TECHNICAL REPORT

95-06

Palaeohydrological implications in the Baltic area and its relation to the groundwater at Äspö, south-eastern Sweden – A literature study

Bill Wallin

Geokema AB, Lidingö, Sweden

March 1995

SVENSK KÄRNBRÄNSLEHANTERING AB
SWEDISH NUCLEAR FUEL AND WASTE MANAGEMENT CO

BOX 5864 S-102 40 STOCKHOLM
TEL. 08-665 28 00 TELEX 13108 SKB
TELEFAX 08-661 57 19

PALAEOHYDROLOGICAL IMPLICATIONS IN THE BALTIC AREA AND ITS RELATION TO THE GROUNDWATER AT ÄSPÖ, SOUTH-EASTERN SWEDEN - A LITERATURE STUDY

Bill Wallin

Geokema AB, Lidingö, Sweden

March 1995

Information on SKB technical reports from1977-1978 (TR 121), 1979 (TR 79-28), 1980 (TR 80-26), 1981 (TR 81-17), 1982 (TR 82-28), 1983 (TR 83-77), 1984 (TR 85-01), 1985 (TR 85-20), 1986 (TR 86-31), 1987 (TR 87-33), 1988 (TR 88-32), 1989 (TR 89-40), 1990 (TR 90-46), 1991 (TR 91-64), 1992 (TR 92-46) and 1993 (TR 93-34) is available through SKB.

PALAEOHYDROLOGICAL IMPLICATIONS IN THE BALTIC AREA AND ITS RELATION TO THE GROUNDWATER AT ÄSPÖ, SOUTH-EASTERN SWEDEN - A LITERATURE STUDY

Bill Wallin

GEOKEMA AB, Lidingö, Sweden

March, 1995

Keywords: Palaeohydrology, saline groundwater, isotopes, Baltic Sea, glaciation, global isotope change

ABSTRACT (ENGLISH)

A literature study of different groundwaters in the circum Baltic region is presented in this work. The study is mainly focused on the isotopic signatures observed in different groundwaters in Sweden and Finland. Several saline groundwaters in the Baltic region at depth of 150 to 500m depth show stable (δD, $\delta^{13}C$, $\delta^{18}O$) and radiogenic ($\delta^{87}Sr$) isotope assembly which is suggestive of a marine origin. However, a discrepancy is sometimes observed between the stable as well as radiogenic isotopes of the intermediate groundwater, which suggest a mixture of fossil marine water and a post-glacial runoff of meltwater. In order to explain this phenomenon, the initial setting in $\delta^{18}O$ may have been depleted due to large input of high latitude marine water or cold meltwaters. A solution to the contradiction between the strontium ($\delta^{87}Sr$) and stable isotope (δD, $\delta^{13}C$, $\delta^{18}O$) signatures of the groundwater and of the calcite fracture fillings at Äspö and other places is attained, if it is assumed that the strontium in Baltic Sea water has undergone a significant decrease in $\delta^{87}Sr$ since the last glaciation. A scenario can be constructed to suggest that the Baltic Sea during the initial stage of the Litorina sea (8000 to 5000 Y B.P.) contained strontium with much larger $\delta^{87}Sr$ values. Another explanation for the positive $\delta^{87}Sr$ values may be due to water/rock interaction between the groundwater and the abundant fracture clay minerals, which are observed at Äspö. Typically most of the saline groundwaters occur both in Sweden and Finland below the highest marine shore line during the Holocene. Almost all inland groundwaters show a totally different pattern which is typically non marine, meteoric in origin. This study also summarises the stable isotope (δD, $\delta^{13}C$, $\delta^{18}O$) geochemistry dependence of the important global and regional environmental changes which may have influenced of the palaeohydrology as well as groundwater formation and in the Baltic region and especially at Äspö.

