

POSIVA-96-04

On the origin and chemical evolution of groundwater at the Olkiluoto site

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June 1996

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ISBN 951-652-003-0
ISSN 1239-3096

The conclusions and viewpoints presented in the report are those of author(s) and do not necessarily coincide with those of Posiva.



Posiva-raportti – Posiva report

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Puh. (90) 2280 30 – Int. Tel. +358 0 2280 30

Raportin tunnus – Report code

POSIVA-96-04

Julkaisuaika – Date

June 1996

Tekijä(t) – Author(s) Petteri Pitkänen *, Margit Snellman ** Ulla Vuorinen * * Technical Research Centre of Finland ** Imatran Voima Oy	Toimeksiantaja(t) – Commissioned by Posiva Oy
Nimeke – Title ON THE ORIGIN AND CHEMICAL EVOLUTION OF GROUNDWATER AT THE OLKILUOTO SITE	
Tiivistelmä – Abstract <p>During the site selection programme for nuclear waste disposal, Teollisuuden Voima Oy has collected groundwater samples from boreholes drilled down to a depth of 1000 m. The former evolutionary interpretation of the Olkiluoto groundwater (e.g. Pitkänen et al. 1994) revealed three different end-member groundwater-types mixing in the bedrock due to the land uplift. These were ¹modern fresh rainwater in the upper part of the bedrock recharged since the island rose above sea level about 3 000-2 500 BP, ²brackish Na-Cl groundwater layer originating from the modern and former Baltic Sea at 100-500 m depth, and ³deep-occurring saline Ca-Na-Cl-type groundwater interpreted as a remnant of ancient hydrothermal processes on the basis of the Br/Cl ratio and stable isotopes of water.</p> <p>The latest comprehensive sampling from multipacked boreholes reveals new details of the brackish groundwater layer in particular. Na-Cl water enriched with SO₄ has been identified at a depth of 100-300 m. The salinity clearly exceeds the present value of the Gulf of Bothnia, whereas the Br/Cl ratio indicates a seawater origin. The ¹⁸O-²H values plot on a mixing line between the samples of the present Baltic (having the highest values at the site) and the group of fresh and other brackish water samples at the site, indicating warmer recharging conditions than today. Below this sulfate-rich layer, firstly Cl (salinity) and ¹⁸O are depleting with SO₄, but the Br/Cl ratio remains stable, reflecting the mixing with colder diluted water in the system. At greater depths, the ¹⁸O and Br/Cl ratio begins to increase with Cl towards the values of the most saline groundwaters (Cl > 20 000 mg/l).</p> <p>According to the chemical characteristics of the SO₄-rich water, it is most likely that it has infiltrated from the Litorina Sea, which was the only more saline stage (7 500-2 500 BP), with an estimated highest Cl content of about 6 500 mg/l (Kankainen 1986), and also a warmer period than the modern Baltic stage during the Holocene in the Gulf of Bothnia (e.g. Eronen 1990). The stage was about 2 °C warmer than today, and ¹⁸O of the Litorina Sea water could have been between -5.2 and -4.7 ‰. The ¹⁴C data of the SO₄-rich layer (20 - 35 pM) coupled with the young age of the overlying groundwaters (3-15 TU with 50-60 pM) support the age of the Litorina Sea. The lighter isotope content than in the modern seawater can be explained by the mixing with a colder, dilute pre-Litorina water, probably melt-water from the Weichselian ice sheet. According to the preliminary mixing calculations using Cl as a conservative tracer, the SO₄-rich layer would contain 55-70% water originated from the Litorina Sea and the rest would be glacial melt-water with ¹⁸O varying between -18 and -23 ‰. The chemistry suggests that the displacement of melt-water by heavy Litorina water decreases below the SO₄-rich layer. In the lower part of the brackish groundwater layer the changes in chemistry imply increasing mixing of saline end-member water. The deep location below the cold end-member and high ¹⁸O content indicate a preglacial origin for saline groundwater. However, the elevated Br/Cl and ²H/¹⁸O ratios do not favour seawater origin as the pre-Weichselian Eemian Sea, which may represent about same salinity as oceanwater during the previous interglacial period (Eronen 1990). As a final conclusion, hydrochemistry of Olkiluoto seems to contain a well developed profile of climatic changes from modern time through former Baltic stages in the area to preglacial times.</p>	
ISBN ISBN 951-652-003-0	ISSN ISSN 1239-3096
Sivumäärä – Number of pages 41 + Appendices	Kieli – Language English



Posiva-raportti – Posiva report

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Annankatu 42 D, FIN-00100 HELSINKI, FINLAND
Puh. (90) 2280 30 – Int. Tel. +358 0 2280 30

Raportin tunnus – Report code

POSIVA-96-04

Julkaisu-aika – Date

Kesäkuu 1996

Tekijä(t) – Author(s) Petteri Pitkänen *, Margit Snellman ** Ulla Vuorinen * * Valtion teknillinen tutkimuskeskus ** Imatran Voima Oy	Toimeksiantaja(t) – Commissioned by Posiva Oy
Nimeke – Title OLKILUODON POHJAVESIEN ALKUPERÄ JA KEMIALLINEN KEHITYS	
Tiivistelmä – Abstract <p>Aiemmat pohjavesikemian tulokset (esim. Pitkänen et al. 1994a) ovat osoittaneet koostumukseen vaikuttaneen voimakkaasti kolme eri päätejäsen vesityyppiä, jotka ovat sekoittuneet keskenään vaihtelevissa suhteissa maankohoamisen seurauksena. Näistä vesityypeistä nuorin on kallion yläosassa vaikuttava sadevesi, jota on suotautunut pohjavedeksi siitä lähtien, kun saari on noussut meren pinnan yläpuolelle n. 3000 - 2500 vuotta sitten. Nykyinen ja aiemmat Itämeren vedet korostuvat 100 - 500 m:n syvyydessä tavattavassa Na-Cl-tyypin murtopohjavedessä ja sen alapuolella olevan suolaisen Ca-Na-Cl-tyypin pohjaveden on tulkittu sisältävän alunperin hydrotermisen toiminnan tuloksena muodostuneita suoloja.</p> <p>Viimeinen, merkittävästi aiempaa täydellisempi näytteenotto monitulpatuista rei'istä toi esiin uusia yksityiskohtia erityisesti murtopohjaveden kerroksesta ja siinä vaikuttavista päätejäsen vesityypeistä. 100 - 300 m:n syvyydessä on tavattu Na-Cl-tyypin pohjavesi, jota leimaa poikkeuksellisen korkea SO₄- ja Mg-pitoisuus ja jonka suolapitoisuus ylittää selvästi nykyisen Selkämeren suolaisuuden. Br-Cl-suhde vastaa kuitenkin meriveden koostumusta ja veden stabiilien isotooppien koostumus asettuu kallion yläpuolisen osan makeiden ja vähäsuolaisten pohjavesien sekä ja nykyisen meriveden väliselle sekoittumissuoralle viitaten osaltaan lämpimämpiin suotautumisolosuhteisiin kuin nykyään. Sulfaattirikkaan kerroksen alapuolella ensivaiheessa Cl, ¹⁸O ja SO₄ köyhtyvät Br-Cl-suhteen pysyessä vakiona, mikä viittaa makean, kylmien olosuhteiden veden sekoittuneen systeemiin. Seuraavassa vaiheessa ¹⁸O, Br-Cl-suhde ja Cl alkavat selvästi rikastua kohti kaikkein suolaisimman pohjaveden arvoja.</p> <p>Sulfaattirikkaan pohjavesikerroksen kemiallisten ominaisuuksien perusteella tulkitaan sen sisältävän huomattavan määrän muinaisesta Litorina merestä suotautunutta vettä 7500 - 2500 vuotta sitten. Tämä Itämeren vaihe oli jääkauden jälkeen Suomen rannikkoalueella ainoa nykyistä tilannetta suolaisempi merivaihe ja myös ilmastoltaan lämpimämpi vaihe kuin nykyinen. Sulfaattirikkaan pohjaveden liuennun karbonaatin ¹⁴C pitoisuus, joka on 20 - 35 pM, vastaa ajaksi muutettuna Litorina meren ikää, koska sen yläpuolella olevien tritiumpitoisuuksiensa perusteella nuoriksi (alle 40 vuotta) tulkittujen pohjavesien ¹⁴C on 50 - 60 pM. Nykyistä merivettä keveämpi happi-isotooppikoostumus tulkitaan olevan seurausta raskaan, Litorina meriveden tunkeutumisesta ja sekoittumisesta aiemmin suotautuneeseen kylmään, mahdollisesti jään sulamisvettä sisältävään pohjavesikerrokseen. Alustavat sekoittumislaskelmat viittaavat sulfaattirikkaan kerroksen sisältävän 55 - 70 % Litorina merestä peräisin olevaa vettä ja loppu olisi glasiaalista sulamisvettä, jonka ¹⁸O koostumus tällöin vaihtelisi -18 ja -23 % välillä. Sulfaattirikkaan pohjavesikerroksen alapuolella Litorina meren vaikutus asteittain vähenee ja vastaavasti sulamisveden kasvaa. Murtopohjavesivyöhykkeen alaosassa tapahtuvat kemialliset muutokset osoittavat suolaisen pohjavesityypin vaikutuksen kasvusta. Suolaisen veden esiintyminen kylmän vaiheen pohjavesien alapuolella ja jälleen kohonnut ¹⁸O pitoisuus viittaavat vesityypin preglasiaaliseen alkuperään. Murtovesiin nähden selvästi kohonnut Br-Cl- ja ²H-¹⁸O-suhteet eivät kuitenkaan tue Veiksel-jäätiköitymistä edeltävään Eem-meriperäiseen veteen, jonka suolaisuus ilmeisesti vastaisi suolaisen pohjaveden arvoja. Olkiluodon pohjavesikemia näyttää sisältävän erinomaisen läpileikkauksen viimeiseen Veiksel-jäätiköitymiseen liittyneistä ilmaston ja meren pinnan vaihteluista.</p>	
ISBN ISBN 951-652-003-0	ISSN ISSN 1239-3096
Sivumäärä – Number of pages 41 + liitteet	Kieli – Language Englanti

PREFACE

The geochemical modelling of the groundwater in the Olkiluoto area started in 1990 at the Technical Research Centre of Finland (VTT), the first step being reported by Pitkänen & Snellman (1990). The geochemical modelling work continued as team work by a group named GEOKEM, formed by scientists from two laboratories at VTT (VTT Chemical Technology, Environmental Technology, and VTT Community and Infrastructure, Rock and Environmental Engineering) and the power company Imatran Voima Oy (IVO) (Pitkänen et al. 1992 a,b). A preliminary model for the probable processes responsible for the evolution of the groundwater at Olkiluoto was presented in 1994 (Pitkänen et al. 1994a). In this report the previous geochemical interpretations on the origin and the evolution of the groundwater at Olkiluoto have been specified based on the new more comprehensive areal data gained during the present detailed site investigation programme.

The contact persons in this study were Juhani Vira from Posiva, Petteri Pitkänen and Ulla Vuorinen (Hilkka Leino-Forsman) from VTT and Margit Snellman from IVO.

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1 INTRODUCTION

Since 1987 the Finnish crystalline bedrock has been studied for the final disposal of spent nuclear fuel. Preliminary site investigations were performed at five sites, of which three sites were selected in 1992 for detailed site investigations (TVO 92). The three sites are Kivetty, Romuvaara and Olkiluoto.

Knowledge on the quality of Olkiluoto groundwater and its chemical interactions have been based on the data gathered during the samplings in 1980 - 1992. In addition to the data gained during the preliminary investigation phase at Olkiluoto (Lampén & Snellman 1993), data has also been obtained from the bedrock investigations for the final repository for low- and intermediate-level reactor waste at Olkiluoto (Pääkkönen 1985, Lampén 1985, Helenius 1991). This data is deficient with regard to its adequacy in depth and especially in the areal completeness. The deep boreholes (500 - 1 000 m) at Olkiluoto, were equipped with multipackers in 1991 - 1992. During the present investigation programme, the areal coverage was significantly improved by the new data on the groundwater samples from the deep multipackered boreholes. Furthermore, the analysis programme was extended in respect of the former one to include more analyses, especially of isotopes and gaseous species (compare Lampén & Snellman 1993, Ruotsalainen et al. 1994, Snellman et al. 1995a). The currently available data gives new insight into the areal picture and the quality of the groundwater, and thus requires the specifying of the previous geochemical interpretations of the origin and the evolution of the groundwater at Olkiluoto (e.g. Pitkänen et al. 1994a).

1.1 Hydrogeological background

The Olkiluoto site at Eurajoki is an island on the coast of the Gulf of Bothnia (Figure 1-1). The area is flat and the highest point is 18 m above the sea level (m.a.s.l.). The site is situated in that part of the Fennoscandian shield where the modern postglacial land uplift is moderate, about 6 mm per year. The latest glaciation in southern Finland lasted over 50 000 years. The ice sheet retreated from the Olkiluoto site about 10 000 years ago leaving the area subaquatic. According to the recent results of Eronen et al. (1995), the highest point of the island rose above sea level about 3 000 years ago.

The soil cover is thin, varying between 2 - 5 m consisting of till and minor peat bogs. Granite-veined micagneiss bedrock outcrops are frequent. The detailed structural information of the site is presented in the report by Saksa et al. (1993).

Calcite, different clay minerals and pyrite are the most common fracture minerals (Lindberg & Paananen 1991). The weathering activity of infiltrating recharge water is consumed in shallow depths according to the fracture mineralogy. However, the detailed investigations of Blomqvist et al. (1992) and Frapé et al. (1992) indicate low-temperature, relatively young (< 300 000 a) water-mineral interaction to cover the depths down to 800 m on the grounds of calcite precipitates and pyrite coating on young calcites. The former hydrogeochemical modelling study (Pitkänen et al. 1994a) also suggests significant water-rock interaction continuing down to 600 m in the modern hydrogeological situation.

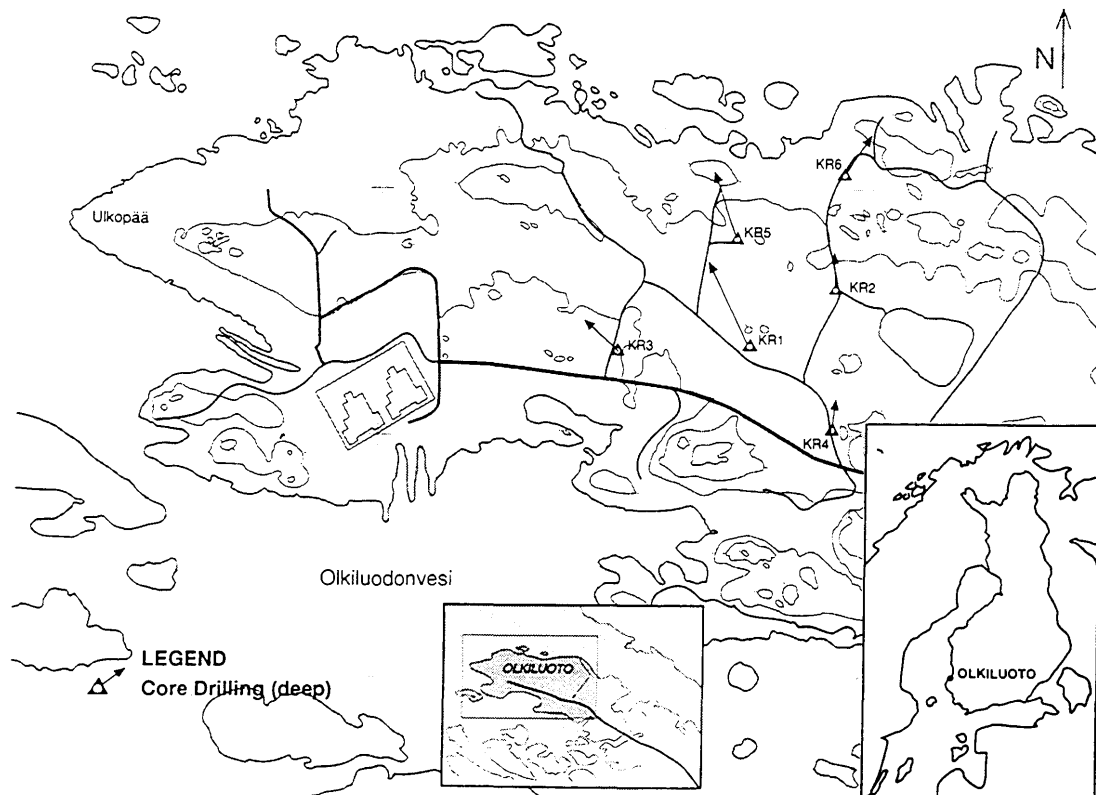


Figure 1-1. Location of the Olkiluoto site.

