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Hydrogeochemistry of deep groundwaters in the central part of the Fennoscandian Shield

Runar Blomqvist



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Abstract

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Saline groundwaters are frequent in the central part of the Fennoscandian Shield. The results indicate large variations in groundwater chemistry and in the spatial distribution of saline groundwaters. The depths of the fresh/saline groundwater boundaries vary considerably but generally the boundary is located at 300-600 m. In some cases fresh bicarbonate groundwaters are encountered throughout the drill hole. More commonly, however, bicarbonate waters occur only as an upper layer, up to a few hundred metres in extent, overlying chloride waters of varying salinity. In coastal areas saline groundwaters are frequently found much closer to ground surface.

Long-term water-rock interaction and incursions of present/ancient sea water are considered the main processes affecting the evolution of the saline groundwater bodies, while isolation from the surface-close hydrological cycle seems to be a prerequisite for the preservation of these waters. Ancient preferential leaching of low-Rb/Sr minerals (most likely plagioclase) and/or fluid inclusions are the main contribution for dissolved solids in water-rock interaction. The strontium isotope results imply that saline groundwaters in crystalline rocks do not evolve as isolated small pockets with a restricted volume of rock but may constitute more open systems in which lateral hydrogeochemical interaction extends over distances of at least hundreds of metres.

One potential mechanism for formation of young calcites is related to glacial rebound where release of stress and increase in temperature in fractures make the groundwaters oversaturated with respect to calcite. δ^{18} O depleted groundwaters have been observed from several sampling sites in Finland, indicative of glacial meltwater intrusion in the bedrock.

As saline waters have been documented to have long residence times and are not associated with active meteoric water circulation, bedrock suites hosted by saline groundwaters could be considered as potential repository environments for nuclear wastes. Due to negligible flow rates, the risk of radionuclide transport to ground surface is small. Also, the reducing conditions associated with the saline groundwaters could be favourable in keeping many of the harmful radionuclides in an insoluble form. A future repository should primarily be targeted to be located within a single groundwater body.

Keywords (GeoRef, Thesaurus): ground water, geochemistry, hydrochemistry, hydrogeology, crystalline rocks, boreholes, saline water, isotopes, water-rock interaction, mixing, residence time, glaciation, calcite, radioactive waste, underground disposal, Finland

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Preface

"The Deep Groundwater Project" was initiated by the Geological Survey of Finland (GTK) in 1985 with a target to study groundwater composition and conditions in various lithological rock units of the Precambrian crystalline basement in Finland. Results from this project make up the dominant part of this thesis.

The project "Hydrogeochemistry of the Outokumpu formation" was initiated by the Finnish Centre for Radiation and Nuclear safety (presently: the Radiation and Nuclear Safety Authority) and offered as a study target to GTK in 1986. The objective of this project was to add to the hydrogeological data from non-granitic rocks. Results from this project have contributed largely to this thesis.

GTK and the Laboratory of Radiochemistry at University of Helsinki jointly initiated "The Palmottu Analogue Project" in 1987, and in 1988 the project was enlarged to incorporate the Laboratory of Engineering Geology and Geophysics at Helsinki University of Technology. This project received a financial support from the Ministry of Trade and Industry in Finland. These three study projects form part of the Publicly financed nuclear waste management research programme in Finland (Vuori, 1992), jointly supported by the Ministry of Trade and Industry and the Radiation and Nuclear Safety Authority in Finland.

The project ordered by Teollisuuden Voima Oy from GTK in 1990 "Dating of fracture minerals" and its extension ordered by Posiva Oy "Fluid inclusion geothermometry of calcites" also created data that later were published. Since 1987 a long-term scientific co-operation has been in progress between GTK and the Department of Earth Sciences, University of Waterloo, Ontario, Canada: "Water-rock interaction: Improvement of methodologies and analytical techniques." The present author has acted as the scientific and technical leader of all these five projects within GTK.

I am grateful to all those persons and organisations that contributed to the successful performance of these projects, especially to my superiors Dr. Martti Salmi (up to June 1986) and Mr. Paavo Vuorela, Phil. Lic., for offering me good opportunities to develop and expand the research opportunities of the Nuclear Waste Disposal Research unit of GTK from 1986 onwards. Additionally, it is my pleasure to thank my many colleagues and staff members of GTK for their contribution during the various stages of these projects.

The permanent scientific support from Professor Heikki Niini, Helsinki University of Technology, is gratefully acknowledged, as well as the scientific support from professor S. K. Frape from University of Waterloo.

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List of Publications

This thesis consists of an introductory review, ten research publications and a discussion part. Reference to the publications in the text is made in Roman numerals as follows.

- Blomqvist, R., Lahermo, P., Lahtinen, R., and Halonen, S., 1989. Geochemical profiles of deep groundwater in Precambrian bedrock in Finland. In: Proceedings of Exploration '87. Third Decennial International Conference on Geophysical and Geochemical Exploration for Minerals and Groundwater, (ed. G. D. Garland). Ontario Geological Survey, Canada, Special Volume 3, 746-757.
- II. Blomqvist, R. G., 1990. Deep groundwaters in the crystalline basement of Finland, with implications for nuclear waste disposal studies. Geologiska Föreningens i Stockholm Förhandlingar 112, 369–374.
- III. Ahonen, L. and Blomqvist, R., 1994. Mode of occurrence of deep saline groundwater in Finland based on hydraulic measurements. In: Salt Groundwater in the Nordic Countries. Proceedings of a workshop, Saltsjöbaden, Sweden, September 30–October 1, 1992, (ed. Bo Olofsson). The Research Council of Norway. Nordic Hydrological Programme NHP Report 35, 49–59.
- IV. Smalley, P. C., Blomqvist, R., and Råheim, A., 1988. Sr isotopic evidence for discrete saline components in stratified ground waters from crystalline bedrock, Outokumpu, Finland. Geology 16, 354–357.
- V. Suutarinen, R., Blomqvist, R., Halonen, S., and Jaakkola, T., 1991. Uranium in groundwater in Palmottu analogue study site in Finland. Radiochimica Acta 52/53, 373-380.
- VI. Ivanovich, M., Blomqvist, R., and Frape, S. K., 1992. Rock/Water interaction study in deep crystalline rocks using isotopic and uranium series radionuclide techniques. Radiochimica Acta 58/59, 401-408.
- VII. Blomqvist, R., Frape S. K., and Lahermo, P. W., 1995. Isotopic evidence for interaction of glacial meltwater with deep groundwaters in the central part of the Fennoscandian Shield. In: Isotopes in Water Resources Management. Extended Synopses of a symposium on Isotopes in Water Resources Management organized in co-operation with the United Nations Educational, Scientific and Cultural Organization and held in Vienna, 20-24 March 1995, (ed. K. Fröhlich). International Atomic Energy Agency (IAEA), Vienna, Austria, IAEA-SM-336, 360-362.

- VIII. Blomqvist, R., Frape, S. K., Nissinen, P., Ivanovich, M., Vuorela, P., Blyth, A., and Ruskeeniemi, T., 1993. Crustal rebound-related groundwater flow and calcite formation in the crystalline bedrock of the Fennoscandian Shield: New observations from Finland. In: Palaeohydrogeological Methods and their Applications. Disposal of Radioactive Waste. Proceedings of a NEA Workshop, Paris, 9-10 November 1992. Organisation for Economic Cooperation and Development (OECD/NEA), Paris, France, 161–167.
- IX. Blyth, A., Frape, S. K., Blomqvist, R. Nissinen, P. and McNutt, R., 1998. An isotopic and fluid inclusion study of fracture calcite from borehole OL-KR1 at the Olkiluoto site, Finland. Posiva Oy, Helsinki. POSIVA 98-04, 41 p. + 2 Appendices (15 p.).
- X. Frape, S. K., Bryant, G., Blomqvist, R., and Ruskeeniemi, T., 1996. Evidence from stable chlorine isotopes for multiple sources of chloride in groundwaters from crystalline shield areas. In: Isotopes in Water Resources Management. Proceedings of a symposium on Isotopes in Water Resources Management organized in co-operation with the United Nations Educational, Scientific and Cultural Organization and held in Vienna, 20-24 March 1995. International Atomic Energy Agency (IAEA), Vienna, Austria, IAEA-SM-336/24, Vol. 1, 19-30.

Introduction

Organisational framework of the study

The results presented in this study are based on the outcome of the following research projects during the years 1986–1998:

- 1. The Deep Groundwater Project, 1985–1994;
- 2. Hydrogeochemistry of the Outokumpu formation (Hydrogeochemistry of nongranitic rocks), 1986–1992;
- 3. The Palmottu Analogue Project (first domestic part: 1987-1991);
- 4. Dating of fracture minerals, 1990–1998;
- 5. Water-rock interaction: Improvement of research methodologies and analytical techniques, 1987-present.

The overall need for these projects was generated by the on-going site selection programme for the deep disposal of high-level radioactive nuclear waste in the crystalline basement of Finland, accordingly these projects deal with the various aspects of deep groundwater in crystalline basement of the Fennoscandian Shield. The project initiators and the funding organisations varied, as can be seen from the following short description of these projects. As a common feature, however, the Nuclear Waste Disposal Research Unit (YST) of the Geological Survey of Finland (GTK) has been strongly involved in the performance of these projects.

"The Deep Groundwater Project" was initiated in 1985 by GTK (Nurmi *et al.*, 1985), and from the beginning of 1986 the present author was nominated the scientific and technical leader of this project. The main target of this project was to achieve an overall view of deep groundwater composition and conditions in lithologically varied crystalline basement units. As such, the project work targeted to supplement and widen the relatively scanty hydrogeochemical information that was available at that time from the central part of the Fennoscandian Shield. The main sampling phase of the project, in 1985–1988, was performed jointly between YST and the Department of Geochemistry of GTK, and the annual personnel resources varied from 18 to 36 manmonths.

