL8-7-6	230	31.0	*<8*	*9.1*	*-14.4*	*-108*
URL10-3-2	80	1.5	*18.3*	*44.0*	-14.1	-109
URL10-6-7	250	155.0	3.5		-16.0	-118
URL11-3-1	45	5.1	51.0		-13.2	-107
URL11-7-7	135	4.3	23.0	48.6	-13.8	-101
URL12-10-19	390	1246	<0.8	*9.2*	-17.5	-128
URL12-11-13	430	96	21.5	*45.3*	-13.3	-103
URL12-13-21	605	2454	14.2		-15.4	*-114*
URL14-8	280	3389	<0.8		-16.6	-121
URL15-1-4	125	191	<6.0	80.2	-13.6	-105
URL16-4-1	85	17.7	20.5		-11.2	-93
Boreholes in other areas at Whiteshell						
WA1-1-3	150	6.9	19.0		-12.0	-99
WA1-2-8	240	1.9	11.1	53.6	-11.3	-95
WA1-3-8	320	10.8	11.1		-13.8	-105
WA1-5-7	630	3800	1.3		-19.0	-140
WB1-1-5	130	56.8	17.3	64.3	-12.4	-95
WB1-2-6	230	300	10.8	67.4	-13.5	-105
WB1-4-SW10	540	9797	13.3		-11.3	-89
WB1-5-21	630	10780	7.3		-14.1	-105
WB1-7-7	1000	30200	2.1		-13.0	-94
WB2-20-12	725	27900	<0.8		-15.4	-102
WD1-110-2	100	2.8	16	40.5	-13.8	-107
WD2-72-5	65	1.6	10.2		-13.5	-103
WD3-895-10	810	11390	5.2		-15.6	-113
WG2-2-8	130	3.3	9.0	32.7	-13.0	-100
WN1-8-17	380	3480	2.6	53.7	-16.2	-117
WN3-90	90	119	<8	47.6	-16.2	-122
WN4-6-8	370	3880	59.0		-16.5	-121
WN4-13-20	650	11091	<0.8		-16.0	-117
WN8-T4	315	2581	1.6	26.2	-16.8	-125
WN10-3-4	245	1350	<0.8		-17.9	-132
WN10-4-3	320	2909	2.3		-18.1	-131
WN11-17-15	1000	18944	3.0		-14.1	-109

Salinity increases with depth or along inferred flow paths at the Whiteshell research area and URL site in the Lac du Bonnet batholith (Table A7; Gascoyne, 1994; Gascoyne and Kamineni, 1994; Gascoyne, 2004). Recharge zones in areas with relatively high topography have dilute (<400 mg/L TDS) groundwaters containing positive ^{3}H and high ^{14}C contents to ~200 m depth (Figures A3 and A4). This is an indication of the depth to which topographically-driven flow circulates relatively effectively in this region. ^{3}H contents decrease to <1 TU at more than 200 m depth and stable isotope composition at 200-400 m depth under recharge areas indicates a glacial meltwater component. Salinity increases heterogeneously below 400 m and groundwaters are mostly saline below 500-600 m.

Discharge zones in areas with relatively low topography were found to have saline waters (>2 g/L TDS) below 50 m depth. This indicates that upflowing saline waters are diluted by dominant volumes of shallow fresh water. The stability of the hydrodynamic regime is therefore likely to be reflected by the variability of compositions over time, though no time series analyses are available. Groundwater compositions evolve from Ca-HCO_3 through Na-(Ca)-HCO_3 to Na-Ca-Cl-SO_4 types with increasing depth and increasing salinity (up to 5-50 g/L TDS). Some deep brackish waters were found to have relatively low δ^{18}O values (up to 7 ‰ lower) at depths between 50-400 m depending on the recharge/discharge flow direction (Figure A5). However deeper saline waters do not have these low δ^{18}O values, indicating that cold climate recharge penetrated only to the intermediate depths. This interpretation is supported by ^{14}C values as low as 3 pmC which were measured on samples from brackish groundwaters at 270 m depth (Figure A4).

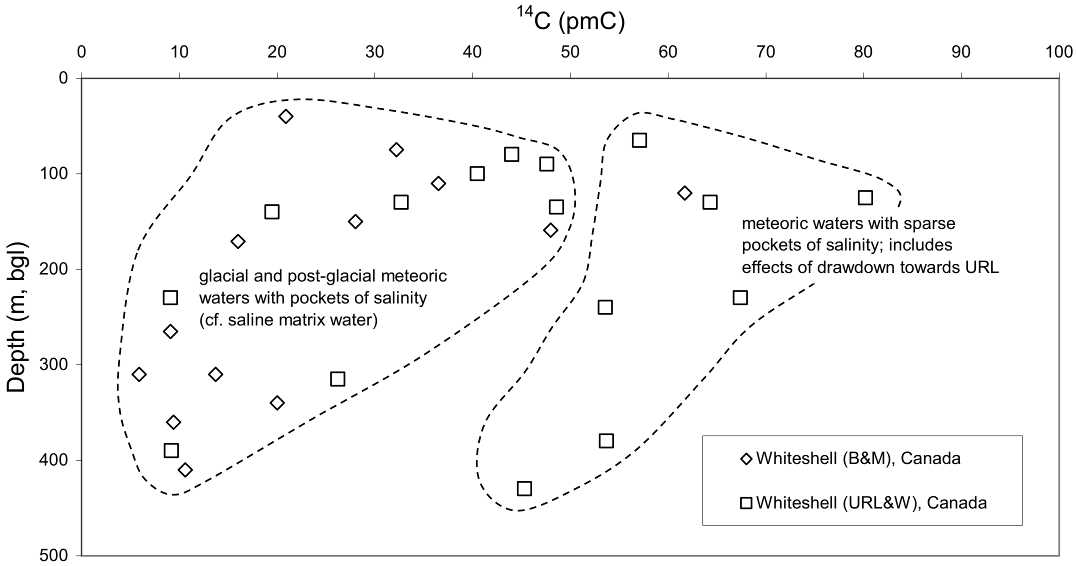

Figure A3. Carbon-14 versus sample depth for groundwaters from the Whiteshell area, Canada. B&M and URL&W refer to samples from different sets of boreholes.