2 GROUNDWATER CHEMISTRY AT OLKILUOTO

The results on former groundwater chemistry at Olkiluoto have been presented in several earlier reports (Lampén & Snellman 1993, Pitkänen et al. 1992a, 1992b, 1992c, Pitkänen & Snellman 1990, Pitkänen et al. 1994a, Blomqvist et al. 1992, Laaksoharju et al. 1994, Wickström & Helenius 1990, Snellman et al. 1995a). The analysis results from 1987 - 1992 on the most representative samples used in the first interpretation are presented in Appendix 1.

A preliminary model on the evolution of the groundwater at Olkiluoto and the probable processes involved has been drawn up, Figure 2-1 (Pitkänen et al. 1994a, b, c), and is principally used as the basis for the present study.

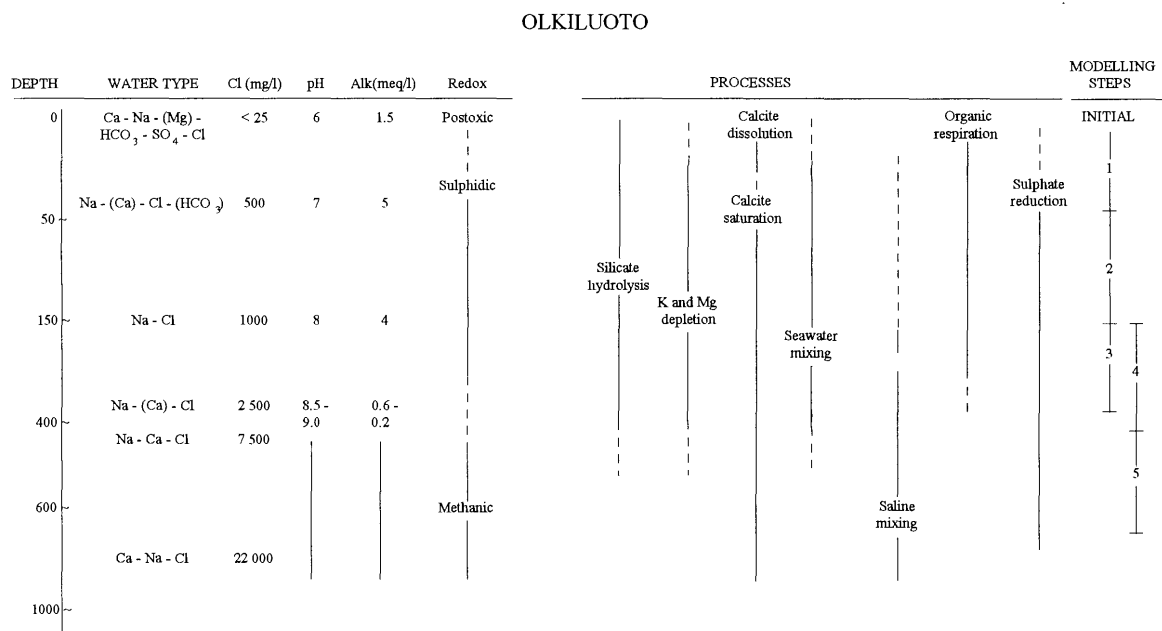


Figure 2-1. Schematic presentation of the variations in groundwater chemistry at given depths at Olkiluoto including the parameters and processes involved (Pitkänen et al. 1994 a, c).

The model indicates that the salinity of the different groundwater-types in present ambient temperature conditions is mainly due to inmixing of Baltic-type seawater and deep saline groundwater to the water infiltrating into the bedrock. The increase in salinity in the groundwater at shallow depths of the bedrock seems to be controlled by the interaction of groundwater and the bedrock, whereas deeper such an influence is only a minor one, but the interaction is, however, important in regulating the pH and redox conditions. The groundwater is buffered slightly basic by the dissolution and

precipitation of calcite as well as the hydrolysis of silicates. The redox conditions seem to be controlled by the anaerobic microbially mediated reduction of sulphate to sulphide while organic carbon (both biogenic carbon and methane) is simultaneously oxidized.

2.1 Representativity of the groundwater samples

The first geochemical interpretation (Pitkänen et al. 1994a,c) was based on the most representative groundwater samples from the samplings from 1987 - 1992.

To prevent open-hole effect and the mixing of different groundwaters the deep boreholes were divided by packers into seven sections in 1991-1992. The deepest section is coded as T1, the following one as T2 and the uppermost one as T7 (Appendix 2).

During the period 1993 - 1995, the criteria for the groundwater sampling (Table 2-1) from the multipackered boreholes (OL-KR1...KR5) were: sufficient exchange of water in the packed-off section, stability of the field measurements, small flushing water contamination, as well as small tritium content (Ruotsalainen et al. 1994). In addition to these requirements, also possible packer leakages and contamination by the cemented upper part of the borehole, as well as the effect of the pumping rate were considered when assessing the representativity of the groundwater samples.

Each sampling was preceded by a pumping period of 5 weeks on average, during which the water in the packed-off section was changed about 8 times.

Contamination by the flushing water was very small in all samples. Generally the flushing water content was about 0.2 - 0.6% except for samples OL-KR1/T4 from borehole KR1, OL-KR3/T3 and OL-KR3/T4 from borehole KR3, and OL-KR4/T3 from borehole KR4, which all contained over 2% of flushing water (Table 2-1). The tritium content of the samples was also very small, falling below the detection limit (7 - 12 TU) of the direct measurement, except for one sample, OL-KR2/T7, from the upper part in borehole KR2, which contained a more pronounced amount of tritium, about 10.7 TU. Especially the brackish groundwater samples and the samples from borehole KR3 had very low tritium contents, often below the detection limit (<0.8 TU) of the enrichment method. In borehole KR1 the measured tritium values are on average between 2 and 6 TU, which is an indication of the samples containing younger water. Conversely, the tritium content of the groundwater samples of relatively low salinity from the upper part of the rock can be considered natural, whereas tritium contents found in the highly saline deep groundwater

samples are most probably a consequence of the investigations disturbing the groundwater system.

The charge balance errors of the groundwater samples are usually within $\pm 5\%$, only in a few samples this specified quality range was exceeded.

Contrary to the expectations, the results on the measured field values of Eh and dissolved O₂ often indicated oxidizing conditions, which gave reason to suspect technical problems in the field instrumentation. While this report is being written, the possible technical defects are being investigated and thus the results and conclusions regarding the redox conditions and species in this report have to be considered preliminary. Based on some preliminary tests, it can be concluded though, that the present instrumentation may have caused too low pH values. Possible additional effects, depending on the chemistry of the groundwater sample, are the too high Eh values, as well as a diminished amount of sulphide due to the diffusion of the atmospheric gases (CO₂, O₂) through the polyamide sampling tube (Snellman et al. 1995b). The preliminary tests with the instrumentation also indicated that sulphide is such a strong buffer that problems with the instrumentation may not, after all, be seen in the measured Eh values. Nevertheless, these technical problems may have influenced other redox parameters and the analysis results of parameters sensitive to atmospheric contamination, especially if the concentration level is low, e.g., the alkalinity of the saline groundwater samples.

Leakage from the protection tube in the uppermost section (inmixing of more surficial water during sampling) may have influenced some samples, especially samples OL-KR1/T2, OL-KR3/T1 and OL-KR4/T4 (Niva & Ruotsalainen, 1995). The influence on samples OL-KR1/T2 and OL-KR4/T4 is particularly strong and is observed in their low-chloride concentration compared to the samples from the neighbouring sections. Also the tritium level of the affected samples is somewhat elevated. The high-chloride concentration and a very low H-3 content of sample OL-KR3/T1 do not indicate any remarkable contamination, but, on the other hand, the pumping rate was very low (6 ml/min) and may have had an effect on the measured pH (low) and Eh (high) value which cannot be corrected with present knowledge. The representativity of the deepest groundwater sample OL-KR1/T1 has also been affected by the very low pumping rate (0.3 ml/min) due to the dense rock. The low pumping rates have not only influenced the measured field parameters but also the other parameters sensitive to atmospheric contamination. Cementation of the upper part of borehole KR4 has influenced sample OL-KR4/T7.

Table 2-1. Basic data on the parameters indicating representativity of the groundwater samples taken between 1993 and 1995 from the multipacker boreholes.

Borehole/ packer interval	Date	Depth (m)	Structure	Con- nec- tions and leaks **)	Pump- ing rate ml/min	Water type	Classifi- cation	TDS*) mg/l	Electr. balance %	Flush- ing water %	pH	EhPt (mV)	Cl (mg/l)	H3 (TU)	C-14 PM
OL-KR1/T7	11.7.94	76-126	R11		20.0	Na-Cl-HCO ₃	Brack.	1370	-0.34	0.54	7.80	100	415	6.20	63.3
OL-KR1/T7	29.3.95	76-126	R11		16.3	Na-Cl-HCO ₃	Brack.	1390	0.68	0.4	7.60	120	430	5.60	63.5
OL-KR1/T6	24.10.94	126-170	R14		25.0	Na-Cl-HCO ₃	Brack.	1070	-3.79	1.4	8.30	120	250	5.80	57.0
OL-KR1/T5	29.8.94	301-392			33.3	Na-Cl-HCO ₃	Brack.	1120	-1.68	1.4	8.36	130	275	5.50	57.2
OL-KR1/T4	14.12.94	497-552	R10		13.3	Na-Ca-Cl	Saline.	14450	0.76	2.2	7.80	-100	8800	2.10	52.8
OL-KR1/T3	15.4.93	612-618	R15		16.0	Na-Ca-Cl	Saline.	20700	-8.37		8.50	-60	13500	<12	
OL-KR1/T3	9.1.95	612-618	R15		17.5	Na-Ca-Cl	Saline.	23750	-1.26	0.6	8.20	-160	14800	3.00	42.4
OL-KR1/T3	15.2.95	612-618	R15		20.0	Na-Ca-Cl	Saline.	23900	-0.57	0.6	8.30	-270	14800	2.80	43.6
OL-KR1/T2	28.9.94	739-804	R9	****	20.0	Na-Cl	Brack.	2040	-4.88	<0.2	8.10	140	940	6.10	
OL-KR1/T1	20.3.95	804-1001	R1,R8		0.3	Na-Ca-Cl	Saline.	26700	2.27	<0.2	7.10 ^D	340	16300	<0.8	79.8
OL-KR2/T7	24.10.94	51-91	R17		5.0	Na-Cl-HCO ₃	Fresh	900	3.69	<0.2	8.00	100	210	10.7	
OL-KR2/T6	9.1.95	91-151			26.6	Na-Cl	Brack.	2800	-5.14	<0.2	8.00	100	1500	2.20	46.8
OL-KR2/T5	29.8.94	196-231	R17		24.0	Na-Cl	Brack.	6500	0.76	0.6	7.70	130	3590	<0.8	26.4
OL-KR2/T4	15.2.95	231-256	R20		16.6	Na-Cl	Brack.	8050	-2.96	0.6	7.50	190	4600	<0.8	28.1
OL-KR2/T3	28.9.94	281-305		HHHH	16.0	Na-Cl	Brack.	7300	-1.09	0.6	7.80	-30	4300	1.30	36.2
OL-KR2/T2	14.12.94	305-350		HHHH	16.3	Na-Cl	Brack.	7000	1.5	0.6	8.45	-210	4200	<0.8	45.8
OL-KR3/T7	29.8.94	86-141	R10		15.0	Na-Cl	Brack.	5900	-2.78	1.6	7.90	120	3420	0.90	18.3
OL-KR3/T6	9.1.95	141-231	R10		23.3	Na-Cl	Brack.	4900	-0.08	<0.2	7.93	-200	2800	<0.8	8.0
OL-KR3/T5	13.3.95	231-261	R10		21.6	Na-Cl	Brack.	4600	1.36	0.8	8.20	-200	2860	<0.8	10.5
OL-KR3/T4	28.9.94	311-356	R10	HHHH	14.0	Na-Cl	Brack.	5300	-3.90	4.2	8.15	50	3250	2.4	
OL-KR3/T3	15.2.95	356-406	R10,R9		21.6	Na-Cl	Brack.	5500	-2.73	2.2	8.00	-120	3400	<0.8	
OL-KR3/T2	28.11.94	416-461	R10	HHHH	11.0	Na-Cl	Brack.	6500	0.16	0.6	8.30	-5	3900	<0.8	22.5
OL-KR3/T1	1.8.94	461-502		****	6.0	Na-Cl	Brack.	9600	-0.68	1.5	7.30	100	5865	0.90	34.7
OL-KR4/T7	11.7.94	72-107	R19		25.0	Na-Cl	Fresh	900	0.12	0.8	9.80	160	368	3.10	49.1
OL-KR4/T6	24.10.94	107-132	R12		8.3	Na-Cl	Brack.	2900	0.23	<0.2	7.90	100	1400	1.30	33.9
OL-KR4/T5	13.3.95	132-192	R12		26.6	Na-Ca-Cl	Brack.	8000	-0.33	<0.2	7.55	140	4500	<0.8	21.4
OL-KR4/T5	9.1.95	132-192	R12		16.6	Na-Ca-Cl	Brack.	8020	-0.13	<0.2	7.80	-50	4500	<0.8	22.9
OL-KR4/T4	28.9.94	282-337	R18	****	8.0	Na-Ca-Cl	Brack.	4300	4.18	0.8	7.80	100	2330	3.20	40.5
OL-KR4/T3	14.12.94	357-382	R15		7.0	Na-Ca-Cl	Saline.	10200	1.5	6.2	8.20	-20	6200	2.30	
OL-KR5/T7	29.8.94	61-91		HHHH	25.0	Na-Cl	Brack.	2100	-3.46	<0.2	7.40	250	910	1.70	41.5
OL-KR5/T6	9.1.95	106-141	R10	HHHH	31.6	Na-Ca-Cl	Brack.	6800	-2.4	<0.2	7.25	200	3800	<0.8	25.1
OL-KR5/T5	28.9.94	191-261	R10,R20		16.0	Na-Ca-Cl	Brack.	7420	-3.21	0.6	7.65	180	4300	1.10	34.8
OL-KR5/T4	28.11.94	261-296	R10,R2		28.3	Na-Cl	Brack.	7000	-0.86	0.4	7.80	-10	4000	1.20	27.9
OL-KR5/T2	24.10.94	376-446	R1		28.3	Na-Cl	Brack.	8100	4.72	0.6	7.60	-100	4700	<0.8	59.7
OL-KR5/T1	18.5.93	446-559	R17,R21		50.0	Na-Ca-Cl	Saline.	13200	7.26	0	8.95	-195	7730	<12	
OL-KR5/T1	1.8.94	446-559	R17,R21		11.3	Na-Ca-Cl	Saline.	12800	3.48	0.3	8.50	-250	7700	2.70	37.9
OL-KR5/T1	29.3.95	446-559	R17,R21		10.7	Na-Ca-Cl	Saline.	13600	-1.2	<0.2	8.30	-270	8500	1.30	39.2

*) TDS < 1000 mg/l Fresh groundwater= Fresh
 1000<TDS<10 000 mg/l Brackish groundwater=Brack
 TDS> 10 000 mg/l Saline groundwater=Saline

D) for KR1/T1 the pH value was measured in the laboratory (field pH was about 6.1)

**)

HHHH

Connection between the packed-off sections

Possible leakage from the protection tube in the uppermost section

2.2 Brackish groundwater at Olkiluoto

Based on both the results of groundwater chemistry (1989 - 1995) and the first interpretations (Pitkänen et al. 1992, 1994a, Lampen & Snellman 1992, Snellman et al. 1995a) *brackish* groundwater ($1\ 000\ \text{mg/l} < \text{TDS} < 10\ 000\ \text{mg/l}$) is encountered at Olkiluoto with a maximum chloride content of $6\ 000\ \text{mg/l}$ (Figure 2-2) at depths varying between 40 m and 500 m. The deepest brackish groundwater has been met in boreholes KR3, KR4 and KR5. The brackish groundwater samples which were included in the geochemical modelling (Pitkänen et al. 1994a) are samples 10, 11, 14, 15, 17 - 20, 22, 23 and 36-37 in Appendix 1.

The brackish groundwater samples are mainly of Na-Cl type and have slightly basic pH values varying between 7.3 - 8.0. Compared to the results from former samplings, a more saline brackish groundwater has been found (Figure 2-2 and Appendix 1). The content of chloride varies up to $5900\ \text{mg/l}$, whereas the former Cl_{max} was $2600\ \text{mg/l}$. The apparent reason for this is the larger number of groundwater samples. Chloride contents are seen to increase up to around $3\ 000 - 4\ 000\ \text{mg/l}$ to the depth of 100 - 200 m and at the depth of 400 - 500 m another strong increase in chloride concentration is in evidence, which in fact occurs at an interpreted chemically metastable transition zone between the brackish and saline groundwater (Pitkänen et al. 1994a).