The Deep Groundwater Project took advantage of existing drill holes that originally were made for ore prospecting purposes and of drilled wells made for supply of household groundwater. In total some 50 drill holes and boreholes were sampled for groundwater and analysed with respect to the major chemical components. As samples were generally collected from drill holes with intervals of 50 to 200 m, the analytical data set became rather extensive, and it includes about 1000 groundwater analyses. The dominant part of the information was preliminary documented as two reports in Finnish (Blomqvist *et al.*, 1986; Halonen *et al.*, 1990). Publications I and VII relate solely to this project whereas publications II, III and VIII have received their dominant contribution or important parts from this project.

The project "Hydrogeochemistry of the Outokumpu formation" was initiated based on an invitation from the Radiation and Nuclear Safety Authority (STUK) (former: Finnish Centre for Radiation and Nuclear Safety) to GTK in 1986. The target of this project was to supplement to the existing hydrogeological data from predominantly granitic rock sites with new information from non-granitic rocks. Senior Inspector Kai Jakobsson from STUK acted as the supervisor of the project while the scientific and technical leadership of the project was given to the author of this thesis. The initial study order was followed by 4 other study orders, accordingly 5 technical reports were produced in 1986–1992 (*cf.* Blomqvist *et al.*, 1989; Ahonen and Hakkarainen, 1992). The volume of these studies varied from 12 to 18 man-months. Publications number IV and VI rely mainly on the results of this project whereas publication VIII has received a dominant contribution from this project. Additionally, publications II and III incorporate significant parts from this project.

"The Palmottu Analogue Project" was established in 1987 based on a joint agreement between GTK and the Laboratory of Radiochemistry (former: Department of Radiochemistry) of University of Helsinki, and with a financial support from the Ministry of Trade and Industry (of Finland). In 1988, the Laboratory of Engineering Geology and Geophysics of Helsinki University of Technology joined the project group. The target of the study was to add to the scientific bases of uranium mobilisation, migration and retardation, based on studies in a natural U-Th bearing geochemical environment. A steering group was established to direct the project work, within which the present author acted as the technical co-ordinator. The resources of the project were up to 50 man-months per year, and 5 annual progress reports were produced (*cf.* Blomqvist *et al.*, 1991; Suksi *et al.*, 1992). Publication number V is based on the outcome of this project.

Based on a request from Teollisuuden Voima Oy, the present author contributed to produce a study proposal relating to dating of fracture-infilling minerals from the Olkiluoto study site in Southwest Finland. This proposal led to an order from Teollisuuden Voima Oy to GTK and the initiation of the project "Dating of fracture minerals" in 1990. The target of the project was to apply direct and indirect dating methods on fracture infilling minerals as well as to improve existing research methodology. As a part of the outcome of this study, a sub-report on the geochemistry of fracture calcites was produced (Frape *et al.*, 1992) and incorporated to the final report of the project (Blomqvist *et al.*, 1992). Later, in order to further classify fracture-infilling calcites, GTK and the Department of Earth Sciences of University of Waterloo (Ontario, Canada), jointly received an additional order from Posiva Oy (the nuclear waste management organisation of Teollisuuden Voima Oy and Fortum Heat and Power) to study the fluid inclusion geothermometry of calcites at Olkiluoto.

Within the framework of the project Dating of fracture minerals also another substudy was conducted: Application of uranium series methods for dating of calcites (Ivanovich, 1992). Based on an exceptionally detailed mineralogical description of various calcite types (by Mr P. Nissinen, GTK), some unique multi-stage calcite samples were observed and sampled using a time-consuming, manual microseparation technique, in order to receive the best available samples for this purpose. Publication number IX is based on the results of this project and publication VIII has a dominant contribution from this project.

Since 1987 a long-term scientific co-operation has been in progress between GTK and University of Waterloo: "Water-rock interaction: Improvement of research methodologies and analytical techniques". The intention was to strengthen the scientific contribution of the research groups involved by adding to the expertise and

sharing with methodology, equipment and samples. Professor S. K. Frape and the present author have acted as the leaders of this co-operation, respectively. Publication number X is a successful expression of this long-term scientific co-operation, as is also publication IX.

The support of the Nordic Liaison Committee for Atomic Energy substantially contributed to the performance of these projects, by being encouraged for international scientific co-operation during the early stages of the Deep Groundwater Project and by getting financial support for the development of essential sampling equipment (*cf.* Björklund, 1990).

Objectives of the study

The main target of these studies can be described as follows:

- 1. To supplement and widen the relatively scanty hydrogeochemical and hydrogeological information of deep groundwater that was available from the Fennoscandian Shield in the mid 80's;
- 2. To draw conclusions with respect to the origin of salinity;
- 3. To draw conclusions with respect to long-term hydrogeochemical stability of groundwater systems;
- 4. To evaluate the implications of new results with respect to the disposal of highlevel nuclear waste in crystalline shield environments.

Summary of Publications I-X

Within the broad field of hydrogeochemistry of deep groundwaters of the central part of the Fennoscandian Shield, several important issues can be distinguished and discussed. In the forthcoming review of the publications, it is convenient to discuss the papers based on the following sub-grouping:

- 1. Hydrogeochemical variability of deep groundwaters (Publications I and II)
- 2. Structural control of deep saline groundwaters (Publications II and III)
- 3. Mixing of groundwaters (Publication IV)
- 4. Residence time of groundwaters (Publications V and VI)
- 5. Palaeohydrogeological implications (Publications VII, VIII and IX)
- 6. Origin of salinity (Publications IV and X)

These issues will be further discussed and emphasised in the next main chapter "Discussion and conclusions".

Hydrogeochemical variability of deep groundwaters (Publications I and II)

Publication I "Geochemical profiles of deep groundwater in Precambrian bedrock in Finland" and publication II "Deep groundwaters in the crystalline basement of Finland, with implications for nuclear waste disposal studies" give jointly an extensive summary of the results of the country-wide survey of deep groundwaters in the Precambrian crystalline basement of Finland, thus adding considerably to the pioneer work by Nurmi et al. (1988). Publication I incorporates data from 20 drill holes or drilled wells and gives the first extensive review of deep groundwater from the central part of the Fennoscandian Shield, as based on a sampling campaign in 1987 and 1988 as well as from the project work dealing with the hydrogeochemistry of the Outokumpu formation.

In total, groundwaters from some 50 drill holes were studied and described. As most of the holes were originally drilled for ore prospecting purposes, they are mainly located in or close to schist belts, or in other ore-potential geological surroundings. The lithological units encountered include mica schists and gneisses with interlayers of quartz-feldspar gneisses, amphibolites, black schists, skarn rocks, serpentinites, and various mineralised horizons, as well as mafic layered intrusions, granitoidic rocks, carbonatites, and an arkosic sandstone.

A very practical groundwater sampler, especially tailored for slim drill holes (Nurmi and Kukkonen, 1986), was successfully used in extracting a continuous profile of groundwater from the drill holes (the tube sampling technique). Some of the drill holes were also sampled with double packer equipment (Laaksoharju *et al.*, 1995). Before sampling groundwater temperature was measured (using intervals of 1-2.5 m) to detect possible flow zones, in order to evaluate the consequences to the representativeness of the samples received. In some cases, *e.g.* in drill hole Po-1, quite distinct groundwater flow situations were detected, but in many cases groundwater flow can

significantly affect the depth location of boundaries between groundwater layers of different salinities (of the order of several tens of metres), as observed during repeated sampling from drill holes in the Outokumpu formation (Blomqvist *et al.*, 1989). The sampling procedure was described in Publication I. Charge balance values (\pm 10 %) were used for analytical quality control of major cations and anions, the dominant part of the samples had a charge balance less than \pm 5 %. Ion ratios were used for controlling the concentrations of certain minor elements, *e.g.* Br/Cl ratios for Br concentrations.

Groundwater types with bicarbonate, sulphate or chloride as the major anion, and various mixtures of these, were found. Bicarbonate waters are characterised by low TDS (total dissolved solids, < 1 g/l), sulphate waters usually have TDS values from 1 to 3 g/l, and the TDS values of the chloride waters vary from a few hundred milligrams to the extreme value of close to 170 g/l. Based on the chemical data collected by the Deep Groundwater Project, 5 g/l is the most frequent chloride concentration in deep groundwater in Finland (Figure 1). This value is higher than the salinity of the present Baltic, but close to that proposed for the Litorina Sea (5–6.1 g/l, Kankainen, 1996). Another, less clear maximum gives a chloride concentration around 30 g/l, a value higher than that for the ocean (cf. Table 1). Examples of chemical and isotopic composition of typical brines (TDS > 100 g/l, Davies and De Wiest, 1966) and saline groundwaters in Finland are given in Table 1, cf. Figure 10).



Figure 1. Distribution of chloride concentrations of deep groundwaters in the Finland based on data from the Deep Groundwater Project (855 samples, logarithmic presentation).

The depths of the fresh/saline groundwater boundaries vary considerably but generally the boundary is located at 300–600 m (Figure 2). In some cases fresh bicarbonate groundwater are encountered throughout the drill hole. More commonly, however, bicarbonate waters occur only as an upper layer, up to a few hundred metres in extent, overlying chloride waters of varying salinity. In coastal areas saline waters are, however, frequently found much closer to ground surface.

Table 1. Chemistry and isotopic composition of typical brines and saline groundwaters of the central part of the Fennoscandian Shield. References for data sources: sample 9 (Nurmi *et al.*, 1988); sample 10 (Blomqvist *et al.*, 1992, Br calculated from Lampén and Snellman, 1993); sample 11 (Rankama and Sahama, 1950, except δ^{18} O and 87 Sr/ 86 Sr from Faure, 1986); sample 12 (Luukkonen *et al.*, 1999).