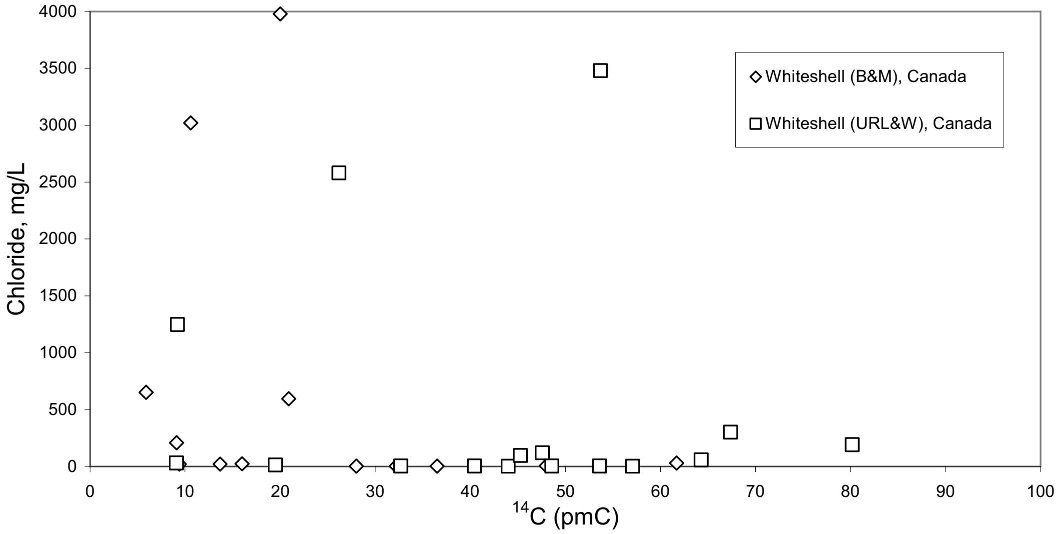

Figure A4. Carbon-14 versus chloride concentrations for groundwaters from the Whiteshell area, Canada. B&M and URL&W refer to samples from different sets of boreholes.

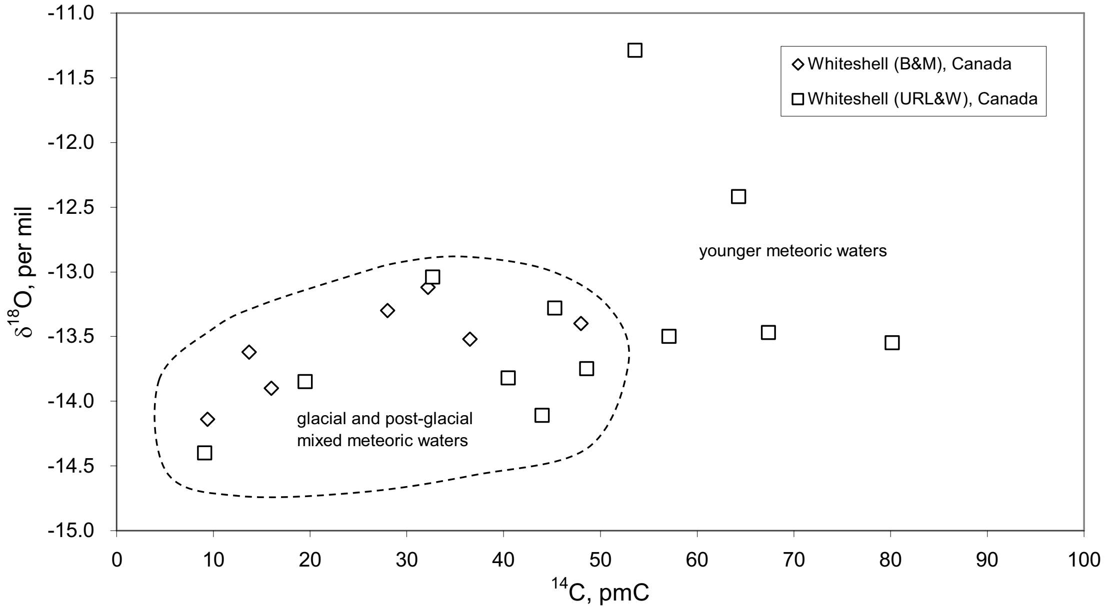

Figure A5. Carbon-14 versus stable oxygen isotope ratio for groundwaters from the Whiteshell area, Canada. B&M and URL&W refer to samples from different sets of boreholes.

In situ experiments to recover samples of matrix pore waters have been carried out in the URL (Gascoyne, 2004). Matrix water samples had higher salinities (up to 90 g/L TDS) than in fracture waters at the same depth (~50 g/L), and also have distinct stable isotope compositions. This implies that the fracture waters have been slightly diluted by ingress of water that occurred within the timescale required for the two types of water to re-equilibrate and homogenise by diffusion.

Several studies of deep groundwaters in deep mines in the Canadian Shield describe the hydrodynamic and geochemical environments resulting from drawdown to mine galleries. In these locations, vertical fracture zones at >1000 m depth have been found to contain fresh/brackish waters whose salinity decreases with time, whilst ^{3}H contents increase (Frape et al., 1984). ^{3}H values greater than 20 TU have been found even at >1000 m depth (Frape and Fritz, 1987; Fritz and Frape, 1982). These fracture zones are believed to connect fairly directly with the surface environment, and are thus pathways for the groundwater system to respond to the imposed hydraulic drawdown and instability.

In one such study at the Con Mine in Yellowknife, Cl^- increases overall to 194 g/L in a log-linear trend with depth, although there is local heterogeneity between individual fault sets (Clark et al., 1999; Clark et al., 2000). ^{3}H was detectable at all depths but was lowest at the greatest sampled depth of 1615 m. The inferred magnitude of isotopic depletion of cold climate recharge at Con Mine was about –10 ‰ δ^{18}O. The conceptual model proposed is that melt water would have been injected into the groundwater system at the end of the last ice age, as the retreating ice sheet passed over the site. A numerical model of this system indicated that the observed depth-trend of salinity could be simulated with a transient top boundary condition of 500 m head of melt water persisting over a relatively brief period, perhaps as short as 50 years, (Clark et al., 2000; Douglas et al., 2000). The preservation of an isotopically-light meltwater in the system indicates that the gradients and dispersive mixing have been consistently low, i.e. stable, since that time.

At the East Bull Lake pluton site, similar trends were found (Bottomley et al., 1986). Salinity increases to 3 g/L TDS below 300 m depth and δ^{18}O values decrease (-17 ‰ to -12 ‰) at depths as shallow as <100 m. ^{14}C values are from 7 to 75 pmC (δ^{13}C from -23 to -12 ‰). However a value of 42 pmC was reported for a sample of isotopically-light water, suggesting an age of a few thousand years at most and thus implying a younger source for cold-climate recharge in this location, but a more probable explanation is that the ^{14}C content is due to contamination.