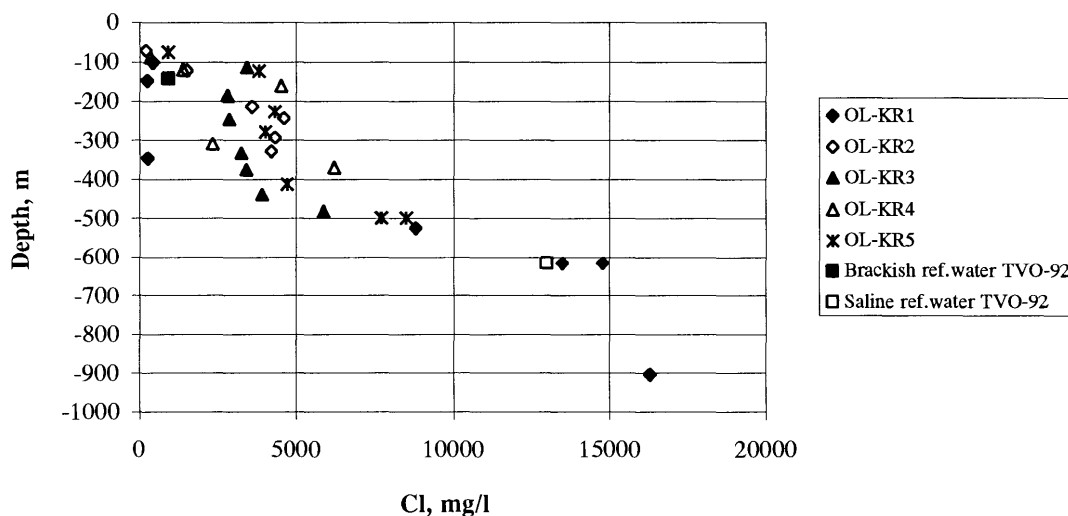


Figure 2-2 Chloride content versus depth of the groundwater samples at Olkiluoto (Depth is expressed as the average depth of the packed-off section in all Figures throughout the report. The two reference waters from Olkiluoto (brackish nr. 23 and saline nr. 24 in App.1) used in the TVO-92 performance assessment (TVO-92 1992) are also included in the Figures).

Data on the new samples complete the former data on Ca (Figure 2-3), Na (Figure 2-4), Br (Figure 2-5) and Cl. According to the mixing calculations (Pitkänen et al. 1994a), the groundwater samples contain seawater, resembling the present Baltic seawater, and the most saline brackish samples reflect minor inmixing of a deeper saline groundwater as well. Support of this interpretation is also obtained from the behaviour of the stable isotopes of water (Figures 2-6 and 2-7). Particularly cold infiltration conditions are indicated by the brackish groundwater samples from borehole KR3, from where also the measured C-14 values (Figure 2-13) indicate a long residence time.

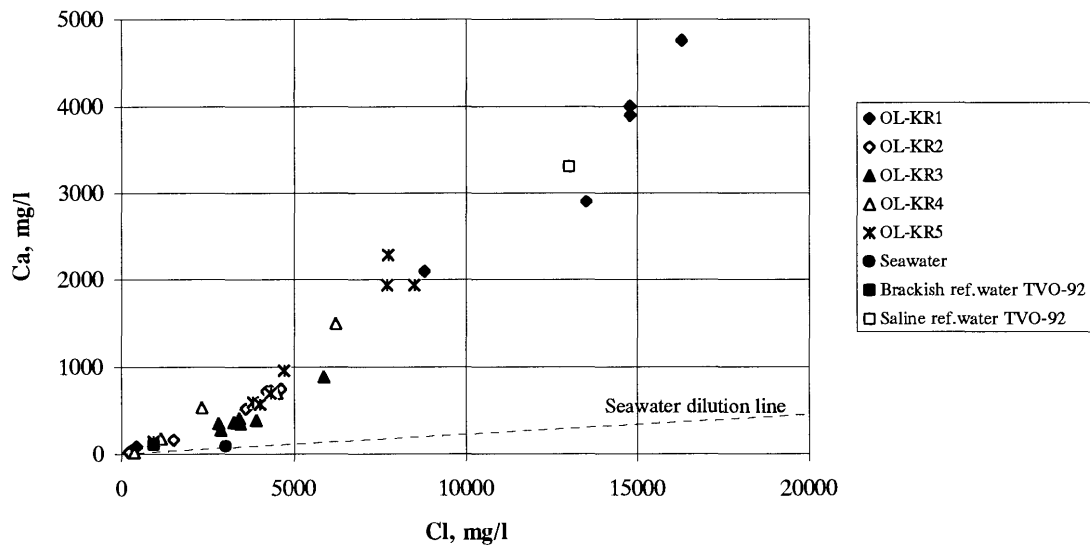


Figure 2-3. *Ca contents versus Cl concentrations of the groundwater samples at Olkiluoto. The seawater samples throughout the report refer to samples taken from the Gulf of Bothnia off shore at Olkiluoto.*

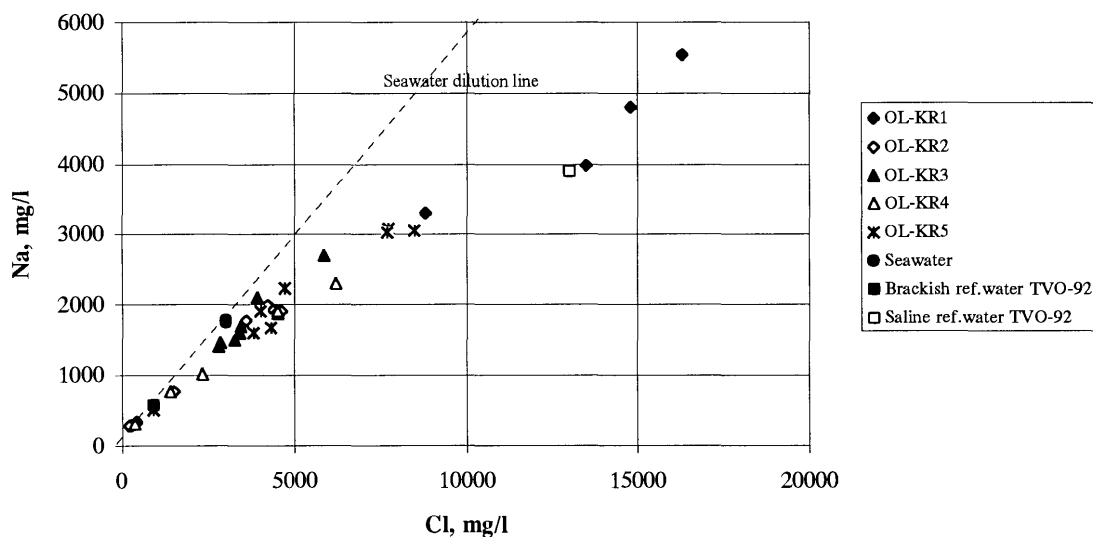


Figure 2-4. *Na contents versus Cl concentrations of the groundwater samples at Olkiluoto*

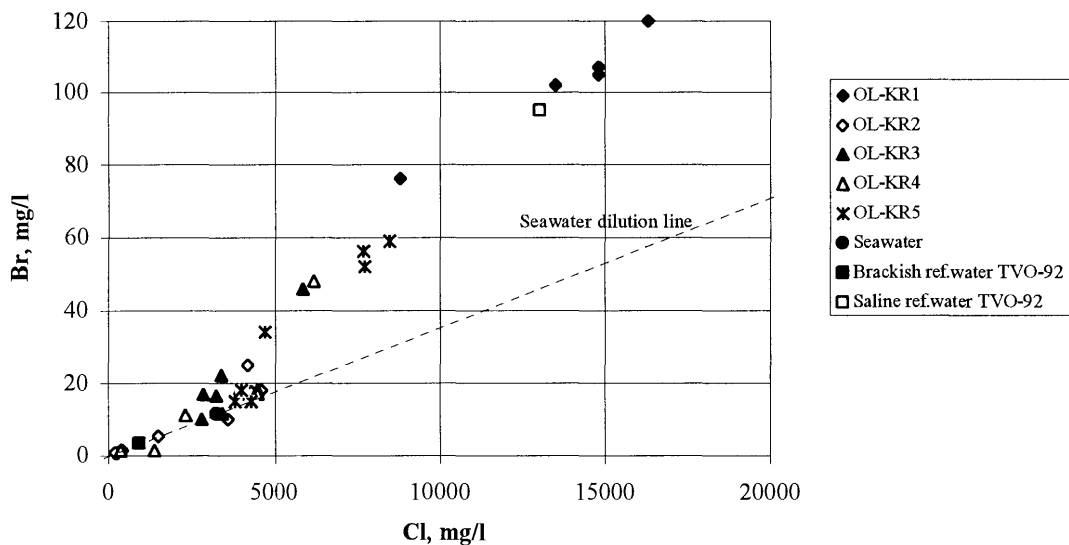


Figure 2-5. *Br contents versus Cl concentrations of the groundwater samples at Olkiluoto.*

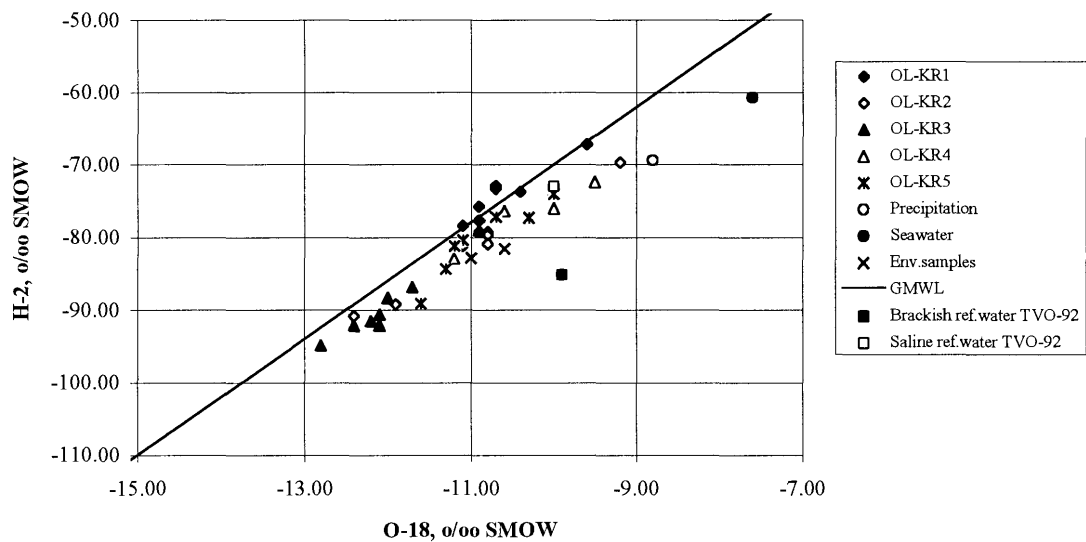


Figure 2-6. *$\delta H-2$ versus $\delta O-18$ of the groundwater samples at Olkiluoto. GMWL = Global Meteoric Water Line; $\delta H-2 = 8 * \delta O-18 + 10$ (Craig, 1961). (SMOW = standard mean ocean water).*

The behaviour of carbonate is probably mainly governed by calcite equilibrium, Figures 2-3, 2-8, 2-9, 2-10, 2-11, and 2-12 (Note! Only those samples which have not been affected by the leakage from the protection tube in the uppermost section or the slow pumping rate (KR1/T1) have been included in the figures). Calcite is in equilibrium or slightly oversaturated in brackish groundwater ($Cl < 6\,000$ mg/l). In the upper part of borehole KR1, alkalinity reaches the highest values in the most dilute brackish groundwater samples. The highest values are about 6.5 meq/l, which are distinctly higher

than the highest values measured (about 4.9 meq/l) during the samplings in 1989 - 1992. The alkalinity of the recharging waters is at the level of 0.3 meq/l.

Within the brackish groundwater zone at chloride contents between 3 000 - 5 000 mg/l, altogether very variable values for both $\delta\text{C-13}$ (-36...-3 ‰ PDB,) and C-14 (7...60 pM¹) (Figures 2-13 and 2-14) were measured, which indicate the origin of carbon to be both inorganic (calcite) and organic. They may also be a reflection of groundwaters mixing to a different degree, as well as the interaction between rock and groundwater. At these chloride concentrations remarkable variations are also seen in the contents of $\delta\text{O-18}$ (Figure 2-7).

According to the results on C-13, several brackish groundwater samples are clearly enriched compared to the recharge conditions (drilled wells Varvinnokka and Helmiranta: -19.8 ...-19.6 ‰ PDB², Tuominen 1994), which is an indication of calcite dissolution. For other brackish groundwater samples, the $\delta\text{C-13}$ (Figure 2-13) values and the remarkable decrease in alkalinity as well as the saturation of calcite suggest precipitation of calcite.

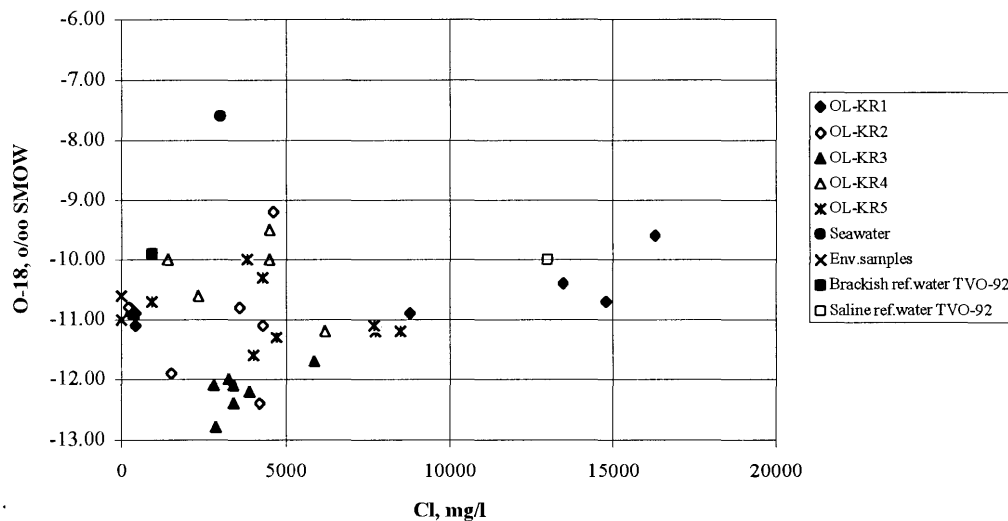


Figure 2-7. $\delta\text{O-18}$ contents versus Cl concentrations of the groundwater samples at Olkiluoto.

¹ pM = % modern, which is defined as the 95% activity of an NBS oxalic acid in the year 1950, that is before anthropogenic carbon was introduced

² $\delta\text{C-13}$ is reported as per mille difference from the PDB standard, a belemnite from the Cretaceous Pee Dee Formation, South Carolina

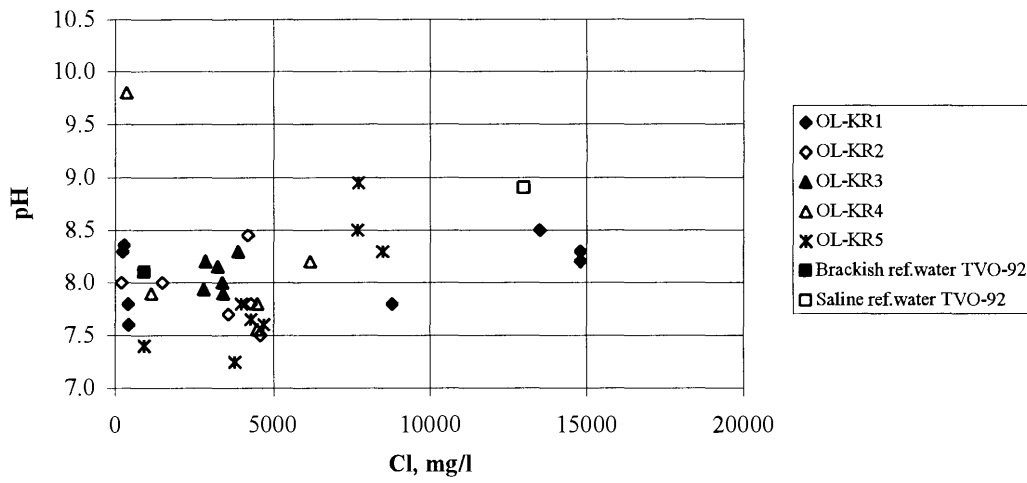


Figure 2-8. pH values versus Cl concentrations of the groundwater samples at Olkiluoto.