Sample	Location, borchole;	Year	pH	TDS	Na	K	Ca	Mg	Sr	Ba
number	sampling section (±10m)			BU	mgA	mg/l	.mg/l	ing/l	mg/l	mg/l
1	Juuka, Ju/Mi-116, 1020 m	1987	9.1	166.2	48000	600	17000	230	188	0.7
2	Pori, Po-1, 600 m	1986	6.7	120.4	9500	5	36000	82	531	8.9
3	Ylivieska, R-313, 620 m	1990	7.3	82.9	16000	96	8550	5230	276	5.6
4	Juuka, Ju/Mi-114, 920 m	1987	6.9	70.2	10800	16	16200	522	116	0.2
5	Kotalahti mine, Ktl-1088, 945 m	1986	9.3	55.8	8200	17	13300	0.9	123	0.3
6	Mäntsälä, Mha-2, 855 m	1991	8.9	50.3	6870	18	12700	17	95	0.3
7	Noormarkku, R-43, 575 m	1987	8.3	46.7	5670	27	10880	52	77	8.4
8	Juuka, Ju/Mi-116, 520 m	1987	10.4	40.2	6300	21	8900	3	51	0.4
9	Liminka, R-60, 720 m	1985	6.8	41.3	8200	51	5500	760	110	1.0
10	Olkiluoto, OL-KR1, 750-1000 m	1990	8.9	34.9	6880	23	6560	52	47	2.1
11	Ocean (average)	1950	-	34.5	10556	380	400	1272	13	0.1
12	Hästholmen, HH-KR4, 882.5-890.5 m	1998	7.4	31.8	7230	39	4400	520	53	-
13	Enonkoski mine, La-375, 419 m	1988	-	27.6	5560	45	3450	1470	206	-
14	Juuka, Ju/Mi-91, 610 m	1987	9.9	9.3	2310	15	1196	39	11	0.1

Sample	Cl	F	Br	HCO3	SO,	Ch.bal.	9	δ ¹⁸ 0 ‰	δ ² H ‰	*7Sr/*6Sr	Watertype		
number	mg/l	mg/l	mg/l	mg/A	mg/l	%	TU	SMOW	SMOW				
1	99500	<0.1	490	146	45	2.7	4.3	-11.8	-4.2	0.71018	Na-Ca-Cl		
2	73660	0.18	550	7	19	3.3	1.4	- 7. 8	-40.8	0.71493	Ca-Cl		
3	52030	0.1	625	51	1	2.8	4.2	-13.5	-20.9	0.70482	Na-Mg-Ca-Cl		
4	42000	0.29	280	83	190	5.2	<6	-9.4	-16.4	0.71381	Ca-Na-Cl		
5	34000	<0.1	120	-	60	3.1	3	-10.6	-57.1	-	Ca-Na-Cl		
6	30300	0.75	253	29	-	4.5	<6	-12.1	-83.9	-	Ca-Na-Cl		
7	29800	0.66	137	21	2	-2.8	3.4	-10.9	-71.2	0.71362	Ca-Na-Cl		
8	24460	<0.1	174	73	200	1.6	<6	-10.2	-21.2	0.71250	Ca-Na-Cl		
9	22140	0.63	295	98	4100	-1.1	11.5	-12.1	-81.0	0.71881 ^b	Na-Ca-Cl		
10	21200	0.94	157	18	•	2.8	<8	-9.0	-70.3	0.71871	Ca-Na-Cl		
11	18980	1.3	65	140	2649	-	-	0.5	-	0.70906	Na-Cl		
12	19430	-	-	26	25	2.6	1.8	-10.9	-77.1	0.73080	Na-Ca-Cl		
13	16690	-	184	13	10	6.6	<6	-13.2	-81.2	-	Na-Ca-Mg-Cl		
14	5630	0.53	38	23	7	1.3	1.6	-13.4	-83.5	0.71395	Na-Ca-Cl		
Change holes of (Chan) (57*(CAA))/(5)/(7)/(7)/(7)/(7)/(7)/(7)/(7)/(7)/(7)/(7													
										b Gram 600 m			
Z = charge value from 600 m													
C = concentration													
M = molar weight													

The new results revealed that layered groundwater structures are common in the central part of Fennoscandian Shield, and, as indicated by results elsewhere from shield areas, are likely to be found globally in crystalline basement areas (*cf.* Juhlin *et al.*, 1998). Groundwaters with clearly elevated sulphate concentrations (> 100 mg/l) are quite rare even though sulphide minerals are found in most of the study sites (Figure 2).

The elemental concentrations and ratios in the surface-close coastal groundwaters resemble the present day Baltic Sea waters, and supported by evidence from ¹⁴C dating (Kankainen, 1986), a Litorina Sea origin has been proposed for such saline groundwaters (Kankainen, 1986; Nordstrom, 1986; Lahermo and Lampén, 1987).



Figure 2. Chloride and sulphate values versus depth from groundwaters at various sites in Finland (Blomqvist, 1990) based on the tube sampling technique. For comparison, a few chloride results received with the double packer sampling technique are also shown. Chloride results from Outokumpu 737 (cross) correspond well, irrespective of sampling technique, but the upper sample from Pori (triangle) show large differences, as a deeper, more saline water discharges onto ground surface via the borehole.

Sporadically saline waters have also been found close to ground surface in inland areas, *e.g.* in the Outokumpu area (Blomqvist *et al.*, 1989), that do not show any indication of seawater coverage since the end of the Weichselian glaciation (Donner, 1995). Surface-close saline waters of the Outokumpu area have elemental ratios that clearly deviate from marine values, in that respect resembling many other saline groundwaters from the deep parts of the bedrock. As some of these deeper groundwaters additionally had salinities that by far exceed the salinity of the ocean, it was concluded that such groundwaters are not likely to have a dominant marine contribution to salinity, and it was considered plausible that diversified water-rock interaction processes had a more marked impact on the salinity than a seawater source (Publication I). This all was in good accordance with previous results from the Canadian and the Fennoscandian Shields (Frape and Fritz, 1982; Fritz and Frape, 1982; Frape *et al.*, 1984; Nurmi *et al.*, 1988).

Structural control of deep saline groundwaters (Publications II and III)

Publication III "Mode of occurrence of deep saline groundwater in Finland based on hydraulic measurements" reviews the distribution of saline groundwater based on hydraulic conductivity studies at three sites where saline or highly saline groundwaters were earlier sampled. The study sites represented different lithological environments: the arkosic sandstone at Pori, a mafic/ultramafic intrusion at Ylivieska, and the schistose rocks of the Outokumpu formation. The study focused on the understanding of the factors affecting the spatial distribution of the saline groundwaters, including the fresh/saline groundwater boundaries, therefore the hydraulic conductivity became an essential parameter to be characterised. The measurements were performed with the double packer equipment that was improved for this purpose. Hydrogeochemical results were used for interpretation of results.

In the arkosic sandstone of Pori, high hydraulic conductivity (close to 10^{-7} m/s) was observed in the upper part of the bedrock whereas deeper down low values were measured (of the order of 10^{-10} m/s). The hydraulic conductivity of the upper part was concluded to be due to fractures with relatively large apertures, as deduced from temperature measurements from the drill-hole water (Kukkonen, 1986) and drill-core observations. Additionally, vertical fractures were shown to be relatively common above 300 m, but quite rare below that depth based on observations by Mr. A. Lindberg, GTK. Also laboratory measurements and galvanic *in situ* measurements indicated that rock porosity decreased from about 7 % in the upper part of the bedrock to about 2 % deeper down in the system (Vuorela *et al.*, 1990). Groundwater sampling had previously shown that highly saline groundwater with total dissolved solids (TDS) exceeding 100 g/l occurred at this site below 300 m (*cf.* Publication I).

The layered mafic/ultramafic intrusion of Ylivieska is composed of serpentinite in its upper part, to a depth of 115 m, and dominantly of peridotitic rocks to 430 m, although olivine and pyroxene gabbros are rather common, too. Deeper down the gabbroic rocks totally predominate. The upper part of the intrusion was characterised by dilute Mg-Na-Ca-HCO₃ groundwater down to approximately 350 m. From 550 m down the groundwater proved to be a highly saline Na-Mg-Ca-Cl brine (TDS: 80 g/l). Drill core examinations indicated moderate fracturing in the upper part of the bedrock, down to 160 m, while below this level mainly a few distinct zones of fracturing were

observed, at 210–235 m, 340–350 m, 370 m, 440 m, and 465–480 m (Ruskeeniemi, *et al.*, 1996). The results of the hydraulic measurements showed that increased hydraulic conductivity $(10^{-8}-10^{-7} \text{ m/s})$ correlated rather well with the reported zones of fracturing (Figure 3). A water-conducting fracture that yielded a highly saline groundwater was also observed from the quite homogenous deeper part of the intrusion at about 550 m. The results showed that one of the most dominant water-conducting zones was located around 350 m, this zone was also interpreted to control the fresh/saline groundwater boundary of the borehole.



Figure 3. Variation in hydraulic conductivity of rock, salinity of water, and main lithological units of drill hole R-313 at Ylivieska. The stippled area is mainly composed of ultramafic rock types, whereas the white area is dominated by gabbroic rocks. Dashed lines indicate major zones of fracturing (Publication III).

In the schistose rocks of the Outokumpu formation hydraulic measurements were conducted from three drill holes: OKU-551, OKU-737, and OKU-740, all located in the same drilling profile. The hydraulic conductivity in drill hole OKU-551, which penetrates mainly mica schist, is generally low, but high hydraulic conductivity (10^{-7}) m/s) was observed at 430-440 m, due to a prominent fracture zone which has been observed from most of the drill holes and cores of the area (Koistinen, 1981). This fracture zone hosts a brackish Na-Ca-Cl groundwater (TDS 1.5 g/l) which shows clearly depleted oxygen isotope values (δ^{18} O: -16.7 ‰) (cf. Publications VI and VIII). The fracture zone also delineates the occurrence of the typical saline groundwater of the Outokumpu formation (Ca-Na-Cl; TDS 7-15 g/l) to the deeper parts of this drill hole. In the two other drill holes, metamorphosed black shales and lithological contacts seem to possess one order of magnitude higher hydraulic conductivity values (10^{-8} m/s) compared to those of the typical mica schist and the interlayers of massive calc-silicate rock and dolomite. The hydraulically most conductive zones, however, are associated with single open fractures. The boundary between fresh/saline groundwaters in drill holes OKU-737 and OKU-740 follow the lithological changes, this contact also has slightly elevated hydraulic conductivity.