A3.2 Sellafield, UK

Boreholes were drilled at Sellafield on the Irish Sea coast of northwest England to investigate groundwater conditions in the fractured basement rock, the Borrowdale Volcanic Group (BVG), which was being investigated as a potential host for a nuclear waste repository until the project was stopped in 1997. Sedimentary rocks, mainly sandstones of the Triassic Sherwood Sandstone Group (SSG), cover the basement over most of the area and are about 500 m thick in the centre of the area. Within the investigated area, the top surface of the basement dips from outcrop in the north-eastern part at 160 m above sea level to more than 1750 m below sea level at the southwestern corner.

The regional hydraulic gradient is generally directed westwards through the area, from the high ground of inland hills towards the coast. The hydrogeological conceptual model has three main groundwater flow regimes: (a) a Coastal Plain regime, in which groundwater flow in the shallow aquifer is topographically driven and groundwater is fresh water derived from precipitation, (b) an Irish Sea Basin regime, in which very slow movement of dense basinal brines is controlled by processes operating in the offshore sedimentary basin, and (c) a Hills and Basement regime, in which groundwaters in fractured basement rocks are mixtures of fresh water with deeper saline waters, and in which groundwater flow is largely topographically driven with the possibility of density variations being significant at depth.

Ice sheets covered this part of north-west England for about 100 of the last 700 ka and permafrost affected the ground for another 200 ka of that period. The most recent glacial stage lasted about 100 ka and ended at about 14 ka ago, during which an ice sheet advanced to cover the East Irish Sea Basin and Lake District massif.

The hydrodynamic stability issues that were pertinent to investigations at this site were: (i) To what extent is the perturbation due to glaciation and potential melt water intrusion detectable by geochemical and isotopic data in deep groundwaters, and (ii) What do geochemical indicators show with respect to stability in the system due to the stratification and compartmentalization of water masses with different origins, salinities and densities?

Water samples were collected by pumping from discrete intervals, 163 tests in all, in nineteen deep boreholes to a maximum depth of 1950 m. Data (Cl^-, ^3H, ^{14}C, $^{18}O/^{16}O$ and $^2H/^1H$) from samples which achieved <5 % contamination are shown in Table A8. Other data that provide information about past groundwater movements and stability include noble gas recharge temperatures (NGTs), ^{36}Cl and ^4He and are reported in Nirex (1997). Overall uncertainties in estimating *in situ* values for ^3H, ^{14}C and $\delta^{13}C$ are dominated by the impacts of contamination by drilling fluids. The inorganic carbon system and specifically $^{13}C/^{12}C$ and ^{14}C were affected non-linearly by the drilling water additives. In a few cases of very low contamination, upper limits on ^{14}C have been inferred that provide minimum model ages.

Table A8. Selected parameters for groundwater samples from Sellafield, northwest England. Data from Bath et al. (2005).

Borehole/test	**Depth[1], m**	**Cl^-, mg/L**	**^3H, TU¶**	**^{14}C, pmC¶**	**$\delta^{18}O$, ‰**	**δ^2H, ‰**
Sedimentary rock formations						
2/DET1A	206.42	12	3.5	46	-6.1	-36.4
2/DET2	314.92	25.2	2.9	25	-6	-34.4
2/DET3	356.92	10			-6.1	-36.2
3/DET4	689.05	64200	0.97	32.5	-6.3	-44.2
3/DET3	772.33	65800			-6.3	-43.4
3/DET1	1105.58	108000	1.83	15	-5.1	-32
10A/DET3	467.22	98.6	0.193	6.18	-6.69	-44.5
10A/DET2	595.99	291	0.06	2.49	-7.2	-47.7
10A/DET1	667.00	1900	0.076	2.2	-7.48	-49.9
11A/DET4	764.03	9451	0.113	6.36	-7.62	-46.8
12A/PCDET1	571.62	176	0.107	11.97	-6.47	-40.8
PRZ2/DET4*	369.00	43.3	0.11	14.05	-6.25	-36.1
PRZ2/CDET2*	369.08	44.3			-6.25	-39.4
RCF3/DET1	387.28	22.3	0.11	20.72	-6.08	-36.9
7A/PCDET2	550.23	17900	0.42	6.2	-7.42	-47

Borehole/test	**Depth^1, m**	**Cl$^-$, mg/L**	**^{3}H, TU¶**	**^{14}C, pmC¶**	**δ^{18}O, ‰**	**δ^{2}H, ‰**
10A/DET4	746.39	20300	0.247	2.03	-7.66	-48.5
10A/DET6*	932.08	31700	0.14	8.55	-7.54	-47.4
10A/DET5*	960.65	37300	0.11	1.46	-7.15	-48
11A/PCDET3	875.42	10800	0.163	62.1	-7.88	-50.8
12A/PCDET4	864.67	28100	0.06	61.3	-7.38	-46.4
13A/DET3	1458.76	82600	0.06	4.62	-6.02	-31.3
PRZ2DET1A*	395.87	956	0.11	7.13	-6.48	-40.3
PRZ3/DET3A*	476.49	1950	0.06	6.66	-6.78	-42.8
PRZ3/DET5	526.26	10200				
RCF1/DET2	437.26	10200			-7.3	-45.3
Fractured metavolcanics basement formation						
2/DET10	542.82	13000			-7.6	-41.7
2/DET9	710.61	12600			-7.5	-41.2
2/PDDET7*	935.23	15800			-7.87	-54.4
2/PDDET2*	1011.71	16700			-7.98	-54.6
2/DET8	1012.39	15700			-7.5	-43.6
2/PDDET6B	1199.75	15200			-7.85	-54.9
2/PDDET5	1441.28	15100			-7.66	-52.4
2/PDDET1	1585.20	17200	0.07	10.6	-7.86	-55.2
2/DET7	1585.80	17400	0.8	11	-7.7	-45.9
3/DET7	1668.33	104000			-5.9	-32.1
4/DET3B	415.87	1140	0.44	9.2	-6.5	-44.7
4/DET2	578.60	12300	0.7	22.2	-7.6	-49.7
4/DET1	801.82	13600	0.42	13.9	-7.6	-50.5
7A/PCDET1	880.33	40000	0.06	30.2	-7	-38.6
8A/DET1	953.16	10000			-7.09	-46.8
9A/DET2	104.40	1780			-6.58	-40.3
9A/DET6B*	347.13	3330			-6.98	-43.7
9A/DET5B	452.36	11500	0.11	8.44	-7.57	-44.9
9A/DET4	485.58	11400	0.115	7.4	-7.51	-45.4
9B/SPFT4*	75.21	916	0.11	9.8	-6.27	-43
10A/PCDET1	1069.38	48910			-6.77	-32.8
10A/PCDET2	1134.46	50792	0.06	37.2	-6.86	-36.6
10A/PCDET4	1240.60	58229	2.74	36.6		
10A/PCDET3	1594.15	77600	17.6	25.1	-6.28	-35.5
11A/PCDET2	989.86	12200	0.06	18.41	-7.94	-47.9
11A/PCDET1	1067.18	12300	0.078	46.9	-8.06	-47.9
12A/PCDET7	1002.40	39400	0.339	23.74	-7.42	-44.1
12A/PCDET6	1108.26	40800	0.073	68.17	-7.1	-46.1
PRZ2/CDET1A	493.48	12400				
PRZ2/DET2	493.48	12400			-7.5	-47
RCF2/DET2	789.17	14200			-7.88	-48.1