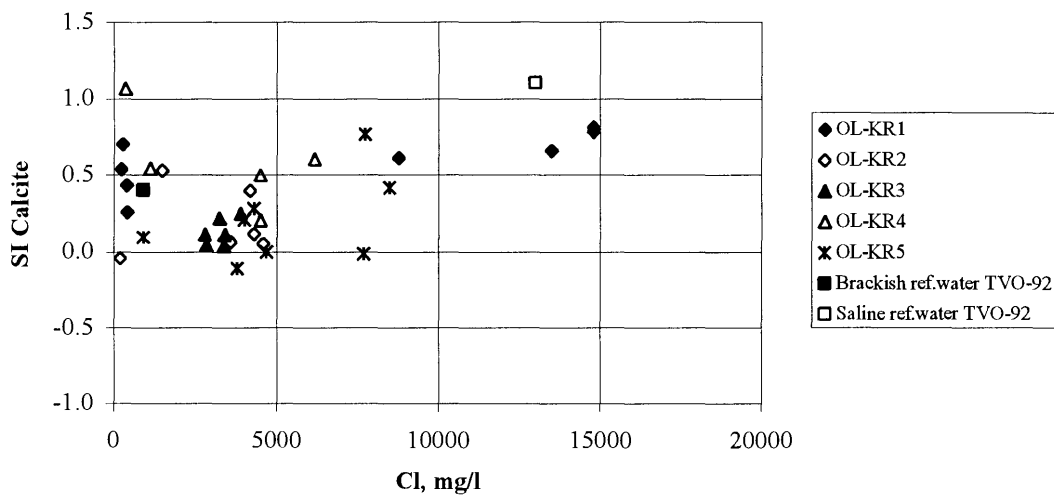


Figure 2-9 Calcite saturation indices versus Cl concentrations of the groundwater samples at Olkiluoto.

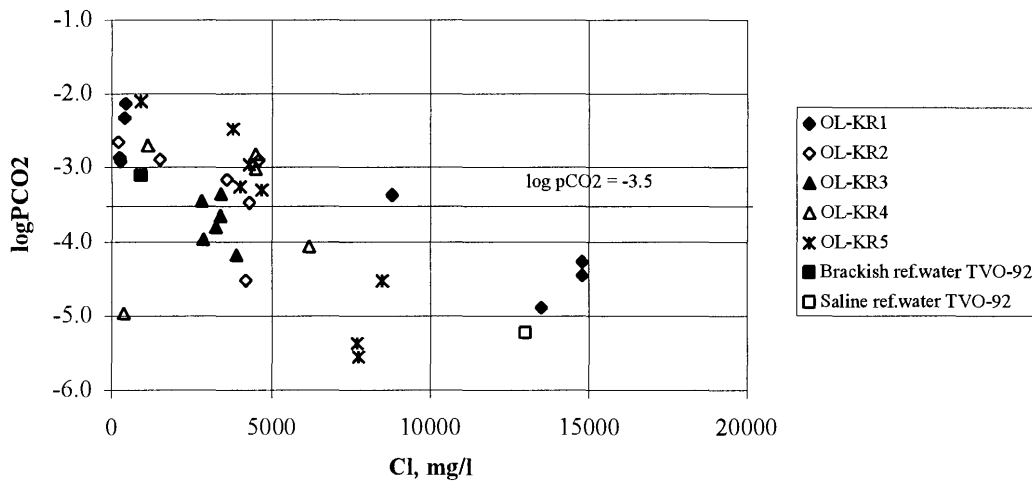


Figure 2-10. Partial pressure of carbon dioxide (calculated $\log pCO_2$) versus Cl concentration of the groundwater samples at Olkiluoto ($\log pCO_2 = -3.5$ refers to the atmospheric partial pressure of CO_2).

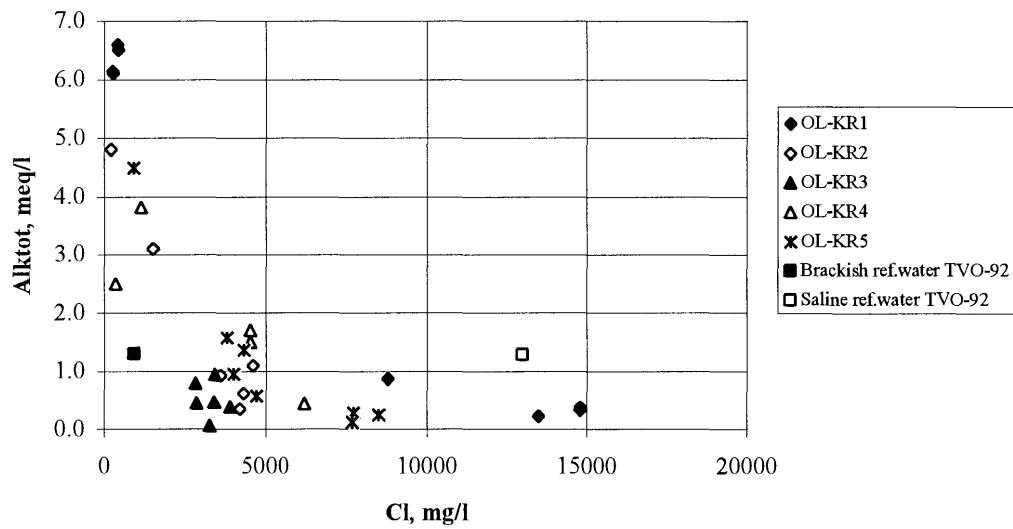


Figure 2-11. Total alkalinity versus Cl concentrations of the groundwater samples at Olkiluoto.

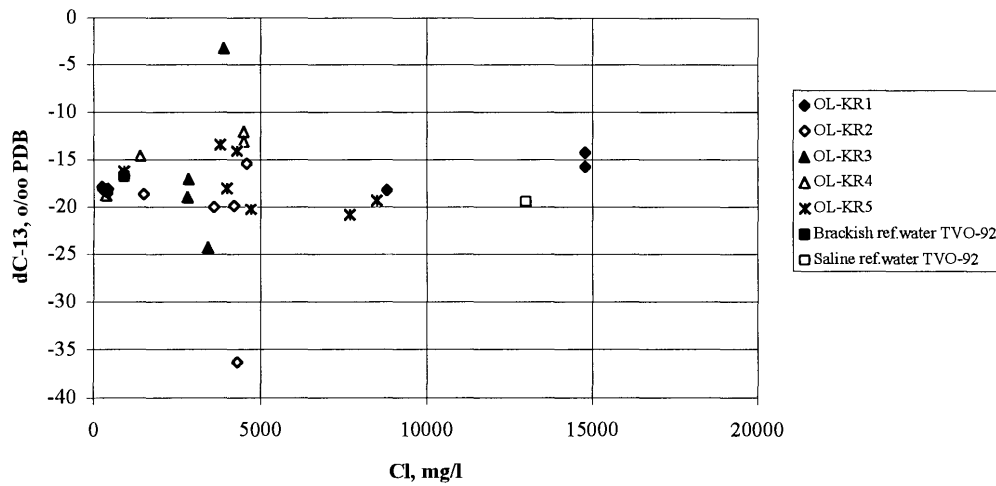


Figure 2-12 $\delta C-13$ contents versus Cl concentrations of the groundwater samples at Olkiluoto.

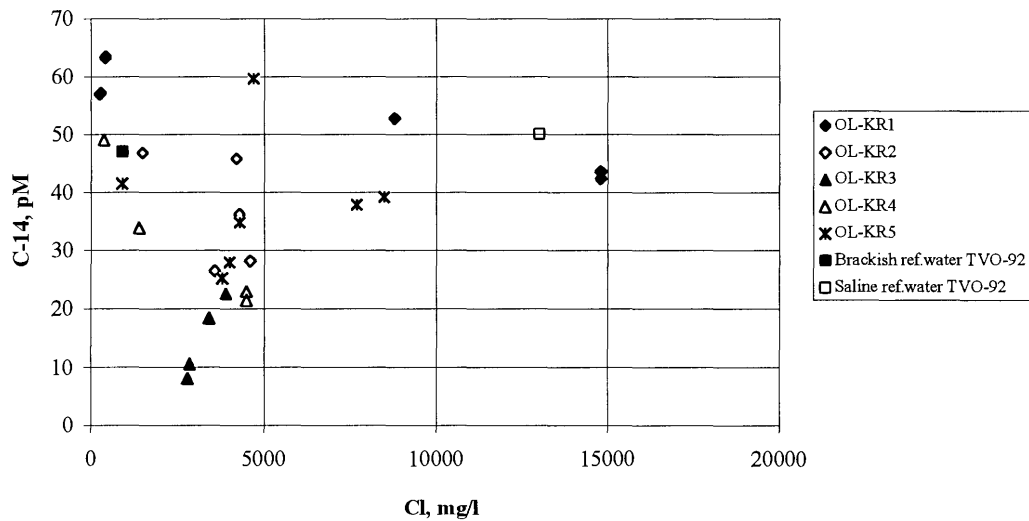


Figure 2-13. C-14 contents versus Cl concentrations of the groundwater samples at Olkiluoto.

In the fresh groundwater samples, as well as in the more dilute (down to about 1 000 mg/l Cl) brackish groundwater samples, the sulphate concentrations show relative enrichment compared to seawater (Figure 2-14). In the most saline brackish groundwater sample, the sulphate concentration is distinctly below the Seawater dilution line. When chloride contents exceed 3 000 mg/l, the concentration of sulphate in a part of the groundwater samples strongly increases to levels higher than obtained in the earlier investigations, reaching levels

even higher than that of the present seawater (500 mg/l). The highest sulphate concentrations are about 520 mg/l in borehole KR2 at the depth of 231 -256 m. A similar concentration (510 mg/l) is also reached in borehole KR4. In borehole KR5 the analysed sulphate concentrations are almost of the same order. The analysed chloride concentrations of these samples are also higher than that of the present seawater (3300-3600 mg/l). The highest sulphate concentrations in borehole KR3 are around 300 mg/l and in borehole KR1 about 100 mg/l. The behaviour of Mg (Figure 2-15) is very similar to that of sulphate, exceeding the concentration level of seawater (230 mg/l) in borehole KR4, but unlike sulphate no systematic increase in Mg concentrations in the boreholes is observed.

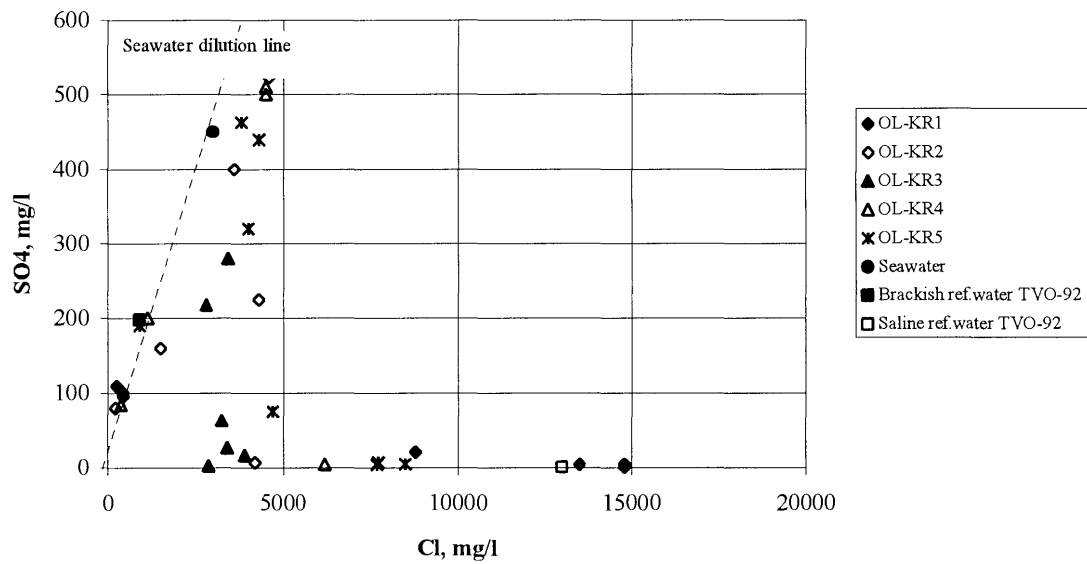


Figure 2-14. *SO₄ contents versus Cl concentrations of the groundwater samples at Olkiluoto.*

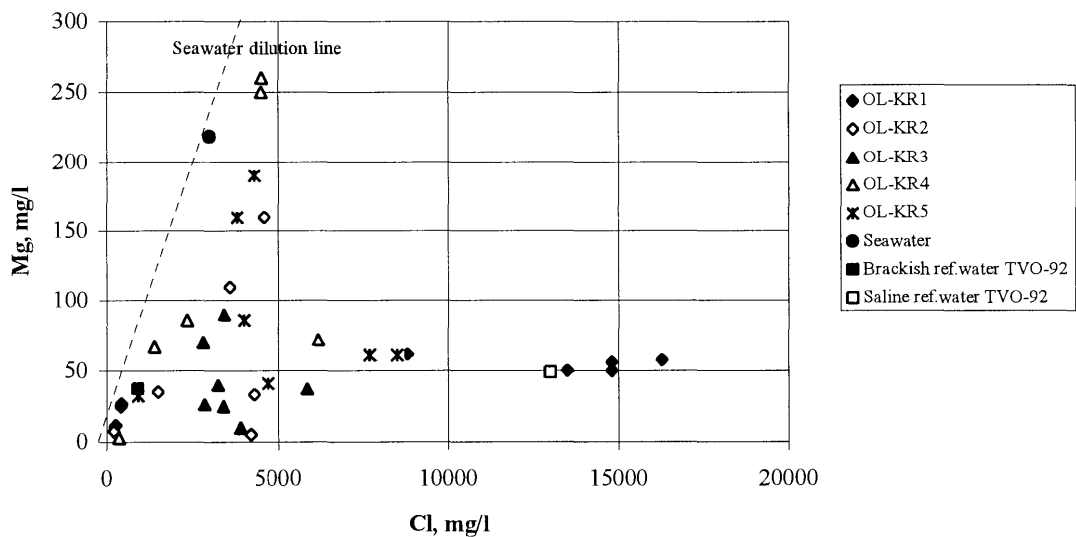


Figure 2-15. *Mg contents versus Cl concentrations of the groundwater samples at Olkiluoto.*

When compared to the results from the previous sampling period (1989 - 1992), the remarkably high magnesium and sulphate concentrations encountered in a part of the new groundwater samples indicate the presence of a new water-type, representing an end-member not observed before in the Olkiluoto area.

The calculated ion-exchange results based on the material from the investigations in 1989 - 1992 support an interpretation of layers of brackish groundwater resembling seawater and surficial fresh groundwater intruding into the bedrock as a consequence of coastal regression (Pitkänen et al. 1994a). Also the most recent results (Na, Mg, SO₄, Br and stable isotopes) indicate the groundwater to have seawater-related origin, however, for the sulphate-rich groundwater distinctly more saline than the present seawater.

The measured redox values for the brackish groundwater samples indicate varied reducing and oxidizing redox conditions, which are most probably caused by technical problems (Figure 2-16). However, the redox values measured for the samples containing sulphide are clearly reducing (Figure 2-17), as well as the values obtained for the samples containing ample amounts of methane (Figure 2-18). Only some of the more dilute brackish groundwater samples contain notable amounts of iron, which is mainly present as Fe(II). However, also these iron-containing samples represent varied reducing and oxidizing conditions and usually the analysed amount of iron is not enough to buffer the system reducing according to theoretical calculations (Fe > 0.55 mg/l, Stumm & Morgan 1981). The most reducing conditions, about -200 mV, were measured for samples having significant amounts of both sulphide and methane. Fe(II) was also somewhat enriched in some of the samples.

The maximum contents of sulphide, 2-3 mg/l are met at depths between 300 and 500 m (Figure 2-19) in the most saline brackish groundwater samples and the most dilute saline groundwater samples (the transition zone), where iron contents are very small (Figure 2-20). The iron content throughout the samples from borehole KR1 is exceptionally high, otherwise the iron concentration is highest at the depth of 100 - 300 m.

Methane concentration distinctly increases with decreasing sulphate concentration (Figure 2-21). Methane is present more remarkably below 300 m (Figure 2-22). The isotopic analysis of methane (Snellman et al. 1995a) indicates its origin to be mostly thermogenic gas of deeper origin resulting from elevated temperatures and abiotic processes. The simultaneous presence of methane and sulphate in the transition zone also suggests a deep origin of methane. Sulphate reduction and methanogenesis are sequential processes and tend to exclude each other (e.g. Plummer et al. 1990).

The increase in S-34 in sulphate shown in Figure 2-23 indicates progressive reduction of sulphate with depth. Altogether the new results support the previous theory (Figure 2-1) and the mass-balance calculations, according to which the probable redox processes governing the conditions in fresh and brackish groundwater are based on the microbially mediated oxidizing of organic carbon and reduction of sulphate in anaerobic conditions, as a consequence of which pyrite precipitates if Fe(II) is present.

When compared with the former investigations (1989 - 1992) more significant amounts of sulphide (1 - 3 mg/l) have been found in several samples (boreholes KR2 and KR5). The former observations on abundant amounts of methane in the evacuated gases gains confirmation. Especially, substantial amounts of methane were found in the saline groundwater samples but also variably in those brackish groundwater samples containing sulphide and only a small amount of sulphate.