Further, with respect to the occurrence of deep saline groundwaters, publication II "Deep groundwaters in the crystalline basement of Finland, with implications for nuclear waste disposal studies" stresses the role of fracturing of various lithological units in controlling the existence of deep saline groundwaters. Saline groundwaters were frequently observed from the drill holes sampled by the Deep Groundwater Project. These drill holes were dominantly located in ore-potential lithological units in, or close to, schist belts with a wide variety of associated rock types. Generally the schistose rocks tend to be intensely foliated and fractured, but the fracture apertures are dominantly small. Within granitic rock types, fracture geometry is characterised by sparsely spaced open fractures that often form an interconnected network suitable for good hydraulic connections, therefore their hydrogeochemistry tend to be characterised by tritium-rich bicarbonate groundwaters. Similar observations of fresh groundwaters in granitic rocks have been described from site selection and characterisation studies for disposal of nuclear waste from many sites in Sweden and Finland (cf. Smellie et al., 1985; Pitkänen et al., 1987, 1996, 1998). The Hästholmen site in Loviisa is located on the coast of the Baltic Sea and here brackish groundwater typical for coastal areas have been reported from the upper part of the rapakivi granite (Kankainen, 1986) whereas saline groundwater prevail from 640 m down (Luukkonen et al., 1999).

Mixing of groundwaters (Publication IV)

Publication IV "Sr isotopic evidence for discrete saline components in stratified ground waters from crystalline bedrock, Outokumpu, Finland" discusses mixing relationships and water-rock interaction of deep groundwater bodies based on ⁸⁷Sr/⁸⁶Sr isotopic results from drill hole OKU-741, the deepest hole of the Outokumpu region (1100 m). The results and implications of water-rock interaction, however, will be discussed later in this thesis, in Chapter "Origin of salinity".

The upper part of the drill hole OKU-741 is characterised by mica gneiss and schist with interlayers of metamorphosed black shale, calc-silicate rock and dolomite, whereas the deepest part is occupied by serpentinite. The groundwater in this drill hole is compositionally stratified as shown by Nurmi and Kukkonen (1986; cf. Figure 2). The fresh water interval (A: 0 to 430 m) contains only trace amounts of Na, Ca, Mg, and Cl. In the first saline water interval (B: 430 to 800 m), the total dissolved solids (TDS) are of the order of 15 g/l, and the element concentrations tend to increase only slightly with depth in this interval. The second saline water interval (C: > 800 m; located in serpentinite) is characterised by higher salinity (TDS = 27 g/l), and here also Mg becomes enriched in the water. The salinity is still increasing as the bottom of the hole is reached. A temperature log (Nurmi and Kukkonen, 1986) indicated no significant flow along the hole. Whereas the element concentrations in interval A remain close to analytical detection limits, the ⁸⁷Sr/⁸⁶Sr drops with depth, even in the shallowest samples analysed (Figure 4). This is because the very low Sr concentration in interval A makes the ratio sensitive to additions of small amounts of saline water from interval B. When an extrapolated ⁸⁷Sr/⁸⁶Sr value of 0.7335 for surface water was used, calculations showed that at 105 m depth the water derived about 5 % of its Sr from the underlying saline water, and at 371 m depth, about 90 % of the Sr content was saline-water derived. Interval A is thus a zone of mixing between the fresh, near-surface water and the underlying saline water. The waters from interval A define a straight ⁸⁷Sr/⁸⁶Sr vs. l/Sr mixing line (A-B) which has a slope of $3.95 \cdot 10^{-4}$ (in Figure 4 this line is curved due to the logarithmic presentation). The 87 Sr/ 86 Sr drops gradually in interval B and more quickly in interval C as Sr concentrations rise concomitantly. These waters also form a well-developed straight mixing line (B–C), but with a much steeper slope than for the interval A waters ($4.53 \cdot 10^{-2}$, see Figure 4).



Figure 4. Mixing relations in groundwater from drill hole OKU-741 based on ⁸⁷Sr/⁸⁶Sr ratios (Publication IV). The three shallowest samples are off scale. The curved mixing lines would appear as straight lines in non-logarithmic presentation. See text for additional information.

This leads to three important conclusions:

- (1) Whereas the element data might give the impression of relatively sharp boundaries between the different water bodies, the Sr-isotope data indicate that mixing is prevalent throughout the sampled interval. This mixing reflects, at least in part, slow diffusive mixing along the drill hole, but the same process may also occur in the rock. Secondly it may also reflect flow disturbances caused by the sampling itself.
- (2) The upward decrease in salinity cannot be explained by dilution of a single saline water by fresh, near-surface water because all the samples would then plot on a single mixing line, two saline waters plus a fresh water need to be involved.
- (3) Because of the close fit of the samples to straight mixing lines, the three waters should be relatively homogeneous in composition and apparently unaffected by local variations in rock composition either within the sampled drill hole or between neighbouring drill holes. The same water end-member compositions have been detected in other drill holes up to 500 m away, indicating that the homogeneous bodies of water are laterally extensive (based on unpublished Sr results from surrounding drill holes).

The implication is that the saline groundwaters in crystalline rocks do not evolve as isolated small pockets with a restricted volume of rock but may constitute more open systems in which lateral hydrogeochemical interaction extends over distances of hundreds of metres. With respect to the origin of salinity of groundwaters, these features stress the importance of relatively large-scale regional processes, but yet, with a certain control from the hosting rock types. This can be deduced by comparing the ⁸⁷Sr/⁸⁶Sr isotopic signatures of the groundwaters from the serpentinite body with the results from the mica schist dominating rock sequence (intervals C and B).

Residence time of groundwaters (Publications V and VI)

Publications V "Uranium in groundwater in Palmottu analogue study site in Finland" and VI "Rock/water interaction study in deep crystalline rocks using isotopic and uranium series radionuclide techniques" deal with the uranium series disequilibrium method and various other isotope techniques (²H, ³H, ¹³C, ¹⁴C, and ¹⁸O) in order to estimate time scales over which recent water-rock interaction processes have occurred. The study sites incorporate the Palmottu U-Th mineralisation at Nummi-Pusula in SW Finland and the Outokumpu formation in SE Finland.

Palmottu was chosen as an analogue study site for the geochemical behaviour of uranium in a natural site (Blomqvist *et al.* 1991). The hydrogeochemical sampling at Palmottu was conducted from several drill holes using both the tube-sampling technique and the double packer equipment. The groundwaters in the upper part of the bedrock were dominantly bicarbonate waters, with tritium values close to those of local precipitation, whereas the groundwaters from the deeper parts of the bedrock (below 100 m) were frequently of sulphate and/or chloride type, with tritium values mostly close to detection limits (3.3, 5.0 and 6.4 TU, respectively). In drill hole DH 346, the first 100 m was occupied by fresh Ca-Na-HCO₃ type water with TDS of 0.3 g/l. From 140 m downward, the water was of a slightly saline Na-SO₄-Cl type with TDS of 1.4 g/l. The pH values of the water increased with depth from values close to 7 at ground surface to values approaching 9 at the bottom of the hole. The redox measurements indicated oxidising conditions in the uppermost part of the bedrock and reducing ones further down.

The high tritium values from the groundwaters of the upper part of the bedrock were indicative of extensive recent surface water infiltration into the bedrock. Here the measured uranium concentrations from fracture groundwaters were up to 54 ppb. The concentrations of dissolved uranium in the deeper, clearly reducing and slightly saline part of the groundwater system were low, 1.4 ppb. Under reducing conditions, the concentrations of uranium are dependent on the low solubility of U(IV). Thus, the reduced groundwaters at Palmottu show low concentrations of dissolved uranium despite large amounts of uranium in the rock.

Water-rock interaction frequently results in 234 U/ 238 U radioactivity ratios greater than unity for dissolved uranium. The radioactive decay of 238 U in rock causes a recoil ejection of its daughter, 234 Th, and radiation damage to the crystal lattice. Each decay of 234 Th and its daughter, 234 Pa, may also cause a loss of an electron so that the 234 U is partly in the more soluble U(VI) valence state. These preferential dissolution processes may increase the amount of 234 U compared to 238 U in reduced groundwaters (Andrews and Kay, 1982; Osmond *et al.*, 1983) and with time the alpha recoil mechanism may result in high 234 U/ 238 U radioactivity ratios. At Palmottu increased 234 U/ 238 U radioactivity ratios of up to 3.7 were observed from the reduced deeper groundwaters, indicating clearly longer residence times compared to those from the groundwaters in the upper oxidising part which tend to be close to 234 U/ 238 U sequential equilibrium. The purpose of the study presented in Publication VI was to combine a variety of isotopic and modelling techniques to estimate time scales during which the most recent water-rock interaction processes have occurred at the Outokumpu site. The isotope methods ranged from ²H, ³H, ¹³C, ¹⁴C, ¹⁸O to U/Th series radionuclides (²³⁸U, ²³⁴U, ²³⁰Th, ²²⁶Ra, ²²²Rn, ²³²Th, ²²⁸Ra, ²²⁸Th, ²²⁴Ra). Two drill holes (OKU-551 and OKU-737) were sampled for groundwater using the double packer technique at depth intervals of 441–447 m and 125–131 m, respectively. The corresponding drill core samples were examined and the fracture minerals studied. Fracture infilling (mainly calcite, prehnite and laumontite) and groundwaters were analysed for major and minor ions and isotopes as listed above. The mineral samples were analysed for U and Th isotopes and ²²⁶Ra.