[1] Average depth of sampled interval

* Denotes test with adverse test-specific comments

¶ ^{3}H and ^{14}C data have large uncertainties because of contamination by drilling water which contained an organic additive and was made alkaline with NaOH, causing non-linear effects on ^{14}C, ^{13}C/^{12}C, pH and HCO_3^-.

The variations of salinity across the Sellafield area are illustrated in Figure A6. Groundwater compositions vary from fresh to brackish waters in relatively shallow (mostly down to at least 300 m depth) groundwaters in the sedimentary aquifer strata of the Coastal Plain regime, to saline waters in the Hills and Basement regime at the eastern part of the area (and also in fairly shallow outcropping basement at the eastern edge of the area), to brines in the deep sedimentary and underlying basement formations of the Irish Sea Basin regime at the western edge of the area where the thickness of sedimentary strata increases westwards under the coast into the East Irish Sea Basin. Note also that the greatest depth of fresh-brackish groundwaters was found to the west of the centre of the area, in borehole 10A, east of where the thickening aquifer formation begins to acquire saline waters from the Basin regime.

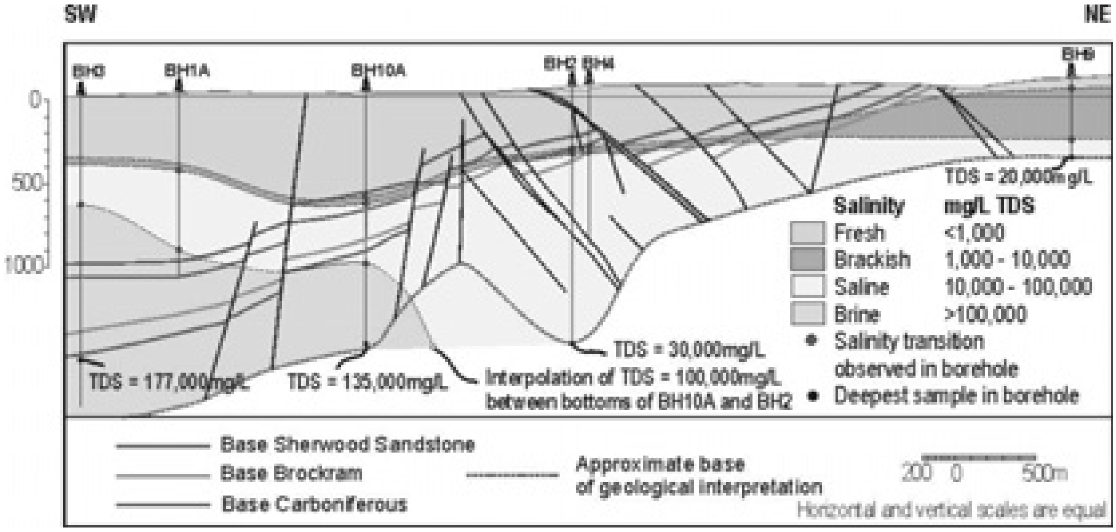

Figure A6. NE-SW section through the Sellafield area, showing some of the deep boreholes and contours of groundwater salinity (as mg/L TDS) superimposed onto lines showing the boundaries of the main sedimentary ands basement formations.

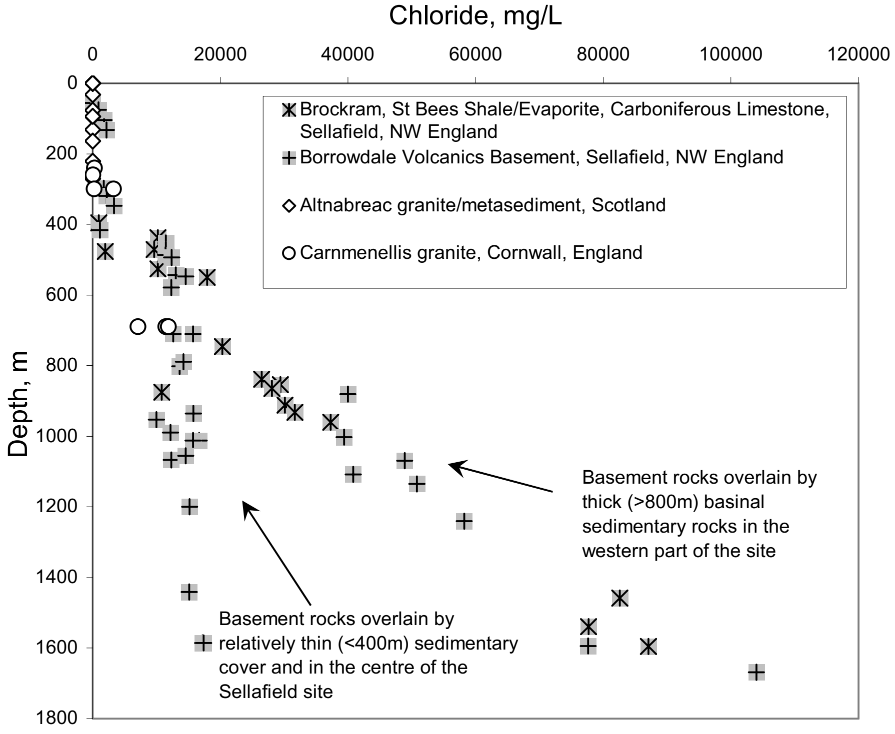

Figure A7. Chloride concentrations versus sample depth for groundwaters sampled in deep boreholes at Sellafield, northwest England and also data from investigations of crystalline rocks in Scotland and southwest England (Kay and Bath, 1982 and Edmunds et al., 1987).