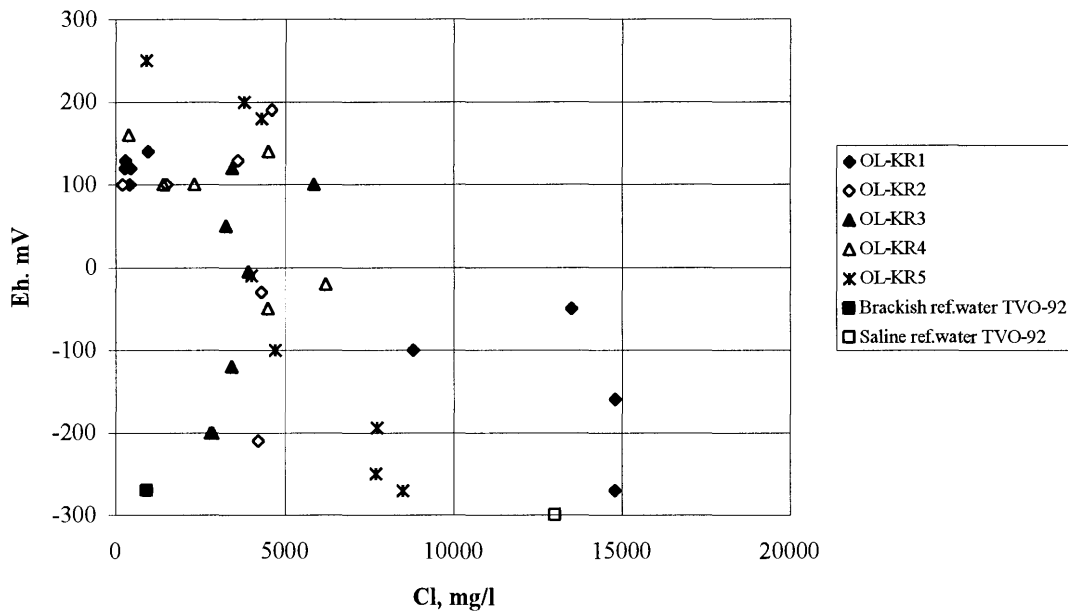


Figure 2-16. Eh values versus Cl concentrations of the groundwater samples at Olkiluoto.

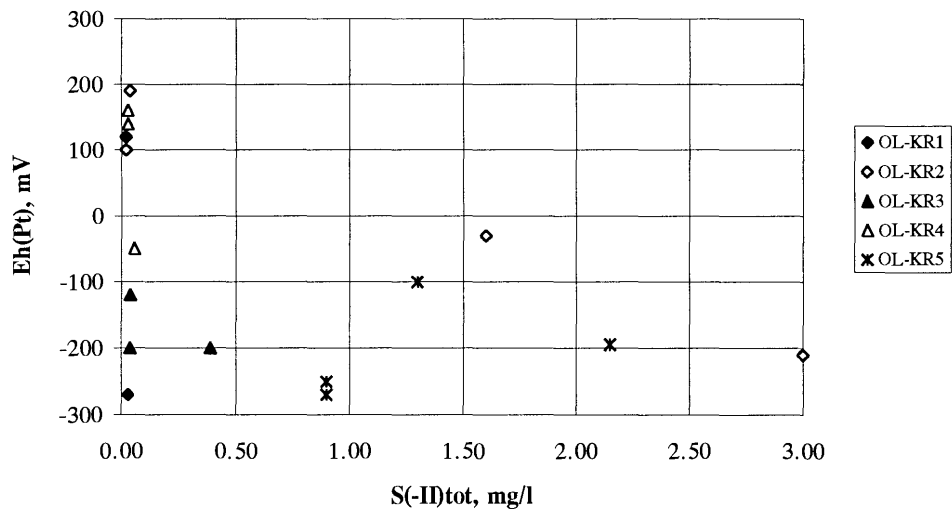


Figure 2-17. Eh values versus S(-II) contents of the groundwater samples at Olkiluoto.

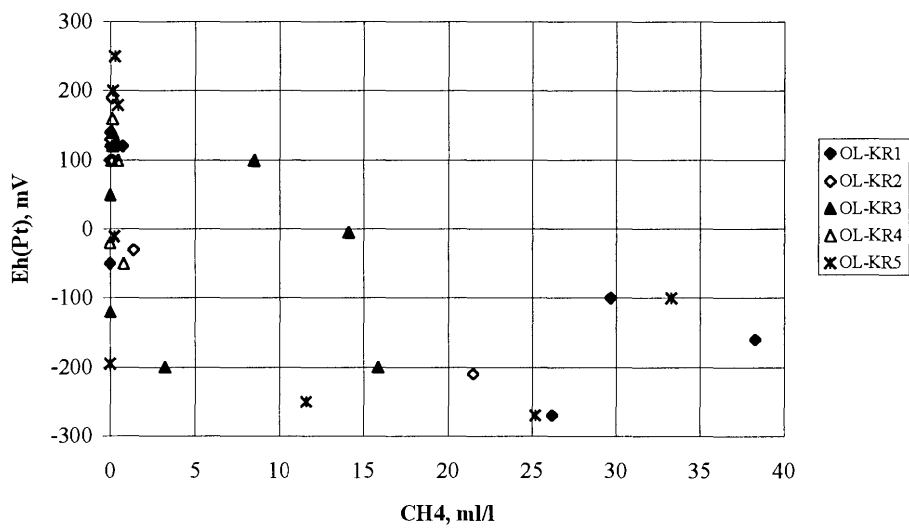


Figure 2-18. Eh values versus dissolved methane of the groundwater samples at Olkiluoto.

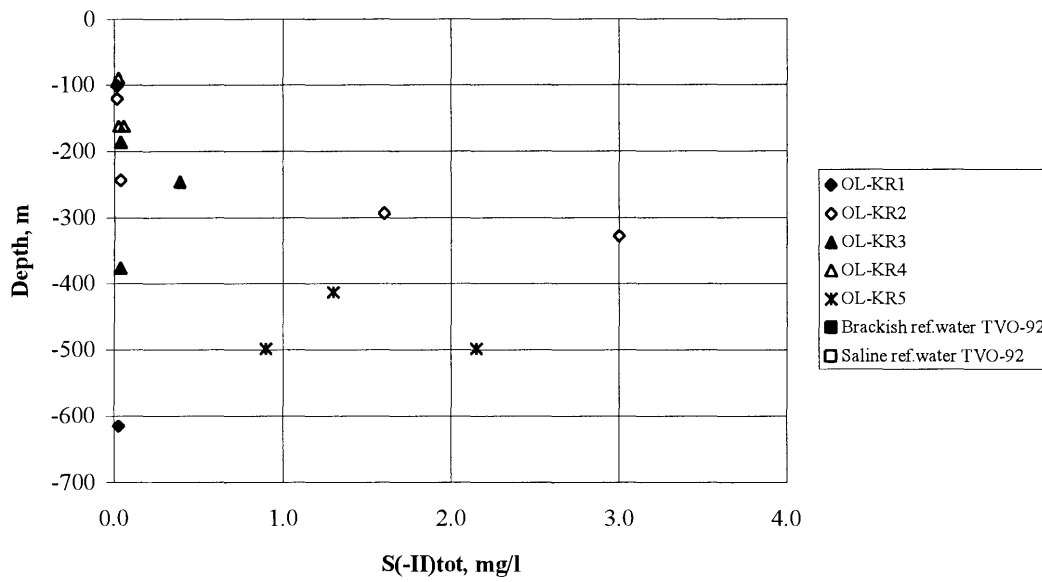


Figure 2-19. Depth-dependence of $S(-II)_{tot}$ of the groundwater samples at Olkiluoto.

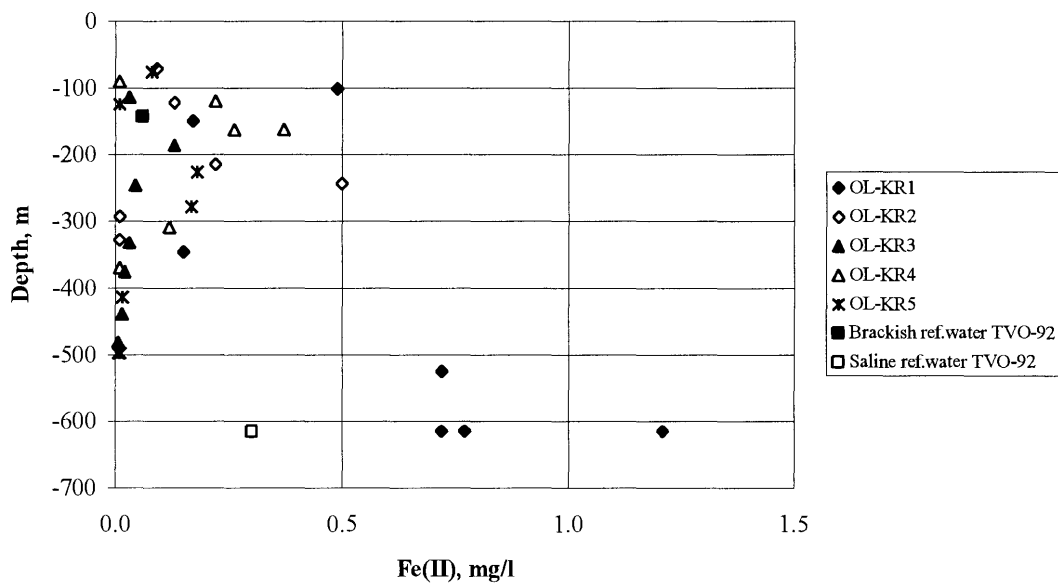


Figure 2-20. Depth-dependence of $Fe(II)$ of the groundwater samples at Olkiluoto.

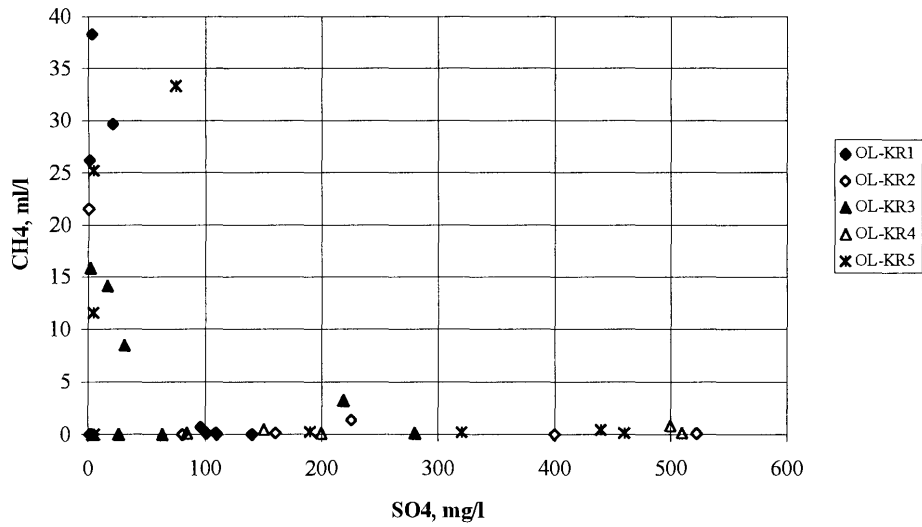


Figure 2-21. Dissolved methane versus SO₄ content of the groundwater samples at Olkiluoto

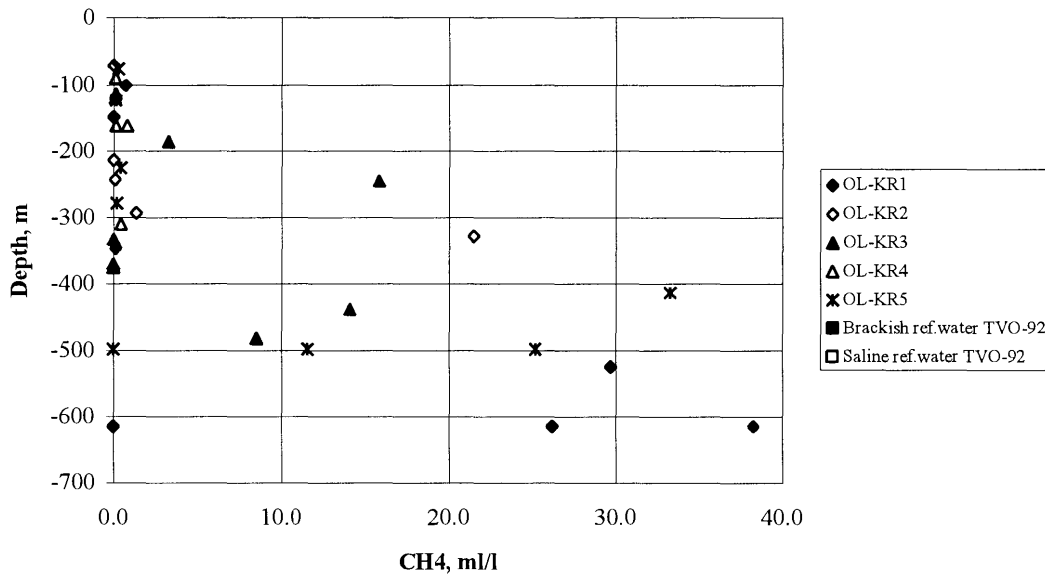


Figure 2-22. Depth-dependence of methane content of the groundwater samples at Olkiluoto.

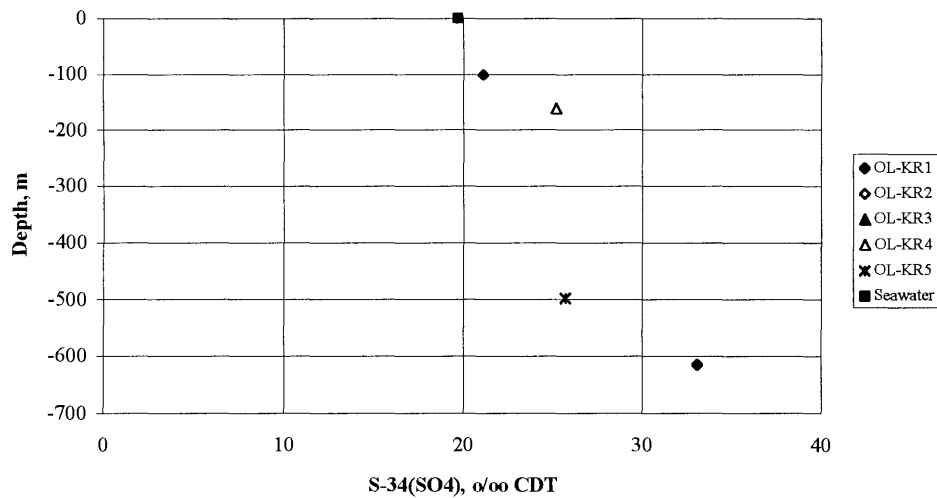


Figure 2-23. Depth-dependence of $\delta S-34(SO_4)$.

2.3 Saline groundwater at Olkiluoto

According to the groundwater chemistry and the interpretation (Lampen & Snellman 1992, Pitkänen et al. 1992a, 1994a) *saline* groundwater (TDS > 10 000 mg/l) is encountered at Olkiluoto below 400 - 500 m. The saline groundwater samples used in the geochemical modelling are given in Appendix 1 (samples 24 - 33 and 38).

The saline Na-Ca-Cl groundwater is basic, having pH values between 7.8 - 9.35. The pH values obtained during sampling in 1993 - 1995 are on average lower (7.8 - 8.95) than those (8.1 - 9.35) obtained in the former samplings. Because the water chemistry otherwise seems to have remained very much the same (e.g. sample from KR1 at 613 - 618 m) the lower pH values obtained indicate a technical problem in the sampling instrumentation. In 1990 salinity (TDS) had its maximum at about 35 000 mg/l below 750 m (Appendix 1). Also in 1993 - 1995, maximum salinity (TDS \approx 27 g/l) was measured from the bottom sample of borehole KR1. The chloride content has somewhat increased in the samples from 612 - 618 m in borehole KR1 when compared with the levels obtained earlier. The alkalinity (mainly carbonate/bicarbonate species) of the saline groundwater samples is very small, the values measured in saline groundwater in 1989 - 1992 were around 0.28 - 0.66 meq/l (Figure 2-11). During the recent sampling period in a nitrogen-protected environment, even lower alkalinities (around 0.12 meq/l) were measured. Silicates, organic anions and even small amounts of flushing water (higher carbonate content) may have influenced the small alkalinity values. Also the measured DIC(CO₂) (Dissolved Inorganic Carbon expressed as CO₂) values give an indication of smaller carbonate concentrations to be truer than those obtained by

titration. Most probably the DIC(CO₂) values represent the maximum carbonate content in the saline groundwater samples. Especially during the sampling period in 1993 - 1995, the DOC (Dissolved Organic Carbon) values obtained were generally higher than those obtained in 1989 - 1992. The saline groundwater samples are saturated in respect of calcite and the partial pressure of CO₂ is low (Figure 2-9, 2-10). The carbon-13 results (Figure 2-12) indicate that the samples from borehole KR1 are somewhat enriched when compared to recharging conditions (drilled wells Varvinnokka and Helmiranta: -19.8...- 19.6 ‰ PDB, Tuominen 1994). Instead, the low-C-13 values (-20.84...- 19.33 ‰ PDB) of the saline KR5 groundwater samples mainly refer to organic origin.