Both the sampled groundwaters represent alkaline, low bicarbonate, and slightly reducing groundwaters. Tritium data suggest no significant presence of modern waters in the samples. Their apparent radiocarbon age is of the order of several thousands of years, consistent with the timing of the last deglaciation in Finland at about 10 000 BP. However, several aspects of carbon chemistry may complicate the detailed interpretation of the data in terms of residence time. First of all, the bicarbonate content in these waters is very low and, secondly the pH measurements at field were much higher than the subsequent laboratory measurements. Geochemical modelling using PHREEOE code (Parkhurst et al., 1980) and the initial water chemistry showed that the groundwaters from OKU-551 and OKU-737 were undersaturated with respect to CO₂ and slightly oversaturated with respect to calcite, partly due to pressurereleased degassing during sampling. Under these conditions, on contact with air, the samples would gain atmospheric CO₂ with concomitant decrease in pH as observed. Because of very low bicarbonate levels, even a small admixture with younger waters rich in bicarbonate (soil or atmospheric CO_2) would probably result in a net gain of carbon from these sources, resulting in dilution of the actual carbon pool and, consequently, underestimated residence times.

One of the fracture infilling samples from borehole OKU-551 yielded a ²²⁶Ra/²³⁰Th activity ratio less than unity implying that Ra is being leached from the surface of the solid sample by saline groundwater flowing through the fracture zone. A mass balance model assuming dynamic equilibrium between the groundwater and the fracture infilling were used together with δ^{18} O and ²²⁶Ra/²³⁰Th data, and data for effective porosity to estimate the timescales of water-rock interaction at this fracture. The model calculations suggest that the groundwater–fracture mineral interaction time in this fracture system (441–447 m of drill hole OKU-551) is of the order of 6 ka or less, and that the effective porosity of this water-rock system is in the range between 0.05 and 0.30 %. Porosity values < 0.3 % have been received using hydraulic testing. The timescales of water-rock interaction at this fracture compared to what could be expected for the δ^{18} O depleted water with the likely glacial melt water signature (see next Chapter). However, when taking in account the uncertainties involved in mixing of groundwaters, the results may be satisfactory.

Palaeohydrogeological implications (Publications VII, VIII and IX)

Publication VII "Isotopic evidence for interaction of glacial meltwater with deep groundwaters in the central part of the Fennoscandian Shield" discusses certain observations based on the δ^{18} O values of groundwater samples from 47 drill holes.

Further on, this publication and publication VIII "Crustal rebound-related flow and calcite formation in the crystalline bedrock of the Fennoscandian Shield: New observations from Finland" document the occurrence of δ^{18} O depleted groundwaters from three regional study areas in Finland. Publication VIII also presents the dating results from a multi-stage fracture infilling calcite of drill core OL-KR1 at Olkiluoto, Eurajoki based on the uranium series disequilibrium method.

The isotopic results of 268 groundwater samples from 47 drill holes from the central part of the Fennoscandian Shield display a broad scatter of δ^{18} O values (Figure 5). The δ^{18} O range from values similar to those of the Baltic Sea (-8 to -7 ‰) to quite strongly depleted δ^{18} O values, around -17 ‰. The calculated regression line of the data set (Equation 1) is very close to the Global Meteoric Water Line (GMWL, Craig, 1961). This calculation excludes the five samples from the Baltic Sea and the brine samples from drill hole Po-1 from the Satakunta sandstone, with δ^{18} O values from -9.5 to -7.5 ‰. A meteoric origin for most of the samples of Figure 5 can be postulated.

 $\delta^2 H = 7.93 \cdot \delta^{18} O + 9.9 \% (SMOW)$ (1)

In the eastern part of Finland, around latitude 63 N, fresh bedrock groundwaters typically show δ^{18} O values of -14 to -13 ‰. In southern and SW part of Finland the δ^{18} O values tend to be between -12 and -11 ‰, as also supported by the results from surface waters (T. Kankainen, GTK) given by Nurmi *et al.* (1988). However, there are several samples within the present data set that clearly deviate from the typical regional values. Besides the heavy δ^{18} O values of deep groundwater from the Satakunta sandstone, the data set of Figure 5 also include several samples with distinctly lighter δ^{18} O values than expected from present climatic conditions at the respective sites. Therefore it was concluded that the samples with light δ^{18} O values were recharged at colder climatic conditions compared to the presently prevailing ones.

At Outokumpu, Sukkulansalo a brackish groundwater was sampled from a major subhorizontal fracture zone penetrated by drill hole OKU-551 at 441–447 m. The depleted δ^{18} O values (-16.7 ‰) of the groundwater differ clearly from the δ^{18} O values of the fresh and saline groundwaters of the five other drill holes studied at the site (*cf.* Blomqvist *et al.*, 1989), and it was concluded that glacial meltwater intruded the fracture zone, probably during a deglaciation-related isostatical bedrock movement, and mixed with the prevailing saline groundwater of the bedrock.

North of Outokumpu at Juuka, the hydrogeochemistry of a massive serpentinite was studied by sampling nine different drill holes. The δ^{18} O values of the majority of the samples plot between -13.8 and -12.2 ‰. The three samples from the uppermost 330 m of drill hole Ju/Mi-86 yielded δ^{18} O values from -17 to -16.4 ‰, whereas the two deeper samples, from 420 and 520 m, plot at -13.2 and -13.5 ‰, respectively. The δ^{18} O depleted groundwaters from Ju/Mi-86 are chemically Na-Cl dominant dilute groundwaters (TDS 0.4 g/l), whereas the deeper groundwaters are slightly saline Na-Ca-Cl groundwaters (TDS 3.5 g/l). The recorded tritium values are low, < 6 TU, except for the groundwater at the interface between these two groundwater types, from which 11 TU were recorded. Therefore the water in drill hole Ju/Mi-86 seem to

represent relic groundwaters, the recharge of the δ^{18} O depleted groundwater being most likely linked to the end of the Weichselian glaciation.



Figure 5. $\delta^2 H$ and $\delta^{18}O$ values for bedrock groundwaters from the central part of the Fennoscandian Shield. Results of 268 groundwater samples from 47 drill holes are given (Publication VII). The samples are classified into three groups according to their chloride concentrations. One sample off the SW coast of Finland ($\delta^{18}O$: -8.4) and four samples from the Baltic Sea south from Finland (Fröhlich *et al.*, 1988) were used as Baltic Sea reference samples. GMWL: $\delta^2 H = 8.0 \cdot \delta^{18}O + 10.0 \%$ (SMOW), (Craig, 1961).

On the western coast of Finland groundwater samples were collected from drill hole Po-1 of the arkosic sandstone of Satakunta using the double packer technique. During a 3-hour sampling campaign and pumping of 300 l of groundwater three samples were extracted from a water-conducting fracture located within the packer interval of 100–106 metres (by Dr. L. Ahonen, GTK). The isotopic results yielded progressively lighter δ^{18} O values with increasing pumping time (-15.3, -15.5, and -15.6 ‰, respectively) whereas the groundwater samples from a deeper fracture of that drill hole yielded the constant δ^{18} O value of -12.8 ‰. During a previous sampling campaign a few years earlier the research group, under the supervision of professor S. K. Frape, University of Waterloo, sampled the same borehole with a down-hole sampling probe designed to collect pressurised gas and water samples in narrow diameter boreholes (Sherwood Lollar *et al.*, 1989). A sample from a depth of 110 m showed the highly depleted δ^{18} O value of -20.7 ‰, but the re-sampling to confirm this exceptional value was not successful.



Figure 6. δ^2 H and δ^{18} O values for groundwaters in the Pori–Rauma region (SW Finland) with focus on Olkiluoto area. A mixing line between δ^{18} O depleted groundwaters and Baltic Sea waters were established (Publication VIII). Additional data from Hyyppä, 1984; Blomqvist *et al.*, 1992; Pitkänen *et al.*, 1992; Lampén and Snellman, 1993).

When presenting the samples from Po-1 on the δ^2 H vs. δ^{18} O diagram (Figure 6), a straight mixing line could be drawn from the δ^{18} O depleted groundwaters of the 100–106 m section via the deeper 195–201 m section to Baltic Sea water, indicating that a δ^{18} O depleted water and a seawater mixed in the fractures (of the arkosic sandstone). The δ^{18} O depleted groundwater was interpreted as glacial melt water that must have recharged before the ice cover had totally retreated from the present coastal area, because the sea immediately covered the low-altitude land after the ice had melted. The δ^{18} O value of the glacial meltwater can be extrapolated based on the intersection of this mixing line with the GMWL: the δ^{18} O value proved to be around –24 ‰. This is in good accordance with other fragmental evidence of the δ^{18} O values of glacial meltwater from the Fennoscandian Shield or neighbouring areas: –19.5– –25 ‰ (Ferronsky *et al.*, 1983; Tullborg and Larson, 1984; Karhu, 1988).

Bedrock groundwaters from drill holes and percussion boreholes close to ground surface down to 400 m at Olkiluoto study site, and from surrounding areas in Eurajoki, also plot below the GMWL of Figure 6, and many samples fall on the mixing line defined by the groundwaters from drill hole Po-1. Therefore it was concluded that the samples from Eurajoki form part a wider mixing system. It was postulated that an extensive regional mixing system between glacial meltwater and Baltic Sea water took place at the end of the Weichselian glaciation on the SW coast of Finland in the vicinity of the present towns of Pori and Rauma. The deeper samples from drill holes both Po-1 and OL-KR1 did not participate in this mixing system.

Fracture calcites were studied from drill core OL-KR1 at Olkiluoto. Four samples exhibiting clear platy or crystal shaped calcite generations suggesting growth in open spaces were selected for dating by the U/Th method. In total, seven calcite specimens from these four samples gave model ages < 300 ka. The results from the sample at 780.5 m, indicated three different calcite generations with model ages of 117 ka (+45, -32 ka), 233 ka (+70, -43 ka), and 285 ka (+160, -60 ka), respectively (Figure 7; *cf.* Blomqvist *et al.*, 1992; Publication VIII). However, as the analytical error is very high for the model age of the third sub-sample, only two separate calcite generations may be present. The model age of the crystal shaped calcite seem to coincide with the Eemian warm stage (the oxygen isotope stage 5e of deep-sea sediments) that followed the Saalian glaciation, whereas the second sample could be correlated to the preceding warm period (the oxygen isotope stage 7) (*cf.* Donner, 1995).