The general salinity gradient with depth in the BVG basement rocks in the eastern part of the Sellafield area is compared with the salinity gradient in the deep sedimentary formations at comparable depths in western parts of the same area in Figure A7. Data from two other areas of outcropping basement crystalline rocks, in southwest England and northern Scotland are also shown, though the maximum depths of investigation are much smaller. The salinity versus depth gradients in basement rocks with relatively thin sedimentary cover (or no cover in some cases) are lower than those in the deep sedimentary and basement formations at Sellafield (there are similar salinity gradients in other basinal sedimentary sequences in Britain).

Salinity in the sedimentary sequences originates from the dissolution of evaporite minerals (mainly halite) and the high salinity gradient as shown in Figure A7 reflects an equilibrium between the maintenance of high salinities at great depth due to dissolution of halite, upwards mixing of saline water by advective and diffusive mixing, and flushing of saline water by natural groundwater circulation. Therefore the regularity of the salinity gradient is an indication of, amongst other factors, the stability of the large scale regional hydrodynamic conditions. Integrated interpretation of geochemical indicators of stability, of water ages and of solute residence times suggests that brines in the basinal sedimentary sequence at Sellafield are probably between 2 and 10 million years old and that movements of both sub-sea brine and onshore saline groundwater are focused towards the mixing zone (shown at the left side of Figure A6) and then flow upwards to discharge.

Salinity in basement rocks at Sellafield may originate partly from downwards movement of dense brines from sedimentary strata where these strata are overlying the basement formations, or have overlain them in the past, prior to uplift and erosion. Some salinity in British basement rocks may also derive from relict traces of ancient hydrothermal and metamorphic fluids and/or water-rock reactions, as is the case in Shield crystalline rocks in Fennoscandia and Canada. The lower salinity versus depth gradient in thinly-covered basement rocks at Sellafield, relative to that in the adjacent basinal sedimentary rocks and deeply covered basement, is related to a faster rate of water 'turnover' in the basement rocks to at least 1500 m depth in the centre of the area than in sedimentary rocks and basement at comparable depths in the western part of the area. The qualitative interpretation of salinity gradients in terms of relative long-term water movements or stabilities is supported by the stable isotope data (see below) which indicate cold-climate origins, i.e. Quaternary ages, for the basement saline groundwaters and older pre-Quaternary origins for water in the basinal brine. It is assumed, but not proven by drilling, that groundwater compositions in deep basement rocks underneath the two types of hydrogeological settings probably converge on a uniformly high salinity at a depth which is beyond transient palaeohydrogeological influences.

$^{18}O/^{16}O$ and $^{2}H/^{1}H$ show that all water types are of dominantly meteoric origins (Figure A8). The composition of present-day recharge is estimated to be between -6.7 and -6.0 ‰ $\delta^{18}O$. Fresh-brackish groundwaters in the sedimentary formation in the centre of the investigated area have stable isotopic compositions in that range and are thus post-glacial, i.e. recharged in the late Pleistocene or Holocene periods. Only where fresh-brackish groundwaters occur locally at >500 m depth down-gradient of the centre of the area and at >200 in the east up-gradient part of the area, do relatively light $^{18}O/^{16}O$ water compositions (-7.5 to -7.0 ‰ $\delta^{18}O$) indicate water that recharged in cold-climate conditions. Saline groundwaters in the basement formation also have relatively light isotopic compositions (-8.1 to -6.8 ‰ $\delta^{18}O$), indicating that they have a large component of cold-climate water mixed in with a saline water component. These interpretations of isotopic data are supported by noble gas concentrations which indicate average recharge temperatures of 4.8 °C for saline groundwaters, in contrast to around 9.0 °C for most fresh waters.

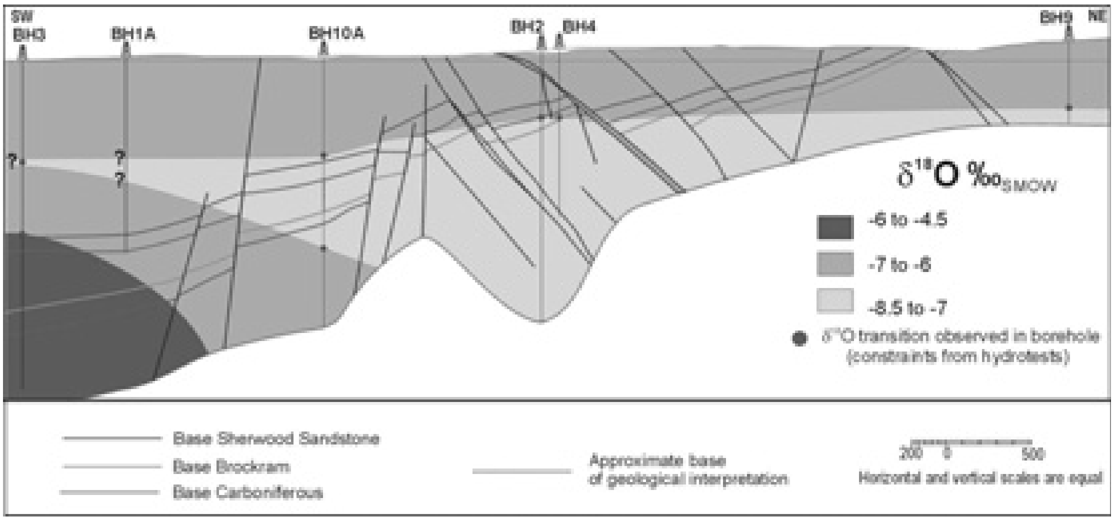

Figure A8. NE-SW section through the Sellafield area, showing contours of stable oxygen isotope compositions.