In the most saline groundwater samples (TDS ~ 35 g/l, in 1990) the sulphate concentration is very low, approaching the detection level (0.01 mg/l). According to the new results, sulphate concentrations vary between 0.8 - 4.2 mg/l in those samples which have TDS values around 27 g/l when highest. The total content of sulphur in these samples is around 0.4 - 3.9 mg/l. Generally the samples also contain small amounts of sulphide, except those in borehole KR5 at 446 - 559 m, which have elevated sulphide concentrations around 0.9 - 2.15 mg/l. These samples, like all the other less saline samples (TDS about 10 - 14 g/l) contain very little iron, whereas in the most saline samples (TDS > 20 g/l) the content of Fe(II) rises to about 0.72 - 1.2 mg/l. According to the redox measurements, reducing conditions exist in saline groundwater and remarkable amounts of methane are present. In addition, small amounts of uranium are encountered, on average 0.01 - 0.04 ppb.

According to the former interpretation (Pitkänen et al. 1994), the microbially mediated reduction of sulphate while methane is acting as a major reductant is occurring in the metastable transition zone between the brackish and saline groundwater. The recent results on methane gas occurrence (Figures 3-18, 3-20 and 3-21) and the isotopic results suggest that methane is mainly thermogenic and originates from deep in the rock. The results also confirm the former interpretation of the dominant role of methane gas as the main electron donor deeper in the bedrock. Also the recent results on both the chemical parameters and the isotopic data refer to the presence of a strong alteration zone. The metastable state, which is reflected in the exceptionally high sulphide concentrations, may be caused by the mixing of brackish and saline groundwaters of different thermodynamic states. Based on reaction path modelling (EQ6, Wolery 1992), the condition is presumed to result from kinetic restrictions of the dissolution of Fe(III) (e.g. iron silicates) (Pitkänen et al. 1994a).

The most saline groundwater samples in borehole KR1 seem to be quite stable chemically (Pitkänen et al. 1994a). The similar Br/Cl ratios in saline groundwater and rock, as well as the heavier stable isotope contents (Figure 2-7) than in the fresh and brackish groundwater, also indicate that the saline groundwater has remained stagnant.

3 VERIFICATION OF THE EVOLUTION MODEL AT OLKILUOTO

3.1 Origin of the sulphate-rich groundwater

Sulphate, magnesium, bromide and chloride indicate the presence of a new previously unknown type of brackish groundwater in the bedrock at Olkiluoto, an end-member which has to be taken into account when further assessing and modelling the evolution of the groundwater at Olkiluoto. The larger number of groundwater samples, both areally and in depth, have helped to find the new water type.

Compared to the material produced during the earlier preliminary site investigations, the new water-type can be distinguished as a small addition in the chloride corner of the anion triangle in the Piper diagram (Figure 3-1). This is due to the significantly higher sulphate content of the new water-type compared to the earlier known brackish groundwater samples (Figure 2-14).

When assessing the origin of the new sulphate-rich water-type, the key components mentioned at the beginning of this chapter refer to seawater-related origin, though significant influence on the total composition of the water seems to result from water-rock interaction and the mixing of groundwater supported for instance by the trends of cations. Especially the ratio between Br and Cl indicates seawater origin (Figure 3-2), since the ratio is very stable as ion ratios in seawater in general and the behaviour of these ions is conservative at the total salinities encountered in Olkiluoto. Thus, co-examination of Br and Cl ions is suitable for checking the mixing of different water-types in the bedrock. The stable isotopes of the new water-type group along the mixing line (Figure 2-6) between the present seawater in the Gulf of Bothnia and the other fresh and brackish groundwater samples in the area, which also supports the interpretation of seawater origin. The high-sulphate concentration, if not having seawater origin, is difficult to explain, because no other significant sulphate resource, e.g., sulphate minerals have not been encountered. The S-34 content of sulphate also refers to seawater origin, whose S-34 content is somewhat elevated due to partial reduction of sulphate. This is also supported by the slight depletion of sulphate in respect of the Seawater dilution line (Figure 2-14). The new water-type is remarkably similar to the most saline groundwater samples from Hästholmen (an island off the south-eastern coast of Finland, which has been investigated as a part of the bedrock investigations for a final repository for low-

and intermediate-level reactor waste), Figure 3-3, which have unambiguously been stated to have seawater-related origin by Kankainen (1986) and Nordstrom (1986).

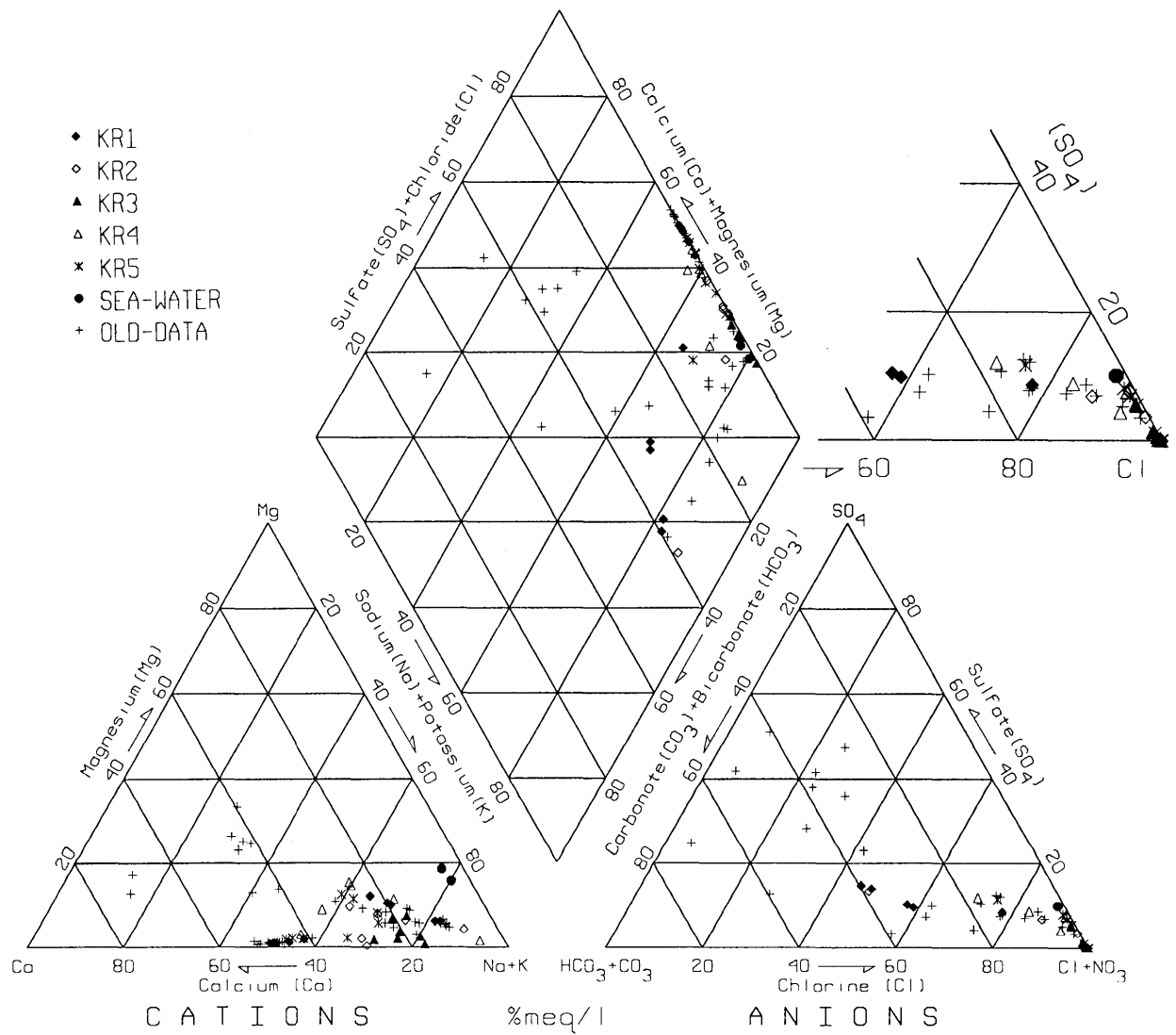


Figure 3-1. Piper diagram and the enlarged chloride corner of the anion triangle of the groundwater samples at Olkiluoto (OLD DATA = material used in the previous modelling, Appendix 1)

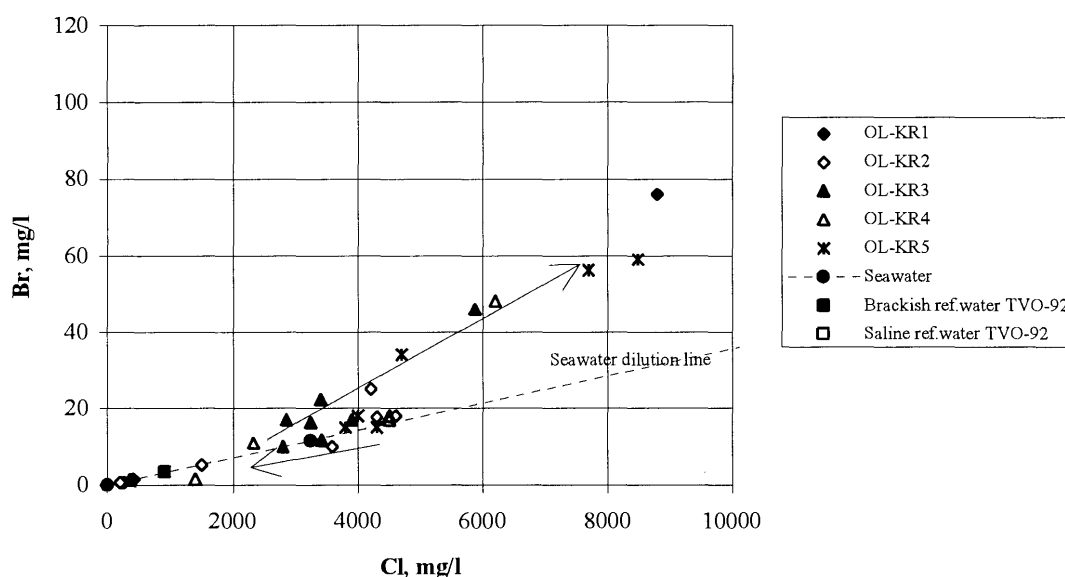


Figure 3-2. *Dependence between Br and Cl in some groundwater samples ($Cl < 10\,000$ mg/l) at Olkiluoto. The new sulphate-rich water-type settles along Seawater dilution line between $3\,500$ mg/l $< Cl < 5\,000$ mg/l. The arrows depict the change in respect of depth in the contents of Br-Cl beneath the sulphate peak.*

The Br/Cl diagram (Figure 3-2) distinctly shows how the new Na-Cl type water is more saline than the present seawater of the Gulf of Bothnia off the Olkiluoto shore and how it retains the Br/Cl ratio typical of seawater (0.00354) at the higher salinities than the other brackish groundwater samples. The behaviour of these is affected by mixing with saline-type of water, which has been set out already in the former groundwater interpretations (e.g. Pitkänen et al. 1994a).

Besides the present Baltic Sea stage, brackish water has been encountered in the Baltic basin twice since the last ice age (Weichselian): The Litorina Sea preceding the present Baltic Sea stage (7 500 - 2 500 BP (= before 1950)) and the Yoldia Stage (10 300 - 9 600 BP). The ice sheet retreated from the Olkiluoto area during the Yoldia Stage. Eronen (1990) states that the water off the Finnish coast was only slightly brackish. The Yoldia Stage was followed by a freshwater period called the Ancylus Lake Stage, which ended at the formation of the Litorina Sea that was distinctly more saline than the present Baltic Sea, with Cl contents varying between 5 000 - 6 500 mg/l (Kankainen 1986) off the Finnish coast. This would, besides Br and Cl, explain the high-sulphate contents of the new sulphate-rich groundwater-type, which exceed those of the present seawater. The highest places at the Olkiluoto investigation site (18 m.a.s.l.) rose above the sea level just at the end of the Litorina period according to the results of Eronen et al. (1995).

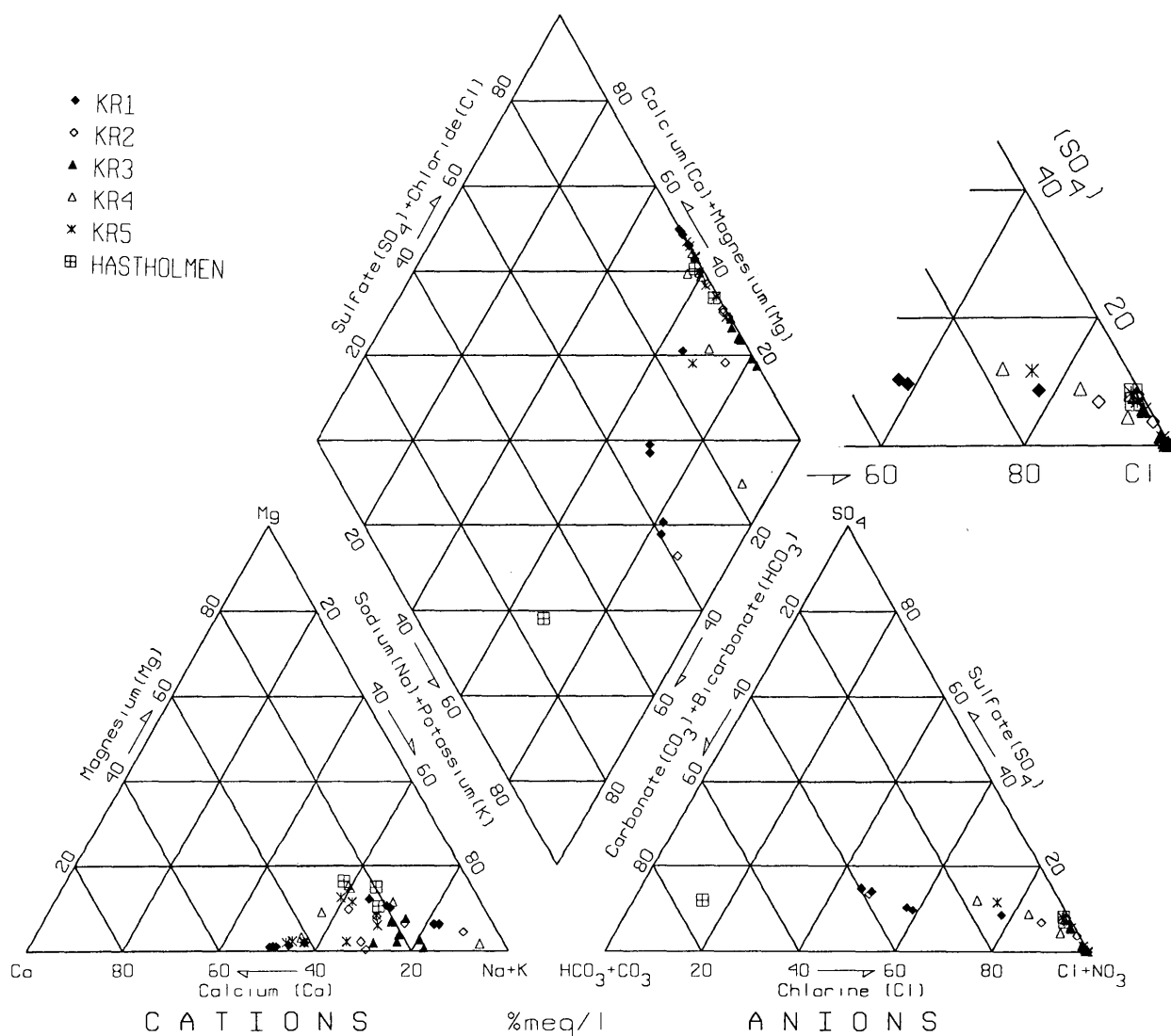


Figure 3-3. Piper diagram and an enlargement of the chloride corner in the anion triangle for groundwater samples from the multipackered system at Olkiluoto and the principal water-types at Hästholmen. Analysis results of the groundwater samples from Hästholmen are from reference Snellman & Helenius, 1992.

Based on the results of Hästholmen water samples, the origin of the referred sulphate-rich groundwater-type has been interpreted as having infiltrated particularly from the Litorina Sea (Kankainen 1986 ja Nordstrom 1986). The most important reasons considered by the researchers were especially the greater salinity than in the present

seawater and changes in the water quality to some extent, which need time to occur, as well as the C-14 concentrations which, combined with the tritium results, refer to the Litorina Sea stage.