One potential mechanism for formation of young calcites is related to glacial rebound where release of stress and increase in temperature in fractures make the groundwaters oversaturated with respect to calcite (*cf.* Ahonen and Blomqvist, 1992). Due to pressure/temperature differences expected to occur during a glacial cycle, calcite may both partly dissolve and re-precipitate (in closed systems), thus being able to generate several generations of young calcite within a single fracture.



Figure 7. Young calcite from a void-type fracture from 780.50 m at OL-KR1 dated by the U/Th method (Publication VIII). Calcite generations 1, 2, and 3 have model-ages of 117 ka (+45, -32 ka), 233 ka (+70, -43 ka), and 285 ka (+160, -60 ka), respectively. However, as the error bars of calcite generation 3 overlaps with calcite generation 2, these two measurements may not represent different calcite generations. Type 4 is a massive old calcite vein that is cut by the fracture with the young calcites, and its U/Th model age is beyond the limits of the dating method (> 300 ka). U/Th model-ages by AEA Technology, Harwell Laboratory, UK. Data by Ivanovich (1992) in Blomqvist *et al.* (1992).

Publication IX "An isotopic and fluid inclusion study of fracture calcite from borehole OL-KR1 at the Olkiluoto site, Finland" points to several periods of formation of fracture infilling calcite in the crystalline bedrock of Olkiluoto site. The study of fracture infilling of calcite provides an opportunity to understand the thermal and fluid history of a rock formation. Based on fluid inclusion analysis of fracture calcite from borehole OL-KR1 three generations of calcite fillings were recorded, each associated with a different fluid. The earliest calcites formed from a high temperature (238–98° C), low salinity Na-Cl fluid that was probably the result of water-rock interaction involving meteoric water or seawater during a hydrothermal event. The next calcite type appears to be the result of a relatively low salinity fluid (98–67° C), probably of a Na-Cl composition and possibly of magmatic or basinal brine origin. The last group of calcites records two distinct fluids: a low-salinity, probably a Na-Cl fluid, and a high-salinity, probably a Ca-Cl dominant fluid. These fluids may be the result of partial dissolution of previous calcites by a magmatic water or basinal brine and seawater/meteoric water mixture. The calcites are associated with hydrothermal minerals, such as albite, quartz, pyrrhotite, illite, laumontite-leonhardite, barite, fluorite, and with clay minerals as kaolinite, montmorillonite, palygorskite, and paragonite (observations by Mr. P. Nissinen, GTK; Blomqvist *et al.*, 1992).

None of the calcites are in equilibrium with current groundwaters found in the borehole OL-KR1 based on fluid inclusion analysis and calculated δ^{18} O values. The waters that precipitated the calcites of the observed groups mostly had δ^{18} O signatures from -1.2 to +12.1 % (SMOW), non-typical for present-day meteoric waters of the Fennoscandian Shield. Calculated δ^{18} O signatures close to present-day meteoric waters were only recorded from the latter subgroup of the third group of calcites: the platy, grey calcites (with calculated δ^{18} O signatures down to -6.1 %), (see Figure 7).

Origin of salinity (Publications IV and X)

Publication IV "Sr isotopic evidence for discrete saline components in stratified ground waters from crystalline bedrock, Outokumpu, Finland" which discusses mixing relationships of the deep groundwater bodies sampled from drill hole OKU-741 (see above), focuses additionally on the issue of the origin of salinity. Publication X "Evidence from stable chlorine isotopes for multiple sources of chloride in groundwaters from crystalline shield areas" discusses the origin of salinity in crystalline rocks based on new data on stable isotopes of Cl from the Canadian and the Fennoscandian Shields.

The groundwaters from the drill hole OKU-741 typically plot on GMWL in the δ^2 H vs. δ^{18} O diagram, whereas the deepest samples plot slightly above the meteoric water line. This indicates that the water molecules are of meteoric origin, with modifications due to water-rock interaction and/or mixing with non-meteoric waters occurring only at the deepest levels sampled. With respect to the source of the main dissolved components (Ca, Na, Mg, Sr, and Cl), the Sr-isotope data preclude the possibility that marine solutes would have contributed to the salinity of these waters, in that the ⁸⁷Sr/⁸⁶Sr ratios of the waters (0.723–0.733) are much higher than the value of seawater during past geological times (Faure, 1986). The most likely origin for the salinity was thus concluded to be due to water-rock interaction.

Rb/Sr systematics were applied to further study this concept. Whole-rock samples from drill hole OKU-741 that were analysed by the Rb-Sr method formed an isochron, yielding 1729 ± 40 Ma and initial strontium-isotope ratio of 0.7094 ± 0.0001 (with main square of weight deviation, MSWD = 5). This age relates to

Sr-isotope resetting during a postkinematic thermal event; presumably, individual mineral constituents would plot on the same isochron. In general, serpentinite samples plot at the low Rb/Sr end of the isochron, ⁸⁷Sr/⁸⁶Sr being about 0.710 (Figure 8); feldspar-rich schists have ⁸⁷Sr/⁸⁶Sr of about 0.750, and micaceous samples have ⁸⁷Sr/⁸⁶Sr as high as 0.80. The different rock types in the borehole thus vary immensely in terms of ⁸⁷Sr/⁸⁶Sr, whereas ⁸⁷Sr/⁸⁶Sr ratios of the water samples have a much narrower range, varying gradually with depth and remaining unaffected by most changes in host-rock composition both on a drill-hole scale and on a scale of hundreds of metres. This indicates that the salinity of the water in the drill hole is not the result of local water-rock interaction with the immediately adjacent rocks (cf. Chapter: Mixing of groundwaters). Furthermore, a simple calculation using whole-rock ⁸⁷Sr/⁸⁶Sr and Sr concentration data together with the relative abundance of the different lithological units of the drill core gives a mean ⁸⁷Sr/⁸⁶Sr of about 0.760, much higher than the water values. The involvement of serpentinite in the ⁸⁷Sr/⁸⁶Sr signature of the deepest groundwater, where Mg exceeds 1000 mg/l, cannot be ruled out on this basis.



Figure 8. Groundwater samples relative to the isochron defined by whole-rock samples from drill hole OKU-741 (Publication IV).

Rather than Sr in groundwater being derived from the leaching of bulk-rocks, a more likely possibility is that Sr in the waters has been derived preferentially from certain rock-forming minerals. The low ⁸⁷Sr/⁸⁶Sr ratio of the waters rules out biotite as the main source of strontium. Although biotite is a mineral that is relatively easily altered, it usually has a low strontium content and, judging by the composition of the biotite-rich rocks, will have ⁸⁷Sr/⁸⁶Sr >0.80. The high ⁸⁷Sr/⁸⁶Sr of biotite is due to high amount of Rb in the mineral lattice (replacing K) and the production of ⁸⁷Sr following the decay of ⁸⁷Rb. Any contribution from biotite to the waters must have been overshadowed by minerals with low ⁸⁷Sr/⁸⁶Sr and thus low Rb/Sr ratios. Minerals that may fulfil this criterion are plagioclase and apatite. Not only could sericitisation of

plagioclase (which composes ~ 30 vol. % of the mica schist) produce Sr with the correct 87 Sr/ 86 Sr, but also the formation of secondary micas/clays could provide a sink for Rb released from the feldspar, leading to the low Rb/Sr in the waters. If apatite were involved, this would also provide a source of Cl for the waters.

An additional possible sources of Sr are fluid inclusions and/or grain-boundary salts. Their contribution to the water cannot be assessed in the absence of fluid-inclusion and salt data. Leaching experiments (Peters, 1986) have shown that fluid inclusions may constitute an important source of salinity, but groundwaters may have an easier access to grain-boundary salts and interstitial waters.

Based on Publication X, the δ^{37} Cl isotopic values of Canadian Shield sites (4 sites) range from -0.51 to +0.17 ‰, being dominantly depleted relative to standard mean ocean chloride (SMOC). Groundwaters from the Fennoscandian Shield sites of Finland (11 sites) have values ranging from -0.61 to +1.97 ‰, and are predominantly enriched relative to the seawater standard and the Canadian Shield fluids. The δ^{37} Cl signature of the Baltic Sea is -0.21 ‰. Data from halite rich salt deposits in Poland and northern Germany was found to range from -0.18 to -0.12 ‰, and a parallel study (Eggenkamp *et al.*, 1995) reports δ^{37} Cl ranging from -0.58 to 0.00 ‰ for evaporate salts from the Zechstein of the Netherlands. The authors of Publication X conclude that the source of Baltic Sea salt, and thus its δ^{37} Cl signature, is most likely related to the extensive Palaeozoic salt deposits, located south of the Baltic Sea in the northern part of Central Europe. Therefore the δ^{37} Cl value of the Baltic would only vary by the degree of Ca-Mg salts (-0.45 ‰) versus halite (+0.15 ‰) dissolved from salt deposits and accumulated in the Baltic Sea basin during past times.

The δ^{37} Cl signature versus chloride concentration for a number of research sites on the Fennoscandian Shield is shown in Figure 9. The most concentrated deeper samples at each site of the Fennoscandian Shield plot in distinct and separate fields on the δ^{37} Cl versus Cl diagram. As quite different lithological units are involved (cf. Figure 11), certain kind of lithological control on the δ^{37} Cl signatures seems likely. However, without additional data for the δ^{37} Cl signatures of host rocks and minerals at each site, the authors of Publication X are partly constrained as to speculation on the primary controls of the δ^{37} Cl values. The concept that a specific lithological unit may have a primary, magmatic or metamorphic chloride signature would appear to be viable. Many minerals such as amphiboles, micas and apatite have been shown to contain considerable concentrations of Cl found both in structural sites (OH-substitution) and as liquid inclusions (Kamineni, 1987). Additional work on continental versus ocean rocks (Eggenkamp, 1994) suggests that mafic rocks may have a heavier δ^{37} Cl signature than felsic rocks. Also, theoretical calculations on fractionation due to Cl volatilisation during volcanic activity suggests that considerable isotopic shifts of both volatiles/condensates and residual fluids may be possible (Kaufmann, 1989; Eggenkamp, op. cit.).