ABSTRACT (SWEDISH)

En litteraturstudie om olika grundvatten i Östersjöområdet och deras paleohydrologi presenteras i följande arbete. Studien har huvudsakligen fokuserats på de isotopsignaturer som observerats i grundvatten i Sverige och Finland. Ett stort antal salta grundvatten på den Baltiska skölden, på ett djup av 150 och 500 m, uppvisar stabila (δD, $\delta^{13}C$, $\delta^{18}O$) och radiogena ($\delta^{87}Sr$) isotopsammansättningar, vilka antyder ett marint ursprung för dessa vatten. Emellertid, föreligger ofta en diskrepens mellan de stabila och radiogena isotopernas respektive "fingeravtryck" i vatten på dessa djup, vilket skulle kunna förklaras av en blandning av "fossilt" marint vatten och glacialt smältvatten. En förklaring till detta fenomen kan vara att den initiala $\delta^{18}O$ signaturen i grundvattnet har ändrats dramatiskt pågrund av inblandningen av kallt smältvatten. En lösning till den diskrepens mellan strontium ($\delta^{87}Sr$) och stabila isotoperna (δD, $\delta^{13}C$, $\delta^{18}O$) i grundvattnet och i kalcitfyllnaderna på Äspö och andra platser, skulle vara att strontium i Östersjön har genomgått en significant minskning i $\delta^{87}Sr$ efter den sista glaciationen. Ett tänkt scenario skulle kunna vara att Östersjön under ett tidigare marint stadium, Litorina stadiet (8000 till 5000 Y B.P.), innehöll strontium med betydligt högre $\delta^{87}Sr$ värden än idag. En annan förklaring till de positiva $\delta^{87}Sr$ värdena kan vara de utbytesprocesser mellan grundvattnet och lermineralen i sprickfyllnaderna i berggrunden som observerats på Äspö. Typiskt nog, förekommer de flesta salta grundvatten både i Sverige och Finland under den högsta marine kustlinjen under Holocene. Nästan alla grundvatten däremot ovanför denna gräns uppvisar totalt olika vatten som är typiskt icke marina och meteoriska i sitt ursprung. Denna studie summerar även de isotopgeokemiska förändringar som kan observeras pågrund av den globala och regionala förändringen i miljön. Dessa förändringar som ofta är kopplade till klimatologiska cycler, såsom glaciation, kan ha haft stor betydelse för paleohydrologin och grundvattenbildningen i Östersjöområdet och speciellt på Äspö.

SUMMARY AND CONCLUSIONS

This literature study is mainly focused on the isotopic signatures observed in different groundwaters in Sweden and Finland. Several saline groundwaters in the Baltic region at depth of 150 to 500m depth show stable (δD, $\delta^{13}C$, $\delta^{18}O$) and radiogenic ($\delta^{87}Sr$) isotope assembly which is suggestive of a marine origin. However, a discrepancy is sometimes observed between the stable as well as radiogenic isotopes of the intermediate groundwater, which suggest a mixture of fossil marine water and a post-glacial runoff of meltwater. In order to explain this phenomenon, the initial setting in $\delta^{18}O$ may have been depleted due to large input of high latitude marine water or cold meltwaters. A solution to the contradiction between the strontium ($\delta^{87}Sr$) and stable isotope (δD, $\delta^{13}C$, $\delta^{18}O$) signatures of the groundwater and of the calcite fracture fillings at Äspö and other places is attained, if it is assumed that the strontium in Baltic Sea water has undergone a significant decrease in $\delta^{87}Sr$ since the last glaciation. A scenario can be constructed to suggest that the Baltic Sea during the initial stage of the Litorina sea (8000 to 5000 Y B.P.) contained strontium with much larger $\delta^{87}Sr$ values. Another explanation for the positive $\delta^{87}Sr$ values may be due to water/rock interaction between the groundwater and the abundant fracture clay minerals, which are observed at Äspö. Typically most of the saline groundwaters occur both in Sweden and Finland below the highest marine shore line during the Holocene. Almost all inland groundwaters show a totally different pattern which is typically non marine, meteoric in origin. This study also summarises the stable isotope (δD, $\delta^{13}C$, $\delta^{18}O$) geochemistry dependence of the important global and regional environmental changes which may have influenced of the palaeohydrology as well as groundwater formation and in the Baltic region and especially at Äspö.