The same reasons support Litorina-related origin also in Olkiluoto. The C-14 concentration in the samples of the new sulphate-rich end-member is 20 - 35 pM and in most samples the H-3 concentration is below the detection limit (<0.8 TU) referring to a possible long residence time. The H-3 content of the samples from the upper parts of the boreholes, in the case of Olkiluoto, the more dilute samples (Cl < 1 000 mg/l), vary between 2 - 11 TU (Table 2-1) indicating unambiguously that they contain a remarkable portion of water formed during the last 30 - 40 years, and thus are interpreted as young waters. In these samples calcite saturates after strong bicarbonate enrichment. The C-14 concentrations in the samples are 42 - 64 pM, which when connected with the tritium results indicate that the C-14 content of Olkiluoto groundwater is diluted roughly to 50 % of the level of the atmosphere and surficial freshwaters (100 - 110 pM) as a result of geochemical interaction, e.g., as a result of calcite dissolution during a short period of time without the influence of radioactive decay. When the half-life of C-14 (5 730 years) is taken into account, the age of the sulphate-rich water-type corresponds to a range of 7 500 - 3 000 BP, in other words, corresponds to the Litorina period. Here, geochemical reactions as crystallization of calcite and the possible oxidation of methane during sulphate reduction causing depletion of radio carbon have not been taken into account. However, the effect of such processes is considered to be fairly limited on the C-14 content, because the fractionation of the carbon isotopes during calcite precipitation is small and the observed trace amounts of dissolved sulphide do not require either substantial oxidation of organic carbon or methane. In the case of the most saline groundwater samples at Hästhölm, Kankainen (1986) came to a similar conclusion of the age. The effect of geochemical isotope dilution at the Romuvaara site was estimated to remain at a somewhat higher level, about 60 pM (Pitkänen et al. 1996), which, based on generally lower carbonate concentrations may result from minor geochemical cycling of carbon.

The results of $\delta\text{O-18}$ in water, show that the samples of the sulphate-rich water represent the heaviest groundwater in the bedrock of Olkiluoto (Figure 3-4). In the $\delta\text{H-2}/\delta\text{O-18}$ diagram (Figure 2-6) the corresponding samples stretch towards the composition of present seawater. Changes in temperature cause changes in the isotopic composition of rain water so that warmer conditions favour the heavier isotopes of water. During the Litorina Sea stage, the temperature was about 2 °C higher than today (Donner 1978). The warm conditions are harmonious with the Litorina connection of the sulphate-rich

end-member (-26...-18 ‰ SMOW) and the ice sheet (-20 ‰ SMOW). In other sulphate-rich samples ($\text{SO}_4 > 250 \text{ mg/l}$) with a Br/Cl ratio resembling that of seawater, the proportion of Litorina Sea seawater would vary from 55 to 70 %. The range of $\delta\text{O}-18$ in the corresponding cold mixed fresh groundwater would be -23...-17 ‰ SMOW the weight being below -20 ‰ SMOW.

3.2 Evolution of groundwater

The trends of SO_4 , Mg and $\delta\text{O}-18$ (shown in respect of depth, Figure 3-5 and 3-6) distinctly reveal the rough position of the groundwater layer most abundant in water infiltrated from the Litorina Sea in the vicinity of boreholes KR2, KR4 and KR5: in the last two at a depth of 100 - 200 m and in KR2 a little deeper at 250 - 300 m. The chloride diagram (Figure 3-6) shows the presence of somewhat less saline groundwater below these depths. In borehole KR3, the sulphate-rich Litorina peak would be placed above the uppermost sample. In borehole KR1 the Litorina peak is not visible, which may be partly due to insufficient sampling (the 130 m-long unsampled section between levels T6 and T5) or disturbance of samples, because the previous brackish reference groundwater (Pitkänen et al 1992b) sampled from KR1 at the depth of 140 - 145 m has features of the Litorina Sea. According to chloride dependencies and isotopes (C-14, S-34(SO_4), H-3, $\delta\text{H}-2/\delta\text{O}-18$), the groundwater above the Litorina peak is mainly a mixture of modern type seawater and fresh young rainwater.

In the structural bedrock model (Saksa et al. 1993), the Litorina peaks in boreholes KR2 and KR5 hit the cross-sections of the subhorizontal fracture zone R20 and in borehole KR4 in the almost horizontal fracture zone R19. Sulphate-rich groundwater types greatly resembling each other, may on the one hand, implicate the existence of a connection between the structures, and, on the other hand, the horizontal structure may enable maintaining the special features of the groundwater as prominent as can be seen here in the area where groundwater flow is in a transient state caused by the effect of land uplift.

What is below the Litorina peak? A decrease in the Cl concentration (simultaneously salinity) to some extent and groundwater becoming lighter in oxygen (Figures 2-7 and 3-6) indicate that the proportion of fresh water, which contains plenty of ice-sheet melt-water preceding the Litorina stage increases at the expense of water originating from the Litorina Sea. This is observed in the Br - Cl diagram (Figure 3-2) as a shift to the left along the Seawater dilution line. Cl concentration begins to increase again below 300 m

but at the same time also the Br/Cl ratio distinctly increases. The samples plot above the Seawater dilution line, the tendency being towards the saline groundwater samples indicating old salts, most probably of hydrothermal origin (Pitkänen et al. 1992a and Pitkänen et al. 1994a), having mixed in the groundwater.

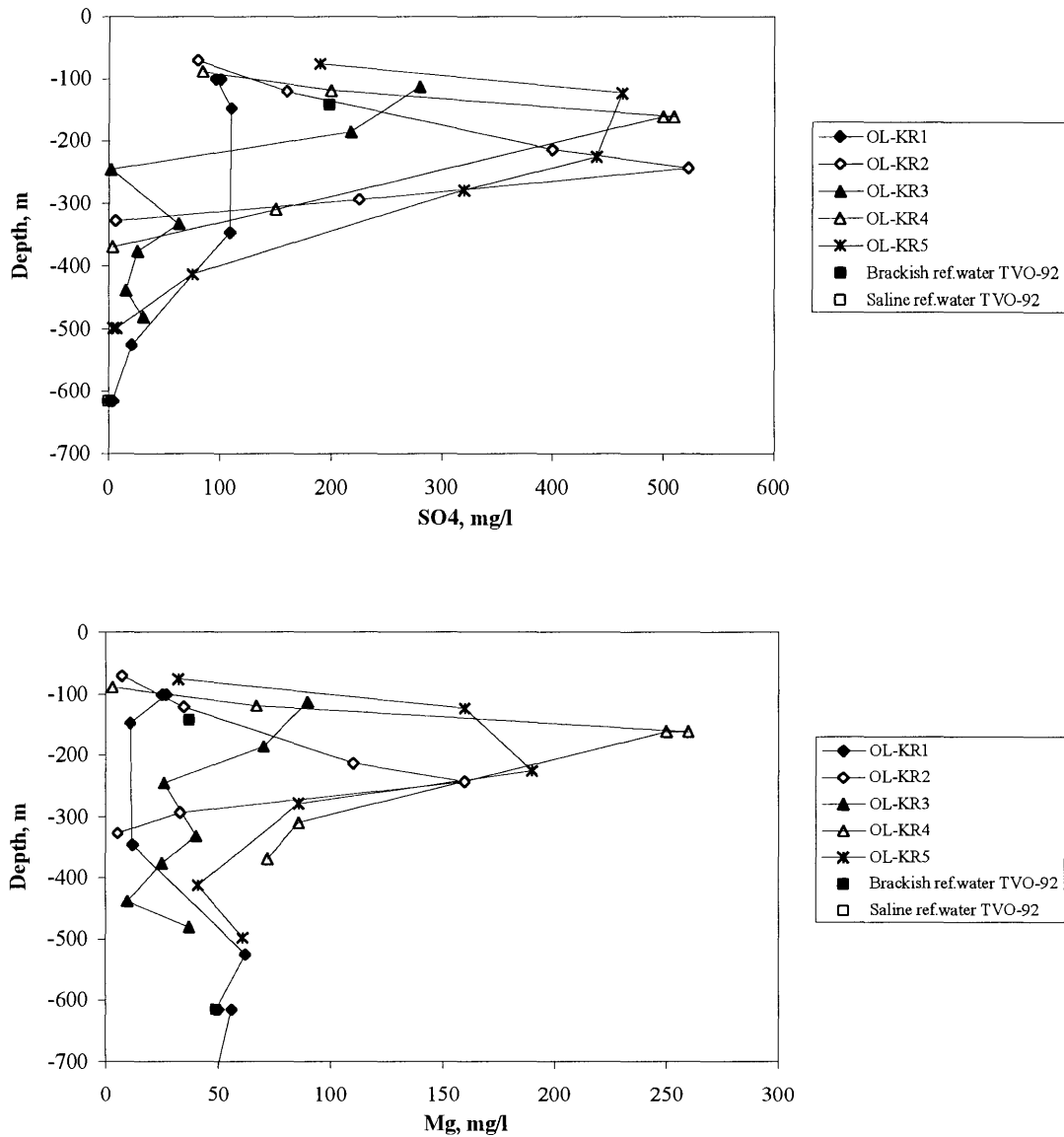


Figure 3-5. Depth-dependence of SO_4 and Mg of the groundwater samples at Olkiuoto.

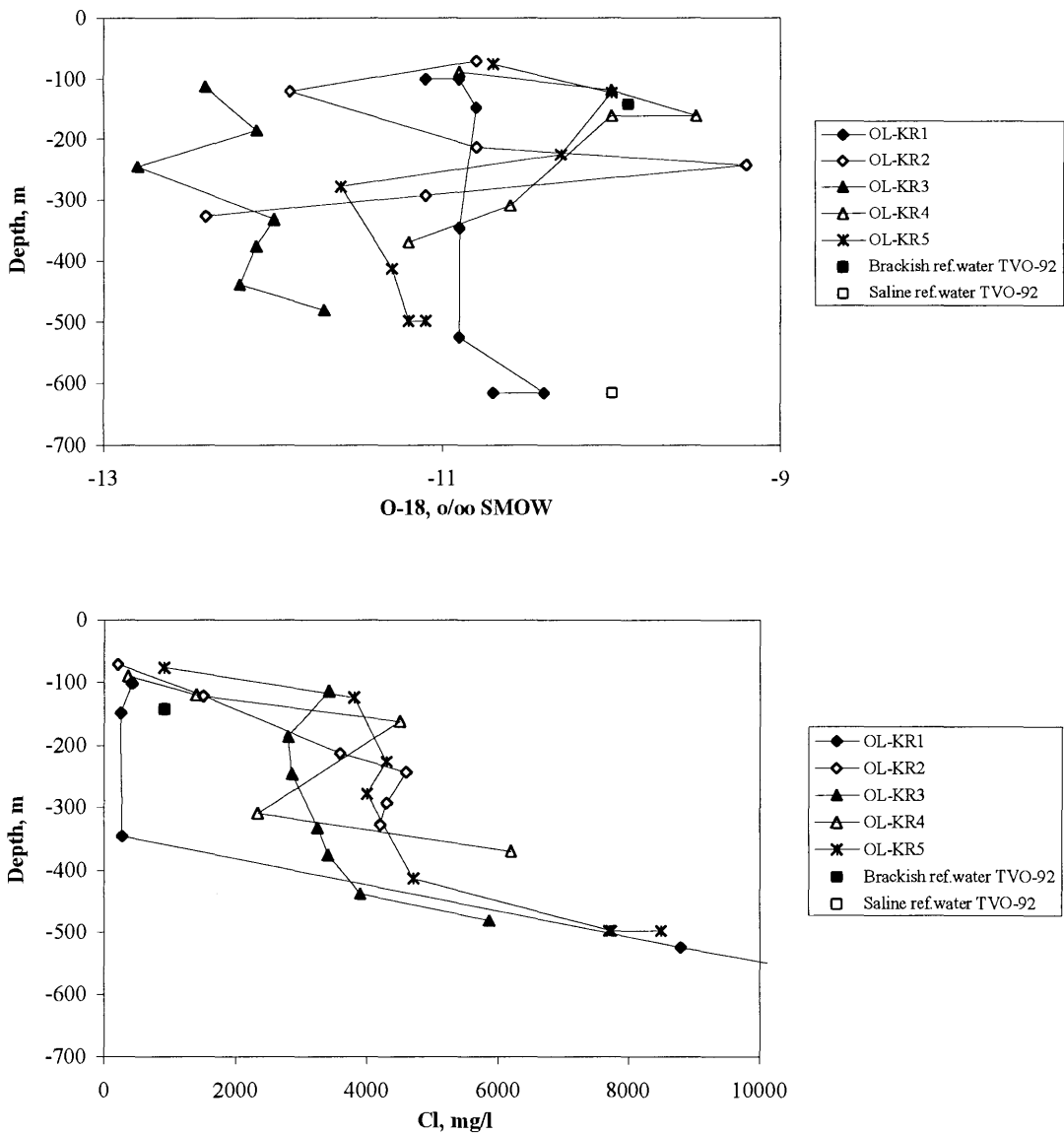


Figure 3-6. Depth-dependence of $\delta\text{O-18}(\text{H}_2\text{O})$ and Cl of the groundwater samples at Olkiluoto. (The Cl diagram is limited to concentrations < 10 000 mg/l).

The diagram of heavy carbon (C-14) and oxygen (Figure 3-7) depicts the apparent residence time of groundwater in the area. The surficial fresh groundwater samples are placed around a point (C-14, $\delta\text{O-18}$) = (45, -10.7) from which the shift is up to the left as the amount of Litorina Sea seawater increases. Below the Litorina peak when depth increases, $\delta\text{O-18}$ quickly depletes while C-14 first roughly retains its level until in the samples representing the coldest stage in borehole KR3 also radio carbon is strongly depleted.

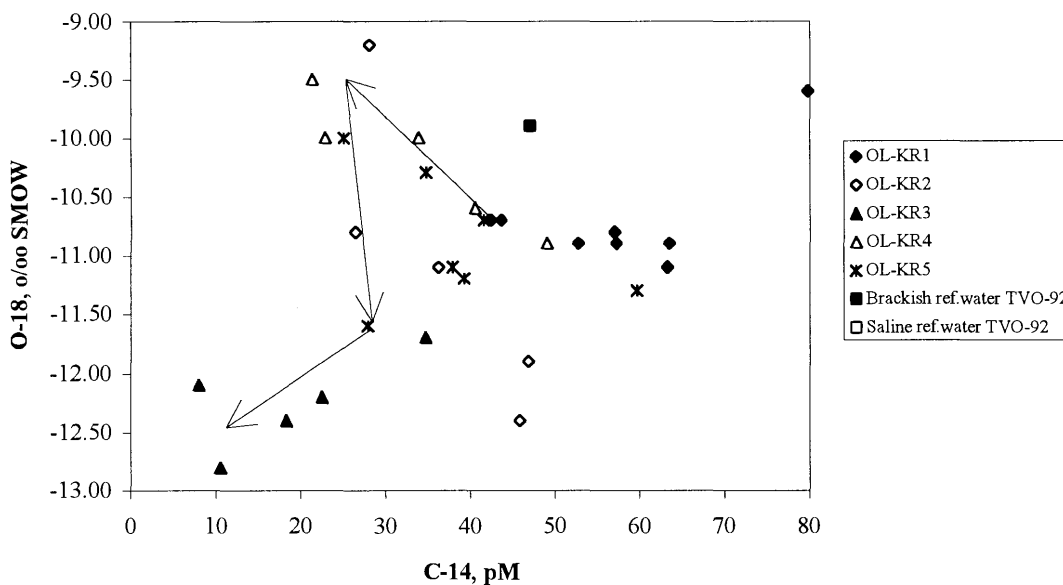


Figure 3-7. *Dependence between $\delta O-18$ and C-14 of the groundwater samples at Olkiluoto. The arrows show the development in respect of depth from the upper part of the bedrock towards the Litorina-originating samples and further to samples containing more abundantly melt-water of the ice sheet.*

The level of C-14 content in the samples from the cold stage is roughly half of the contents of those originating from the Litorina period. If roughly one half-life is added to the formerly presented estimate of the age of the sulphate-rich groundwater sample, it would at the lowest C-14 concentrations lead to ages obviously too high, 13 000 -15 000 BP. The area was at that time covered with the ice sheet and had been in principle already for over 50 000 years closed to radiocarbon formed in the atmosphere, which is the time period to the previous interstadial (Eronen 1990). The age estimate of the Litorina stage does, however, include provises of geochemical processes which can bias the age estimates towards younger ages, and which have not been taken into account in the presented age range. The oxidation of methane may be substantial in this light water zone diluting C-14 content. The smallest C-14 concentrations in the groundwater samples at Olkiluoto have been determined from the alteration region of Br/Cl ratio in the samples from borehole KR3, which implies also mixing of carbonate of presumably radiocarbon-free saline groundwater and dilution of C-14 in the samples to some extent. The alkalinities in these samples are fairly low (0.5 - 0.9 meq/l) and thus already small amounts inmixed can be significant.

In the saline groundwater samples, the alkalinity and the partial pressure of CO_2 are so low that various contamination possibilities, e.g., intrusion of CO_2 into the strongly

unsaturated samples during sampling can be the major factor controlling the concentration of C-14 (Snellman et al. 1995b).

Plausible results are, however, believed to be obtained by taking into account the interaction reactions more exactly in the reaction path modelling of both the samples originating from Litorina stage and the brackish groundwater samples older than those. An example from the preliminary site investigation phase is the calculated value of 8 300 years (Pitkänen 1994) for the packer interval 388 - 393 m in borehole KR3 (Appendix 1). This reaction adjusted age corresponds very well to the average age evaluated in this work for the brackish groundwater below the sulphate-rich groundwater layer originating from the Litorina stage.