'Cold-climate water' is thought to contain a component of melt water from the ice sheet. It signifies that melt waters penetrated to these depths and replaced, either partially or fully, the pre-existing groundwaters. This would have happened during the several glacial periods in the Quaternary when the area was covered by ice, or in the periods of much shorter duration when the wet-based front of the ice sheet was over the Sellafield area. It is hypothesised that the penetration of melt water was promoted by abnormally high hydraulic gradients deriving from the head of the water column in the ice sheet. Therefore these indications of cold-climate water at depth in the present-day groundwater system may be the most compelling indication of a period of palaeohydrogeological instability. It is probable that pure melt waters would have had much lighter isotopic compositions than is seen in the present-day groundwaters, perhaps between -20 and -30 ‰ $\delta^{18}O$, so there has been substantial mixing of water from different sources, either at the time of melt-water intrusion and/or over the subsequent periods of 'normal' hydraulic conditions.

The uniform distribution of relatively light $^{18}O/^{16}O$ ratios in deep saline groundwaters in basement rocks in the eastern part of the Sellafield area indicates that pre-existing groundwaters were flushed out, to the depths investigated, during the Pleistocene period. $^{36}Cl/Cl$ ratios for these saline waters are at or close to secular equilibrium with the U and Th contents of the present host rocks indicating that, in contrast to the probable late-Pleistocene timing of water movement, chloride ion has resided in these basement rocks (or rocks with similar in situ neutron flux) for at least 1.5 million years. The contrasting residence times of water and chloride indicate that meteoric water became saline after recharge, probably by mixing with relatively minor proportions of ancient saline groundwaters or brines that have been preserved at depth in the basement. Water movements in the basement rocks have been sufficient to produce the fairly uniform salinity now seen down to at least 1700 m depth in the centre of the area, but were also low enough not to flush completely the deep source of salinity. Thus the deep groundwater and solute system has an inherent stability relative to shallow groundwaters.

The basinal brine has a range of stable isotopic compositions that is heavier, -6.3 to -5.1 ‰ $\delta^{18}O$, than the other groundwater types and is on the meteoric water line. Therefore water in the basinal brines had a meteoric origin prior to salinization by dissolution of halite. The relatively heavier isotopic compositions suggest recharge in warmer climatic conditions which is supported by noble gas temperatures which have an average of 12.0 °C.

$^{36}Cl/Cl$ ratios in saline waters and brines across the brine-saline water interface in the western part of the area are not in secular equilibrium with the host sedimentary host formations. This suggests that Quaternary water is mixing with pre-existing Tertiary brines in this interface between water masses with different salinities in the western part of the area. The variation of $^{36}Cl/Cl$ with respect to Cl is close to linear, indicating that brine and saline groundwater have moved between the different formations and mixed within the last 1.5 million years. Thus the brine is not truly 'stagnant' within that timescale but has been moving continually along a very small hydraulic gradient induced by mixing and upwards flow in the brine-saline water interface.

Although a few samples from deeper fresh-brackish groundwaters in the centre of the area were obtained with low levels of contamination (Figure A9), there is still poor knowledge of in situ ^{14}C contents and $\delta^{13}C$ values because of large uncertainties due to drilling fluid contamination. Thus calculated model ^{14}C ages are always minimum ages and are between 0 and 30 ka. These very uncertain interpreted age ranges add little if anything to the water ages that are inferred from the inferred correlation between $^{18}O/^{16}O$ data and palaeoclimatic episodes.

The depths to which 'modern' groundwaters, i.e. recharged within the last 50 years, have penetrated in the shallow fresh-brackish groundwaters are uncertain because high levels of sample contamination by drilling fluid raised the threshold for reliable detection of in situ tritium (^{3}H). Most of the less contaminated samples from underlying saline groundwaters which were analysed for ^{3}H gave contamination-corrected values which are zero within the uncertainty range.

Detailed morphological observations by SEM have shown that the crystal morphology of the recently-formed secondary calcite in fractures in Sellafield rocks varies systematically in relation to the salinity of present-day groundwaters (Milodowski et al., 1995; 1997; 1998; Nirex, 1997c; Bath et al., 2000). The calcite morphology varies progressively from 'c-axis flattened' forms at shallow levels in the freshwater zone, through intermediate crystal forms, to 'c-axis elongated' at deeper levels, as the salinity increases from fresh to brackish (from about ≥0.3 g/L to 2 - 3 g/L Cl^-) (Figure A10). The c-axis flattened calcite has a flattened stubby or equant shape when seen under the scanning electron microscope, whilst the c-axis elongated calcite has a more prismatic shape (Figure A10). Changes in the morphologies of successive growth zones in late calcite from Sellafield generally suggest that salinity of groundwater at intermediate depths (ca. 300 m depth in the centre of the area) decreased at some time in the past (Bath et al., 2000). Conversely, the absence of c-axis flattened calcite from the present saline groundwater zones suggests that fresh water has not previously flushed the deeper zones where groundwater is presently saline (assuming that calcite has been preserved throughout the period of interest).

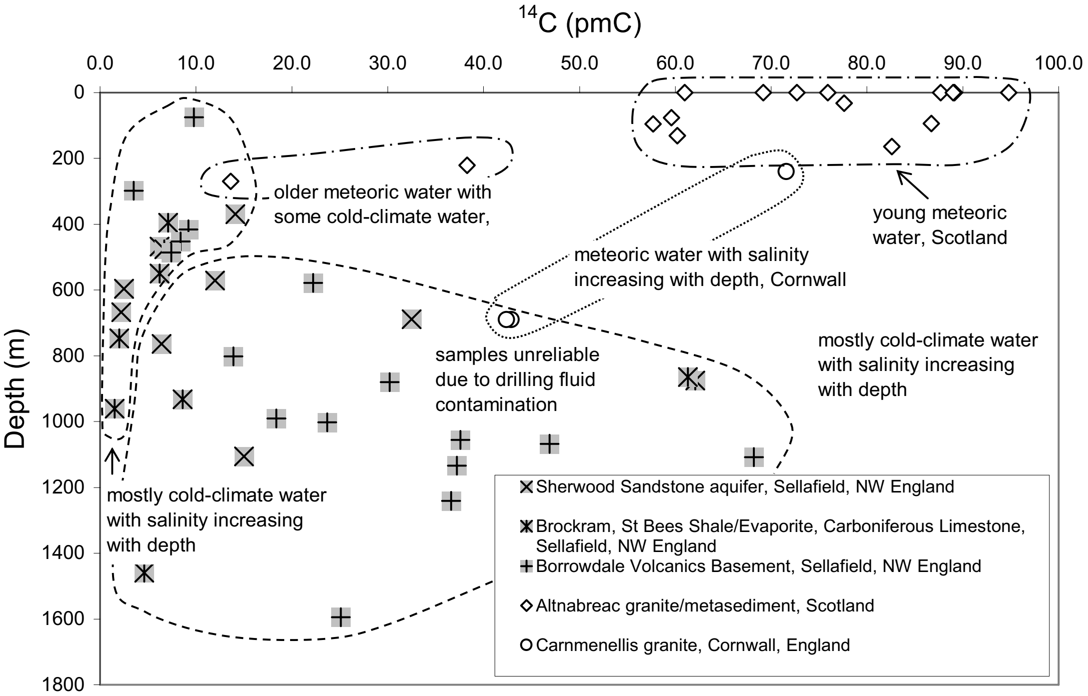

Figure A9. Carbon-14 versus sample depth for groundwaters sampled in deep boreholes at Sellafield, northwest England and also data from investigations of crystalline rocks in Scotland and southwest England (Kay and Bath, 1982 and Edmunds et al., 1987).