Examinations in a large number of groundwater wells in Finland and Sweden suggest a multiple source for the saline waters in the circum-Baltic area. However, most the groundwaters found in the coastal areas below the highest marine transgressions during the Holocene, strongly suggest that saline water intrusions have been responsible for the groundwater formation at intermediate depth, between 150 and 500 m. The saline groundwaters have most likely been formed at different times at different sites due to the prograding isostatic movement during the post-glacial period. Early transgressions (8000 Y, B.P.) during the Litorina stage as well as later transgressions (3000 - 3500 Y, B.P.) during the Limnea stage seem to be important events in the groundwater formation. Moreover, this literature study has shown that there is an extensive ongoing recharge of meteoric water in most of the wells in the circum-Baltic area. Mixing processes between saline groundwaters and the ambient meteoric recharge produces waters of different salinities.

Isotope signatures from the coastal areas reveal a pattern supporting the hypothesis that continental runoff of meltwaters have been in-mixed with the saline waters of the pre-Baltic stages. The discrepancies between, $\delta^{18}O$ and $\delta^{87}Sr$ from several groundwaters support this idea. It therefore, seem to be extremely important to understand the interaction between the melt water runoff and mixing with the saline waters during the Yoldia and Litorina stages of the Baltic Sea, in order to interpret the origin of the saline coastal groundwaters.

CONTENTS

1 INTRODUCTION

Palaeohydrology is a widely used term for the description of the hydrology in the past. During the last decade the international hydrological scientific community have focused their efforts on specific paleohydrological studies as well as the understanding of the processes behind groundwater formation. As we know, many of the processes which are involved in the groundwater formation can be understood by using the chemical and isotopic data of the different waters. The isotopes in combination with the dissolved components often produces a "fingerprint of the past" which can be used for future predictions of the groundwater situation for a certain repository. Hence, in order to predict the future changes of the ground water a good understanding of the palaeohydrology and the regional influence of the groundwater in the past is necessary.

2 BACKGROUND

Isotopic and geochemical examinations of the groundwater at Äspö indicate that several waters have been involved in the groundwater formation. Different sources are distinguished, including meteoric water, fossil marine waters and glacial meltwater and continental runoff. The variation within the groundwater indicate at least two larger end-members; namely a shallow recharge water body and the deep water at Äspö and especially at Laxemar. This deep groundwater, which appears to be a very stagnant, may be very old and possibly originate from leached sedimentary halites or evaporates. Moreover, the discrepancy of the observed in stable isotopes as well as radiogenic isotopes of the intermediate groundwater suggest a mixture of fossil marine water and a post-glacial runoff of meltwater. In order to understand the future changes of this groundwater a detailed understanding of the groundwater situation at Äspö and its palaeohydrology is needed.

The following work is a review and summary of the knowledge we have about different groundwaters in the circum Baltic region. It also summarises the isotope geochemistry dependence of the important global and regional environmental changes which may have influenced of the palaeohydrology as well as groundwater formation and in the Baltic region and especially at Äspö.

3 GROUNDWATER WELLS IN SWEDEN AND FINLAND

3.1 GROUNDWATER WELLS IN SWEDEN

In Sweden several studies of shallow groundwater wells have been performed by *SGU* (Swedish Geological Survey) which are reported by

Knutson and Fagerlind, 1977; Lindewald, 1981; Lindewald, 1985; Enqvist et al., 1985; Johnson et al., 1985 and Gustavsson et al., 1988. Approximately 5200 wells have been sampled and analysed from all over the country and treated in different ways in a computer (Enqvist et al., 1985). The country has been