The more dilute groundwaters, found at shallow depths at many sites, show several types of mixing trends (Figure 9). Firstly, simple dilution by chloride-free groundwaters (line 3a), secondly mixing between a saline groundwater and dilute chloride bearing water with distinctly different δ^{37} Cl signatures (*e.g.* with Baltic Sea water, line 1), and thirdly mixing between different dilute groundwaters (line 3b). The

 δ^{37} Cl signature in many of the shallow groundwaters may be related to previous stages of the Baltic Sea. The present coastal zone and some inland areas of the Fennoscandian Shield where covered by seawater during the recent Litorina stage (7500-4500 BP) and by the more extensive Eemian Sea during the previous interglacial stage about 120 000 BP (*cf.* Eronen, 1974; Forsström and Eronen, 1985; Donner, 1985). During these stages seawater infiltration was possible at parts of the shield.



Figure 9. The δ^{37} Cl signature versus chloride coded for depth (deep/shallow, dividing line at 300 m) for a number of research sites on the Fennoscandian Shield. Numbers and lines represent possible mixing scenarios (Publication X).

Several aspects of shield groundwaters have been revealed using stable Cl isotopes:

- (1) The δ^{37} Cl signature of shield brines is variable and dominantly non-marine, neither present-day seawater nor standard mean ocean chloride (SMOC);
- (2) Canadian Shield waters generally have depleted δ^{37} Cl signature compared to SMOC and Fennoscandian Shield brines;
- (3) Fractionation of 37 Cl/ 35 Cl by primary processes such as magmatic/hydrothermal activity may be responsible for the distinctive δ^{37} Cl signatures associated with the most concentrated fluids at each site;
- (4) In Finland evidence exists for the modification of the δ^{37} Cl isotopic signature at some sites by mixing with Baltic Sea water and dilute glacial melt waters.

Most rock types and areas seem to have a unique δ^{37} Cl signature. However, the fact that signatures of the Baltic Sea and possibly older interglacial seawater can be identified from rocks of the Fennoscandian Shield would indicate that shield environments are susceptible to sea water/surface water infiltration during periods of favourable tectonic conditions *e.g.* during isostatic rebound.

Discussion and conclusions

Chemical characteristics of saline groundwaters

The chemical composition of some of the most saline groundwaters sampled from Finland are presented as Mg-Ca-Na-SO₄-Cl histograms in Figure 10, in comparison to ocean water. This figure includes groundwaters from very different lithological units.

The most saline site is Ju/Mi-116, which has a TDS value of 170 g/l and is located within the Miihkali serpentinite in Juuka, as is drill hole Ju/Mi-91, too (Samples 1 and 14). Both these groundwaters have similar ion ratios despite large differences in concentrations, and are clearly Na-dominant. Due to their high proportion of Na, the serpentinite groundwaters closely resemble the ocean water (Sample 11). The second most saline groundwater in Finland, from the arkosic sandstone of Satakunta at Pori (Sample 2, 120 g/l), is clearly Ca-dominant, and resembles some of the highly saline brines from the Canadian Shield (Frape and Fritz, 1987). The groundwaters from the Ylivieska and the Enonkoski drill holes (Samples 3 and 13) show mutually similar ion ratios and both samples have been taken from the gabbroic parts of Ni-critical maficultramafic intrusions. So far, this highly saline Na-Mg-rich groundwater of Ylivieska (80 g/l) seems to be quite unique, as such water has not been recorded from any other site, neither from the Fennoscandian nor the Canadian Shields (Frape and Fritz, *op. cit.*).

The next five sites in order of salinity (Samples from 4 to 8) are Ca-Na-Cl waters that all have approximately the same ion ratios and TDS values of similar order. The lithological units incorporate amphibolite and hornblende gneiss from the Kotalahti mine, amphibole gabbro from Hirvihaara, Mäntsälä, and pyroxene gabbro embedded in mica gneiss from Noormarkku, and calc-silicate rocks of the Outokumpu type formations from Juuka, Miihkali (two drill holes). All these rocks are characterised by Ca-rich minerals, particularly plagioclase, amphibole and pyroxene and, calcite and calc-silicate minerals as fracture infilling. One of the most saline groundwaters from Olkiluoto (Sample 10) resembles to some extent the groundwaters of the five sites mentioned above, but it has slightly higher proportions of Na. The Olkiluoto site is situated close to the Gulf of Bothnia, and its slightly elevated Na proportions may reflect a prolonged interaction with seawater. The most saline groundwater from the Hästholmen site in Loviisa displays elevated Na and Mg proportions (Sample 12). in that respect mimicking ocean water. The groundwater from the Jotnian shale-siltstone in Liminka additionally has pronounced proportions of SO₄ (Sample 9), and its chemical composition resembles relatively closely the composition of the ocean, with the exception of its high proportion of Ca.

In Figure 11 the Ca/Na versus Br/Cl relationships for saline groundwaters from nearly 40 sites in Finland are shown. The figure is based on the results collected during the Deep Groundwater Project and the hydrogeochemical project of the Outokumpu formation. Additionally, Figure 11 includes chemical data of groundwaters from the following drill holes: Kerimäki KRM/Hä-32, Liminka R-60 and Parainen R-311 (Nurmi *et al.*, 1988), Eurajoki, Olkiluoto OL-KR1 (Blomqvist *et al.*, 1992; Pitkänen *et al.*, 1992), Sievi, Syyry SY-KR1 (Pitkänen *et al.*, 1992), Loviisa, Hästholmen HHKR1 (Luukkonen *et al.*, 1999). Ocean and the Baltic Sea values are from Rankama and Sahama (1950) and Lahermo and Lampén (1987), respectively. Only samples from

the saline groundwater types of each drill hole are used, and samples clearly representing mixtures between different groundwater types have been omitted. Therefore a great part of the samples located within the interface between fresh and saline as well as between brackish and saline water bodies have been taken off.

In Figure 11, previous versions of which were shown in Blomqvist *et al.* (1993) and Ruskeeniemi *et al.* (1996), groundwaters from different rock types and lithological associations plot on discrete fields. For example, the groundwaters from the massive Miihkali serpentinite in Juuka (from six drill holes) form a distinct cluster (marked in green) and having Ca/Na and Br/Cl ratios close to those of ocean water. The maficultramafic intrusions of Perkkiönperä in Ylivieska, Enonkoski mine, Hälvälä in Kerimäki, Vammala mine and Suhanko in Ranua form another clearly defined group (marked in pink red) in which Br/Cl ratios are 2–3 times higher compared to those of the ocean. Pitkänen *et al.* (1993) points out that the groundwaters from the gabbro formation at Syyry plot in this field, too. Still higher Br/Cl ratios are found in the groundwater of the Jotnian shale-siltstone in Liminka (marked in dark green). The Ca/Na ratios of both of these latter groups are low, of the same order as in the groundwaters of the Miihkali serpentinite.

A major part of the sampled groundwaters, however, plot within a large field defined by elevated Ca/Na ratios from 0.5 to 1.6. This group (dominantly marked in light blue) includes groundwaters from most of the felsic rock types as mica schist and gneiss, also with calc-silicate mineral bearing interlayers, from various granitoidic rocks, and from hydrothermal altered rock types. Additionally, the groundwaters from the amphibolite-hornblende gneiss suite from Kotalahti (from the vicinity of the Jussi and Huhtijärvi ore bodies), from the small intrusion of pyroxene gabbro embedded in mica gneiss from Noormarkku, and from the amphibole gabbro in Mäntsälä plot within this field (all three marked with brown colour). Of these latter sites, the amphibole gabbro at Mäntsälä displays elevated Br/Cl ratios, of the same order as in the groundwaters from the mafic-ultramafic intrusions described earlier.

The highest Ca/Na ratios in groundwater are found in rock types that are mainly composed of quartz, feldspar and muscovite (sericite): in the Jotnian arkosic sandstone of Satakunta and in the volcanic-sedimentary quartz-feldspar schist at Tipasjärvi in Sotkamo (the field marked in orange in Figure 11).



Figure 10. Saline groundwaters in Finland (up to 170g/l). The upper diagram shows the concentrations of dominant cations and anions (eq/liter), while the lower diagram gives their proportional values. Location of drill holes, sampling depth and main lithology as follows: 1. Juuka, Miihkali Ju/Mi-116, 1020 m, serpentinite; 2. Pori, Pinomäki, Po-1, 600 m, arkosic sandstone; 3. Ylivieska, Perkkiönperä, R-313, 620 m, peridotite, olivine and pyroxene gabbro; 4. Juuka, Miihkali, Ju/Mi-114, 920 m, calc-silicate rocks and talc-chlorite schist; 5. Leppävirta, Kotalahti mine, vicinity of Jussi and Huhtijärvi ore bodies, Ktl-1088, 945 m. amphibolite and hornblende gneiss; 6. Mäntsälä, Hirvihaara, MHa-2, 855 m, amphibole gabbro; 7. Noormarkku, R-43, 575 m, pyroxene gabbro within mica gneiss. 8. Juuka, Miihkali, Ju/Mi-116, 520 m, calc-silicate rock; 9. Liminka, Tupos, R-60, 720 m, shalesiltstone with gypsum and anhydrite layers (Nurmi et al., 1988); 10. Eurajoki, Olkiluoto, OL-KR1, 750-1001 m, migmatitic mica gneiss with pegmatite and tonalite (Blomqvist et al., 1992; Pitkänen et al., 1992); 11. Ocean water (Rankama and Sahama, 1950; 12. Loviisa Hästholmen, HH-KR4 882.5-890.5 m, rapakivi granite (Luukkonen et al., 1999); 13. Kerimäki, Enonkoski mine La-375, 414 m, norite; 14. Juuka, Miihkali Ju/Mi-91, 610 m, serpentinite.