When seen by cathodoluminescence microscopy, c-axis elongated calcites from Sellafield were found to have well-developed concentric growth zoning, correlated between calcites in different boreholes and over substantial depth intervals (Bath et al., 2000). This suggests that they relate to broad patterns of groundwater compositional variation rather than to local fracture features. Analyses across the zoning showed varying Mn- and Fe-contents that have been interpreted to indicate fluctuating redox conditions.

Fluid inclusions in late-stage calcite from Sellafield were found to be monophase aqueous inclusions, i.e. probably formed below 80°C (Bath et al., 2000). Estimates of salinity from ice melting temperatures (T_{ice}) were between 3 and 120 g/L TDS, similar to the range of present-day groundwaters in the area (<0.2 to 135 g/L TDS). Higher salinities (up to 250 g/L TDS) were occasionally found in late-stage calcites from boreholes in the southwest part of the area and are significantly higher than present-day co-existing groundwaters. For example, fluid inclusion salinities above 50 g/L TDS were measured where present groundwaters are about 25 g/L TDS, indicating that groundwaters in these locations were more saline in the past.

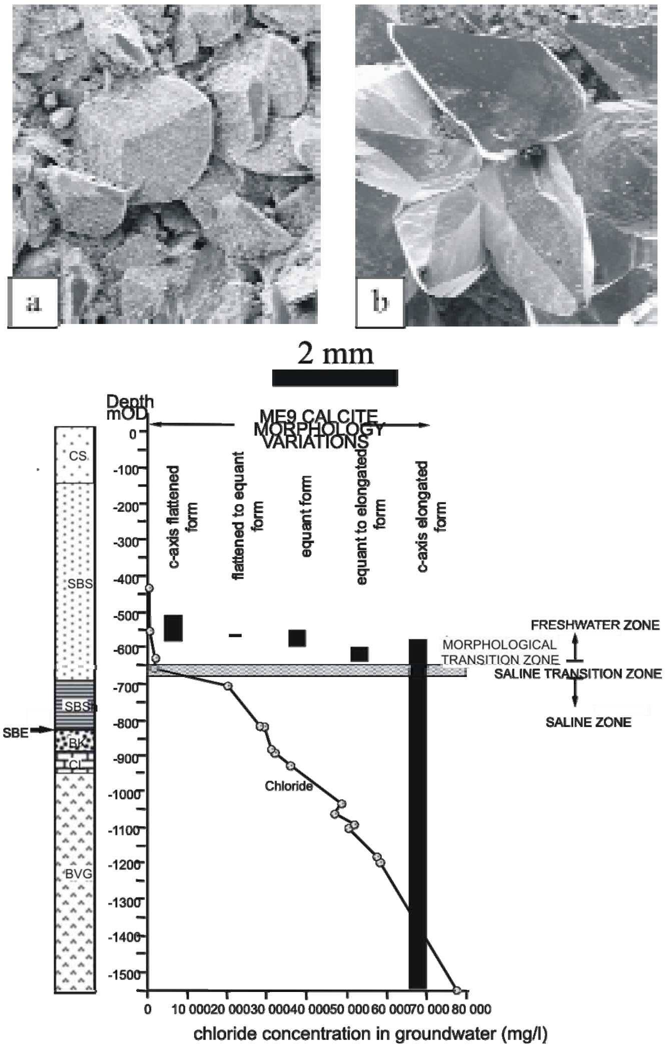

Figure A10. The two types of crystal morphology for secondary calcite at Sellafield and the systematic variation of calcite morphology as salinity increases with depth (from Milodowski et al., 1997). The 'c-axis flattened' morphology (a) corresponds to precipitation from fresh-brackish groundwater and the 'c-axis elongated' morphology (b) corresponds to precipitation from saline groundwater. The depth profile of chloride concentration and calcite morphology is for a borehole drillcore from the central-western part of the Sellafield area.

A3.3 Tono Mine and Underground Laboratory, Japan

Hydrogeology and geochemistry in sedimentary rocks and underlying fractured granite have been studied by JNC in the Tono area, central Japan, for many years. Both formations have been accessed by deep boreholes and an underground laboratory that has been developed in 1990 from uranium mine workings originally excavated in 1972. The sedimentary rocks are <200 m thick at Tono and they overlie the Cretaceous Toki granite which outcrops within a few kilometres of Tono. In principle, the palaeohydrogeology of the granite may be quite simple – any pre-existing brackish/saline formation waters in the upper accessed part of the granite, down to 1000m depth, having been flushed by fresh meteoric water which is topographically driven (Iwatsuki et al. 2002).

Table A9. Selected parameters for groundwater samples from Tono area and URL, Gifu, Japan. Data from Iwatsuki and Yoshida (1999), Iwatsuki et al. (2000, 2001).