The enrichment of the heavy isotopes of water (Figures 2-6, 2-7 and 3-4) starting again from the depth of 300 - 400 m downward presumes the origin of the saline groundwater to be from the warmer climatic conditions preceding the ice age, the first one of which is the Eem interglacial 130 000 - 100 000 BP. During the interglacial, more saline water than the present was present in the basin of the Baltic Sea, as the basin obviously also had a connection through a strait to the White Sea (Eronen 1990). The relatively stronger enrichment of deuterium than $\delta\text{O-18}$ (the samples tend to plot above the GMWL line in Figure 2-6) does not, however, support seawater origin of the saline component, because seawaters, due to evaporation, plot below the GMWL line, but the enrichment implies interaction between meteoric water and bedrock as has been presented in former investigations (e.g. Pitkänen et al. 1992a).

4 CONCLUSIONS

The latest groundwater samples reveal new chemical characteristics of the brackish groundwater layer at Olkiluoto (Figure 4-1).

DEPTH (m)	WATER TYPE	Cl (mg/l)	pH	Alk (meq/l)	Redox
0 ~	Ca - Na - (Mg) - HCO ₃ - SO ₄ - Cl	< 25	6	1.5	Postoxic
50 ~	Na - (Ca) - Cl - (HCO ₃)	500	7	5	Sulphidic
200 ~	Na - (Ca) - Cl	4 500	7,5	1,5	
	Na - Cl	3 500	8	0,8	
400 ~	Na - Ca - Cl	8 000	8.2 - 9.0	0.5 - 0.1	
600 ~	Ca - Na - Cl	22 000			
1000 ~					

Figure 4-1. *New modified version of the vertical variation of the main hydrochemical parameters at Olkiluoto. Compare to Figure 2.1.*

A groundwater-type originally infiltrated from the Litorina Sea has been identified among the groundwater-types at Olkiluoto. The new water-type improves significantly the preliminary vertical concept (Pitkänen et al. 1994a) of the origin and evolution of the groundwater. The present interpretation indicates the influence of five end-member water-types on the groundwater chemistry:

modern

- fresh rainwater infiltrated from the surface and
- seawater from the Gulf of Bothnia (0 - 2 500 BP),

relictic

- Litorina Sea seawater (2 500 - 7 500 BP),

- freshwater prior to the Litorina stage containing ice sheet melt-water (7 500 - 10 000 BP) and
- saline water formed under the influence of hydrothermal salts (preglacial).

The hydrochemistry of Olkiluoto seems to contain a well-developed profile of climatic and shoreline changes from modern times through former Baltic stages in the area to preglacial times (Table 4-1). In the upper part of the bedrock reaching the depth of 100 - 150 m quite young, generally fresh groundwater occurs, which is a mixture of Baltic seawater and water infiltrating from the surface. Deeper at 100 - 300 m the sulphate-rich brackish groundwater-type representing the Litorina peak is present, and below this at 100 - 500 m the brackish groundwater alters to a brackish-saline water-type containing more abundantly ice sheet melt-water. Below 500 m there is saline groundwater containing increasing amounts of water older than the Weichselian glaciation.

Table 4-1. *Main water-types at Olkiluoto, giving the original source and the estimated formation-age of the water-types*

Depth of occurrence	Water-type	Origin of dominant end-members	Age estimate of dominant end-member type
above 150 m	Fresh-slightly brackish HCO ₃ -rich water	Rain water and present Baltic water	0 - 2 500 BP
100 - 300 m	SO ₄ -rich brackish Na-Cl water	Litorina Sea water	2 500 - 7 500 BP
100 - 500 m	Brackish Na-Cl water	Pre-Litorina water containing fresh melt-water of the ice sheet	7 500 - 10 000 BP
below 500 m	Saline Ca-Na-Cl water	Preglacial meteoric water possibly influenced by hydrothermal salts	> > 10 000 BP

The different groundwater-types form a layered structure in a constricted area but areally the occurrence depths coincide on top of each other. Considerable mixing of the main water-types occurs between the different layers, because, e.g., the groundwater representing the Litorina peak seems to contain 30 - 40 % of ice sheet melt-water. The brackish groundwater layer below it contains saline groundwater in increasing amounts based, among other things, on the study of Br/Cl and $\delta\text{H-2}/\delta\text{O-18}$ ratios

Based on the new data no significant alterations are presupposed to the previous interpretation of the reactions and mixing affecting the evolution of the groundwater (Pitkänen et al. 1994a and Figure 3-1 on p.3), because also the newly identified groundwater from the Litorina stage has seawater-related origin even though it is more

saline than the present seawater in the Gulf of Bothnia, which is used in the model calculations. Besides, the behaviour of the dissolved material (e.g. Cl dependencies) and processes occurring (e.g. microbially mediated oxidising of organic carbon and reduction of sulphate in anaerobic conditions, as well as the dominant role of methane as the main electron donor deeper in the bedrock) correspond to the former results, only the concentration ranges have extended compared to the previous ones. The new data affects both the conservative mixing calculations and the mass-transfer in reaction calculations. Because of this the groundwater originating from the Litorina Sea may have significance also in respect of safety assessment, e.g., when considering how extensive the reduction of sulphate and production of sulphide may be, or what the significance is of the groundwater originating from the Litorina Sea lying over the less dense groundwater when flow aspects are considered. The role of deep-seated methane in the reduction of sulphate is another process which has to be evaluated.

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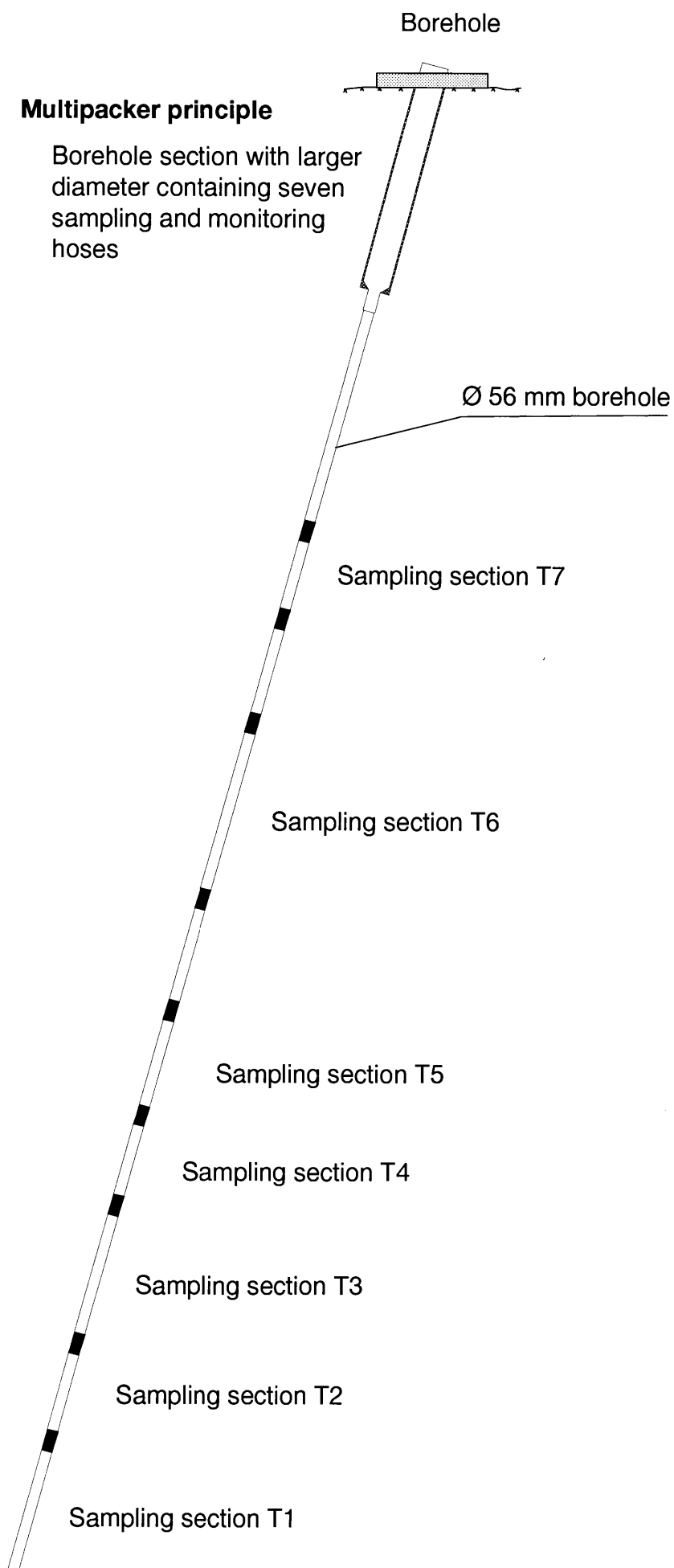
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6 APPENDIX

- Appendix 1 The analysis results of Olkiluoto groundwater samples from 1981-1992 for those which were used in the geochemical interpretation (Pitkänen et al. 1994a).
- Appendix 2 The multipacker system.

Sampl. No	Sampl. date	Sampling interval (m)	Eh(Pt) mV	Cond. mS/m	pH field	pH lab.	O2f mg/l	Alk. meq/l	Acid. mmol/l	CO2free mg/l	TOC mg/l	SiO2 mg/l	Fetot mg/l	Fe2+ mg/l	Al mg/l	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	Mn mg/l	Sr mg/l
1	OL-SEAW	22/8/89		1010.0		7.7		1.63		4.40	4.4	0.6	<0,10		<0,4	1730	61.40	91.0	227.00	<0,05	
2	OL-ENV	22/8/89		24.4		7.1		1.52		7.00	7.7	9.0	0.96		<0,4	20	4.78	23.0	3.92	<0,05	
3	OL-ENV	22/8/89		29.3		7.6		1.62		3.50	7.5	11.4	2.11		1.40	28.80	6.57	25.0	5.16	0.16	
4	OL-ENV	23/8/89		17.4		6.3		1.24		16.30	2.1	24.2	<0,10		<0,4	5.09	1.60	25.0	2.79	<0,05	
5	OL-ENV	23/8/89		25.2		5.9		1.15		40.50	3.2	17.6	0.14		1.50	6.07	2.41	34.0	5.14	<0,05	
6	OL-ENV	31/5/89		12.5		6.9		0.40		1.80	5.8	<0,1	0.067		0.063	6.37	2.00	10.5	3.60		0.042
7	OL-ENV	4/7/89		11.8		7.6		0.45		1.30	3.3	<0,1	0.077		0.054	7.08	2.00	9.5	3.40		0.043
8	OL-ENV	15/8/89		13.5		7.1		0.32		1.30	6.3	0.3	0.051		0.026	7.63	2.30	10.8	3.40	<0,05	0.047
9	OL-ENV	24/4/90		15.1		7.5		0.32		3.52		1.0	0.080		0.030	8.67	2.50	10.7	3.87	0.01	0.033
10	OL-PVA1	6/4/89	37.5	253.0		7.9	2.00	4.90	0.06	2.60	5.1	13.0	0.61F		0.224	435	10.60	45.7	16.10	0.150	0.38
11	OL-PVA1	31/5/89	37.5	297.0		7.7	<0.1	5.10	0.08	3.50	2.3	12.6	0.52F	0.33F	0.064	562	13.50	61.4	24.50	0.240	0.615
12	OL-PVA2	6/4/89	58.7	118.0		8.5	2.30	3.90	0.09	4.00	10.5	12.5	1.45F	1.3F	1.100	195	2.70	21.0	6.39	0.050	0.23
13	OL-PVA2	31/5/89	58.7	128.0		8.3	1.20	3.90	0.08	3.50	11.4	12.5	0.95F	0.47F	0.509	178	2.40	18.1	5.55	0.035	0.235
14	OL-YD1	10/11/80	79.2-82.9	280.0		7.9	1.30	2.80		21.00		15.0	2.700	2.10		500	13.70	88.0	20.00	0.110	
15	OL-YD1	20/5/81	79.2-82.9	280.0		8.4	2.40	3.70		4.00		39.0	15.700	11.90		480	13.00	53.0	17.00	0.240	
16	OL-YD1	23/8/82	79.2-82.9	121.0		8.0	0.30	3.10		14.00		51.0	6.800	4.80		180	6.80	63.0	14.00	0.270	
17	OL-YD1	10/11/80	146.4-149.9	430.0		8.0	0.53	2.50		7.20		7.5	1.200	0.90		780	17.50	145.0	33.00	0.140	
18	OL-YD1	20/5/81	146.4-149.9	260.0		8.5	1.10	3.40		0.00		17.0	11.800	8.00		430	8.20	51.0	16.00	0.220	
19	OL-YD1	23/8/82	146.4-149.9	440.0		7.8	0.40	1.25		5.00		14.0	1.000	0.60		980	8.90	190.0	21.00	0.240	
20	OL-YD7	30/5/81	87.1-90.5	480.0		8.3	1.50	3.00		0.00		11.0	0.950	0.68		640	15.00	170.0	42.00	0.150	
21	OL-YD7	8/7/85	133.5-138.3			7.7	1.28	3.70		19.00		13.0	0.390	0.16	0.100	146	8.70	68.0	15.00	0.270	
22	OL-KR1	16/11/89	140.0-145.0	-280	339.0	8.1	8.1	0.07	4.90	<.05	10.4	11.2	0.14F	0.09F	0.260	585	7.00	110.0	37.10	0.100	1.18
23	OL-KR1	28/11/89	140.0-145.0	-270	265.0	8.1	7.9	0.17	4.18	0.07		11.8	0.05F	0.06F	0.057	565	6.70	110.0	37.40	0.100	1.14
24	OL-KR1	28/2/90	613.5-618.5	-290	2780.0	8.9	7.1	0.10	0.4F	0.08F	5.9	3.1	0.38F	0.3F	0.180	3902	19.00	3275.0	49.30	0.390	29.9
25	OL-KR1	17/8/90	613.5-618.5	-210	2620.0	9.3	6.8	0.02	0.28			3.3	0.01		0.23	4300	21.60	3270.0	53.70	0.28	25.70
26	OL-KR1	27/8/90	613.5-618.5	-300	2750.0	9.4	7.4	0.03	0.29			2.9	0.01		0.27	4310	23.70	3410.0	53.00	0.39	26.70
27	OL-KR1	28/6/90	754.0-1001.0	30	4690.0	8.5	6.5	4.68	.48F	.14F	71.0	2.5	0.99F	0.58F	0.170	5688	15.80	5263.0	55.40	0.370	46.9
28	OL-KR1	27/7/90	754.0-1001.0	-140	5220.0	8.8	7.0	-0.20	.44F	.12F	44.0	5.5	0.38F	0.02F	0.170	6622	15.60	6214.0	59.80	0.400	56
29	OL-KR1	25/4/91	754.0-1001.0	-10	3450.0	8.6	7.9	0.02	.36F	<.05F	5.9	4.3	0.22F	0.19F	0.025	4621	17.40	3575.0	65.50	0.530	33
30	OL-KR1	25/7/90	754.0-1001.0	-140	4980.0	8.9	6.7	-0.20	0.29			3.4	0.10		0.37	6880	22.70	6560.0	51.60	0.29	47.20
31	OL-KR1	26/3/91	754.0-1001.0	-50	3300.0	8.6	6.7		0.30			3.7	0.05		0.19	4800	20.90	3810.0	53.20	0.40	30.20
32	OL-KR1	8/4/91	754.0-1001.0	-30	3550.0	8.6	6.7	0.12	0.26			3.9	0.02		0.24	4880	20.90	3880.0	54.10	0.41	30.90
33	OL-KR1	26/4/91	754.0-1001.0	-22	3440.0	8.0	7.3	0.01	0.27			4.3	0.02		0.23	4980	20.90	4030.0	55.00	0.41	32.40
34	OL-KR2	24/4/90	235.0-240.0	-50	233.0	9.0	8.2	0.43	4.74	<0.05	11.2	10.1	0.3F	0.23F	0.27	386	4.91	76.8	22.80	0.14	0.76
35	OL-KR2	8/5/90	235.0-240.0	-160	221.0	9.1	8.0	0.30	4.87	0.30	11.6	10.1	0.23F	0.16F	0.27	386	4.69	76.9	22.60	0.14	0.76
36	OL-KR3	22/5/90	388.0-393.0	-70	540.0	8.7	8.0	0.93	0.82		5.5	2.5	0.12	0.075F	0.09	907	9.02	231.0	32.60	0.07	1.94
37	OL-KR3	7/6/90	388.0-393.0	-250	793.0	8.6	6.5	-0.18	.67F	<.05F	3.8	3.8	0.17F	0.14F	0.007	1253	10.30	347.0	55.30	0.130	3.14
38	OL-KR5	11/6/92	446.0-558.5	-244	1970.0	9.0	7.9	0.02	0.664F		0.4	6.6	0.21	0.007	0.050	2795	13.9	1654.0	57.00	0.26	15

F = analysed in the field



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