Figure 11. Ca/Na vs. Br/Cl molar ratios for deep saline groundwaters of different host rocks in Finland.

Implications for origin of salinity

With respect to the origin of salinity in crystalline rocks, water-rock interaction reactions during prolonged time scales under hydrological closed conditions have been favoured as the most likely process, as postulated for the Canadian and Fennoscandian Shield brines (Frape *et al.*, 1984, Frape and Fritz, 1987; Nurmi *et al.*, 1988; Publication I; Lamminen, 1995). Strontium isotope studies point to alteration of plagioclase (and other minerals *e.g.* apatite) as a major source for increased concentrations of the saline components in groundwaters (McNutt *et al.*, 1984; Publication IV; McNutt *et al.*, 1990), followed by the formation of secondary minerals in the rock or in fractures. Incursion and mixing of past/present Baltic Sea waters and/or past ocean water has been considered as another dominant mechanism of producing saline groundwaters (*cf.* Kankainen, 1996; Nordstrom, 1996; Lahermo and Lampén, 1987; Nurmi *et al.*, 1988; Smellie *et al.*, 1995; Laaksoharju *et al.*, 1999).

Additionally, many other external processes have been postulated of being involved in producing the saline waters (for an overview of this issue, *cf.* Nurmi *et al.*, 1988). More recently, freezing of sea water (Herut *et al.*, 1990) has also been proposed as a dominant process for producing Ca-Cl brines, typical for the Canadian Shield, in glaciated regions of the earth. This theory, however, has the severe drawback of not being able to satisfactory explain the lithologically controlled chemical variation of brines and highly saline groundwaters, that seem so evident for most of these groundwaters according to the data of the present study from the Fennoscandian Shield.

Based on results using δ^{37} Cl signatures, the following aspects of deep groundwater evolution were drawn with respect to the Fennoscandian Shield (Publication X):

- (1) The δ^{37} Cl signature of shield brines and highly saline groundwaters is variable and dominantly non-marine;
- (2) Fractionation of 37 Cl/ 35 Cl by primary processes such as magmatic/hydrothermal activity may be responsible for the distinctive δ^{37} Cl signatures associated with the most concentrated fluids at each site;
- (3) Strong evidence exists for the modification of the δ^{37} Cl isotopic signature of the groundwaters of the upper part of the bedrock by mixing of combinations of Baltic Sea and dilute glacial melt waters.

The conclusive summary of the Sr isotope study (Publication IV) indicates that saline groundwaters in crystalline rocks do not evolve as isolated small pockets with a restricted volume of rock, but may rather be created in more open systems in which lateral geochemical interaction extends over distances of at least hundreds of metres. The homogeneous bodies of water do not necessarily relate to the composition of the immediately adjacent rock, but may incorporate characteristic features of certain local geological units. As examples the mica schists and gneisses of the Outokumpu formation, with their associated metamorphosed black shales and calc-silicate rock interlayers, host Ca-Na-Cl groundwater that significantly differs with respect to proportions of anions and TDS values from the Ca-Na-Mg-Cl water of the deeper Mg-rich serpentinite body of the site.

Further on, the Sr isotope data for both of these groundwaters strongly points to non-marine origin for Sr (and other cations). Therefore it is proposed that alteration of plagioclase with the formation of sericite, is the most likely process to increase the dissolved load of the saline groundwaters, but apatite may also be involved. The involvement of fluid inclusions or interstitial grain-boundary salts can neither be excluded based on the present data. A pervasive alteration of the rock, *e.g.* alteration of part of plagioclase to sericite, would require long-term, large scale, or regionalscale processes and elevated temperatures.

The fluid inclusion study of fracture infilling calcites at OL-KR1 from Olkiluoto showed that 50 % of the studied samples had homogenisation temperatures > 150° C (up to 240° C) whereas the other 50 % had been crystallised at $70-100^{\circ}$ C (Publication IX). Mineralogical characterisation of the fracture infilling showed a large variety of hydrothermal minerals that gave convincing support for the measured homogenisation temperatures: Calcite was accompanied with albite, quartz, pyrrhotite, illite, laumontite-leonhardite, barite, fluorite, adularia and with the following clay minerals: kaolinite, montmorillonite, palygorskite, and paragonite. The amount of species and volume of fracture-infilling minerals proved to be quite impressive, indicating that significant volumes of fluid were mobilised and crystallised during the past hydrothermal (and slightly lower) temperatures. Part of the residual fluids were obviously also preserved as fluid inclusions or in voids or closed pockets associated with fractures and shear zones.

Rb/Sr dating of fracture-infilling illite gives important temporal constraints of the past hydrothermal system at Olkiluoto. Dating of three illite samples from OL-KR1 from depths of 362–615 m yielded model ages of 1350–1370 Ma, except for a sheared illite sample dated at 1030 Ma (O'Brien, 1992, in: Blomqvist *et al.*, 1992).

Based on the results of a study of Br/Cl ratios of six mafic--ultramafic rock formations from the Canadian and Fennoscandian Shields (Kamineni *et al.*, 1992), the Br/Cl ratios in rock samples varied generally from 4.0–6.7 (expressed as molar units). The two measurements from the mafic-ultramafic intrusion of Ylivieska yielded Br/Cl ratios of 6.2 and 6.7, respectively. These rock values are very similar to the Br/Cl ratios of the highly saline water from the Ylivieska drill hole (R-313), (Br/Cl: 5.5–6.8; with ratios down to 4.5 for the less saline waters) of Figure 11. As stated by Kamineni *et al.* (*op. cit.*), also the groundwaters of mafic-ultramafic rock suites of the Canadian Shield have similar, high Br/Cl ratios as observed in their host rocks. The results invariably point to rock-derived halogenides in the saline groundwaters and brines of the mafic-ultramafic intrusions.

The lithological control for the geochemical characteristics of some of the rock types are very pronounced. The saline groundwaters sampled from the five mafic-ultramafic intrusions in Finland display mutually similar Ca/Na and Br/Cl ratios (*cf.* Figure 11) despite huge differences in elemental concentrations and TDS values. The highly saline groundwater of R-313 at Ylivieska has a TDS of > 80 g/l whereas the groundwater from drill hole YP-128 of Suhanko intrusion at Ranua is dilute with a TDS of 0.5 g/l. Additionally, groundwaters from quite different rock types, but having Ca-rich minerals in common, such as plagioclase, amphibole, pyroxene and calcite, tend to have mutually similar main chemical features, as shown in Figure 10 for samples 4–8. In Figure 11 these groundwaters also form a coherent group and plot on

the lower half of the field occupied by felsic rocks. In this case the alteration of Carich minerals and the formation of secondary minerals is likely to be the crucial factor controlling the chemistry of the saline groundwaters.

It is plausible that the lithological signals produced during hydrothermal alteration have been preserved in the rock throughout their history, predominantly as "fluid inclusions of variable sizes", *i.e.* as fluid inclusions proper, as voids or void-type open spaces in the rock, and as closed pockets associated with fractures and shear zones. It is even possible that extensive "hydrofractured zones" generated by metamorphic dewatering, as shown for the Kola deep borehole (Kremenetsky and Ovchinnikov, 1986), have contributed to the characteristics of the present saline groundwaters in central part of Fennoscandian Shield. The deep groundwaters that have been sampled and presented in this study, just represent more or less strongly diluted fractions of these primordial hydrothermal or metamorphic fluids. Under such circumstances, the highly saline Na-Ca-Cl brine (TDS: 170 g/l) from the Miihkali serpentinite in Juuka may be the closest example to a primordial fluid that has been observed from the central part of the Fennoscandian Shield so far. In the upper part of the bedrock where the samples of present study have been collected, mixing of groundwaters is a process that continuously modifies the saline groundwaters, as shown for the Äspö site (Laaksoharju et al., 1999). Brines and highly saline groundwaters can therefore be expected only in especially well-isolated geological formations.

Implications for nuclear waste disposal

It can be postulated that isolation from the surface-close hydrological cycle is a prerequisite for the preservation of saline groundwaters in the bedrock. This point of view incorporates interesting potential applications with respect to the disposal of nuclear wastes in the bedrock. As saline groundwaters have been documented to have long residence times and are not associated with active meteoric water circulation, bedrock suites hosted by saline groundwaters could be considered as potential repository environments (Nurmi et al., 1988; Anttila, 1988; Publication II). Due to negligible flow rates, the risk of radionuclide transport to ground surface is small, also in the extreme conditions of canister failure. Additionally, the strongly reducing conditions associated with the saline groundwaters would contribute significantly in keeping many of the harmful radionuclides in an insoluble form. Therefore more detailed studies in saline water environments were recommended in Publication II. Presently, ten years later it is interesting to note that the extensive site-selection process for a repository of high-level nuclear waste in Finland has recently culminated in a statement by Posiva Oy that recommends the Olkiluoto site at Eurajoki as the first candidate for a future repository location. This site hosts saline groundwater at depth below 500 metres (Pitkänen et al., 1999).

The boundary between fresh and saline groundwater bodies in inland areas are frequently located at depths from 300 m to 600 m, and in coastal areas the boundary between fresh and brackish groundwater is often still closer to ground surface (*cf.* Figure 2). The geochemical stability around a future repository for high-active nuclear waste is generally considered an important issue. Therefore, it should primarily be targeted to locate the repository clearly within a single groundwater body and to avoid locations where the hydrogeochemical stability could be seriously disturbed during

future climate changes. Additional work to improve the understanding of mechanisms and processes related to glacial events are considered important in order to increase the demonstration credibility of the long-term performance of a future repository.

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