Borehole/test	**Depth, m**	**Cl^-, mg/L**	**^{3}H, TU**	**^{14}C, pmC**	**δ^{18}O, ‰**	**δ^2H, ‰**
Toki granite						
DH-3	122		2.9	99.0	-8.2	-53.7
DH-3	754		2.7	55.3	-8.5	-53.2
DH-5	290		<1	45.5	-8.2	-56.7
DH-6	688		2.1	37.5	-8.2	-52.5
DH-7	494		2.3	50.6	-8	-53
DH-7	767		3.4	22.5	-8.5	-58
DH-7	813		2.1	39.0	-8.2	-54.7
DH-8	645		<1	36.7	-8.5	-54
DH-8	697		1.8	31.3	-8.4	-54
DH-8	749		3.7	27.2	-8.4	-55
DH-8	872		<1	18.8	-8.6	-56
DH-8	978		<1	29.9	-8.6	-58
DH-4	0	1.43			-8.1	-51.7
DH-4	186	2.74	4.6		-8	-52.5
DH-3	208	2.3			-8.2	-53.7
DH-3	330	3.69			-8.3	-53.6
DH-3	840	3.11			-8	-53.2
TH-6 G	177		<0.3	10.0	-8.5	-55.7
TH-8 G (1990)	160		1	28.7	-8.6	-53.7
TH-8 G (1993)	160		<0.3	8.0	-8.7	-55.1
Sedimentary rock formations						
TH-4 TL	153		2	21.7	-8.7	-55.4
TH-6 O	68		1	35.4	-8.4	-53.8
TH-8 O	28.5		1	31.4	-8.5	-55.8
TH-8 A	64		5	49.6	-8.6	-54.2
Gallery TL	125		0	10.8	-8.5	-52.8
TH-3 A	46.5		<0.3	31.0	-8.4	-55.5
TH-3 TU	85.5		<0.3	2.0	-8.8	-59.2
TH-3 TL	124		<0.3	27.0	-8.5	-58.7
TH-4 A	83		<0.3	29.0	-8.2	-54.4
TH-4 TU	99		<0.3	18.0	-8.4	-58.2
TH-4 TL	153		<0.3	14.0	-8.6	-57.5
TH-6 A	104		<0.3	31.0	-8.7	-58.3
TH-6 TU	132		<0.3	27.0	-9.1	-58.8
TH-6 TL	153		<0.3	12.0	-9.2	-58.1
TH-8 A	64		<0.3	32.0	-8.5	-56.5
TH-8 TU	91		<0.3	24.0	-8.3	-56.2
TH-8 TL	121		<0.3	6.0	-8.4	-57.1

Geochemical indicators of groundwater ages and of past hydrochemical conditions have been reported in a number of papers (Mizutani et al., 1992; Iwatsuki et al., 1995;

Iwatsuki and Yoshida, 1999a,b; Iwatsuki et al., 2000; Sasamoto et al. 2002, 2004; Morikawa, 2004; Yoshida et al., 2005). A selection of these data is shown in Table A9. The questions regarding stability of the groundwater system concern the evolution of the meteoric water system in the late Pleistocene and Holocene periods and specifically whether there is evidence of step changes in the hydrodynamics or in the hydrogeological properties of the system over that timescale.

Episodic movements of groundwaters stimulated by seismic activity have been reported for an active fault zone in another part of Japan (Lin et al., 2003). In that case, stable O and C isotopic data and ^{14}C data for vein calcites were interpreted as evidence of infiltration of meteoric and/or seawater into the deep fault zone during the last 35-60 ka, stimulated by a seismic pumping process. On the other hand, mineralogical and geochemical studies of fracture fillings in plutonic rocks of varying ages from >100 Ma to <1 Ma in Japan, including the Toki Granite, have indicated that fractures are relatively stable physically and maintain their hydrogeological transmissivities for long timescales (Yoshida et al., 2005).

Groundwater samples from boreholes in the Tono mine, and also from deep boreholes drilled from the surface into the Toki Granite at distances up to several kilometres from the mine, were analysed for ^{3}H, ^{18}O/^{16}O, ^{2}H/^{1}H, ^{14}C and ^{13}C/^{12}C. Positive ^{3}H (4.6 TU) detected at around 180 m depth in one borehole would indicate that topographically-driven groundwater circulation penetrates to this depth within 30 years of recharge – the sampled borehole in this case is about 2 km from the mine so it is uncertain whether this represents flow that has been perturbed by the mine or not. Stable isotopic compositions of deep fresh groundwaters in the outcropping granite (>200 m depth) are insignificantly different from those for shallow groundwaters (<200 m depth) and inferred modern recharge (-8.1 to -8.0 ‰ δ^{18}O versus -8.3 to -8.0 ‰ δ^{18}O), suggesting that the waters are all of Holocene age (Iwatsuki and Yoshida, 1999). The most plausible conclusion to be drawn is that recharge and groundwater flow rates are relatively rapid where the granite is not covered by a substantial thickness of sedimentary rocks.

In contrast, groundwaters from the sedimentary cover rocks at the Tono site have stable isotopic compositions that are slightly lighter (-9.2 to -8.2 ‰ δ^{18}O) (Iwatsuki et al., 2001). ^{14}C contents of these groundwaters are quite low, 6 to 50 pmC, which give model ages from 4,000 to 19,000 years. Two groundwater samples from the underlying granite (at 160 and 177 m depth) also have light stable isotopic compositions (-8.7 ‰ δ^{18}O) and low ^{14}C (8 and 10 pmC) corresponding to model ages of 18,700 and 13,100 years. This leads to a conclusion that groundwaters in the granite where it is overlain by sedimentary cover are significantly older, with lower flow rates, than deeper groundwaters in the outcropping granite (although this is based only on the interpretation of δ^{18}O values and a single ^{3}H measurement). It is noteworthy that the older groundwaters from the covered granite are from boreholes within a few hundred metres of the mine and URL excavations at Tono, suggesting that groundwater flows in these locations have not been substantially affected by the excavations, or alternatively that the drawdown at these locations is fed by old water from the overlying sedimentary rocks rather than by younger water from nearby outcropping granite.

Secondary calcites on fracture surfaces have been distinguished and categorised according to their $^{13}C/^{12}C$ and $^{18}O/^{16}O$ compositions (Iwatsuki et al., 2002). There are three main origins for these calcites: hydrothermal solutions, seawater of Miocene age, and Quaternary fresh waters. ^{14}C was also measured on many calcites, showing contents of <4.5 pmC and mostly <1 pmC. It was concluded that these calcites were mostly older than the present groundwater regime, confirming their mixed origins and ages, with a fraction having been precipitated within the last 50,000 years. Of greatest interest with respect to hydrodynamic and geochemical stability of the system is the observation that the Miocene marine calcites have retained their original crystal morphologies and have not been corroded or dissolved.

Concentrations of radiogenic ^{4}He were found to vary by 2-3 orders of magnitude in Tono groundwaters, further confirming that groundwater ages through the system have a fairly wide range (Morikawa, 2004). ^{4}He concentrations increase with depth in groundwaters in the sedimentary formations, whereas they vary less systematically in groundwaters in the granite. Overall, the pattern of ^{4}He variation was considered to reflect the distribution of topographically-driven groundwater movements. The apparent pattern of ^{4}He accumulation and retention is further evidence of the stability of the topographically-controlled flow system over a considerable period of time.

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