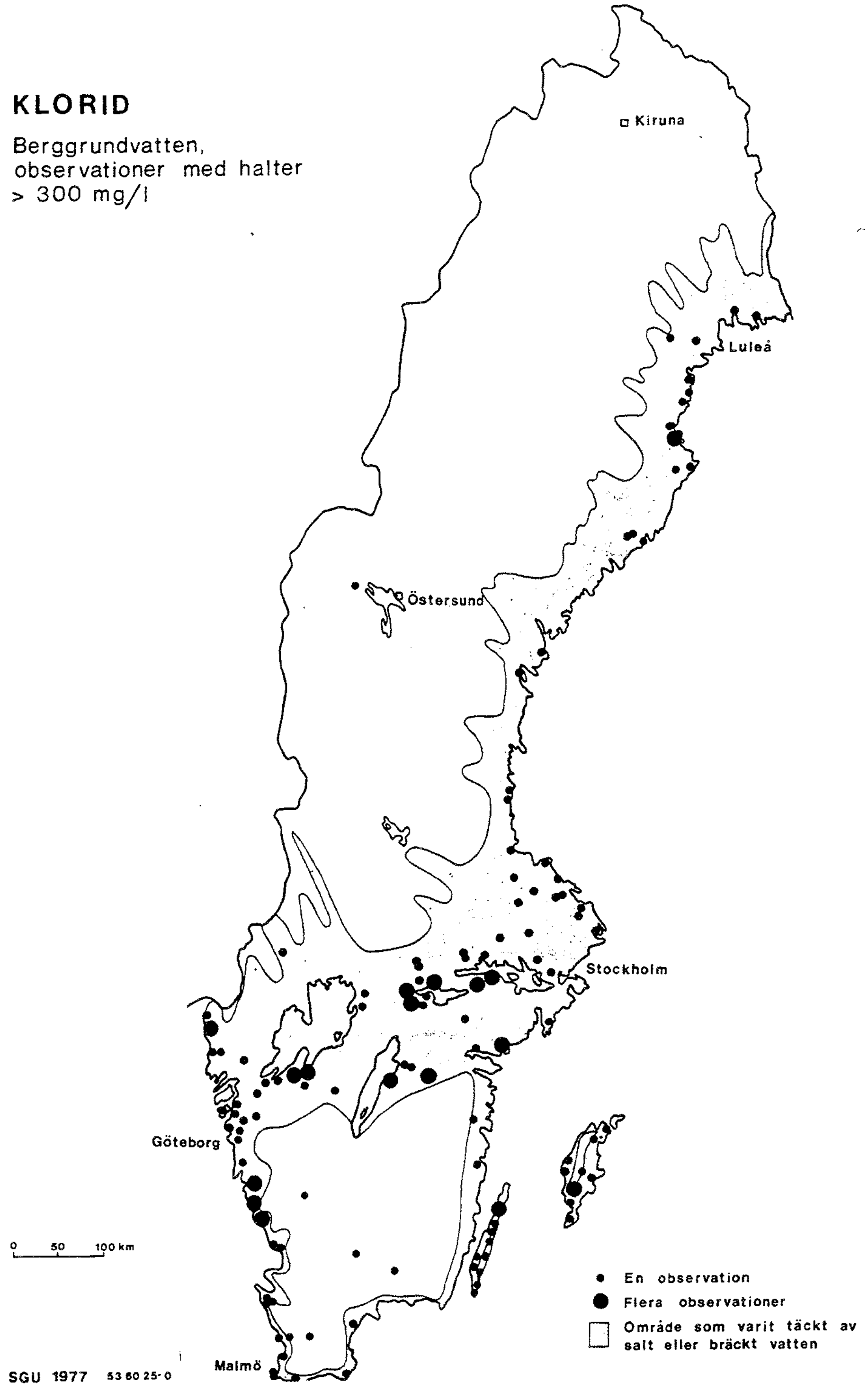

Figure 3-1. *Distriburion of chloride rich wells below the highest marine shore line during Holocene in Sweden. After .*

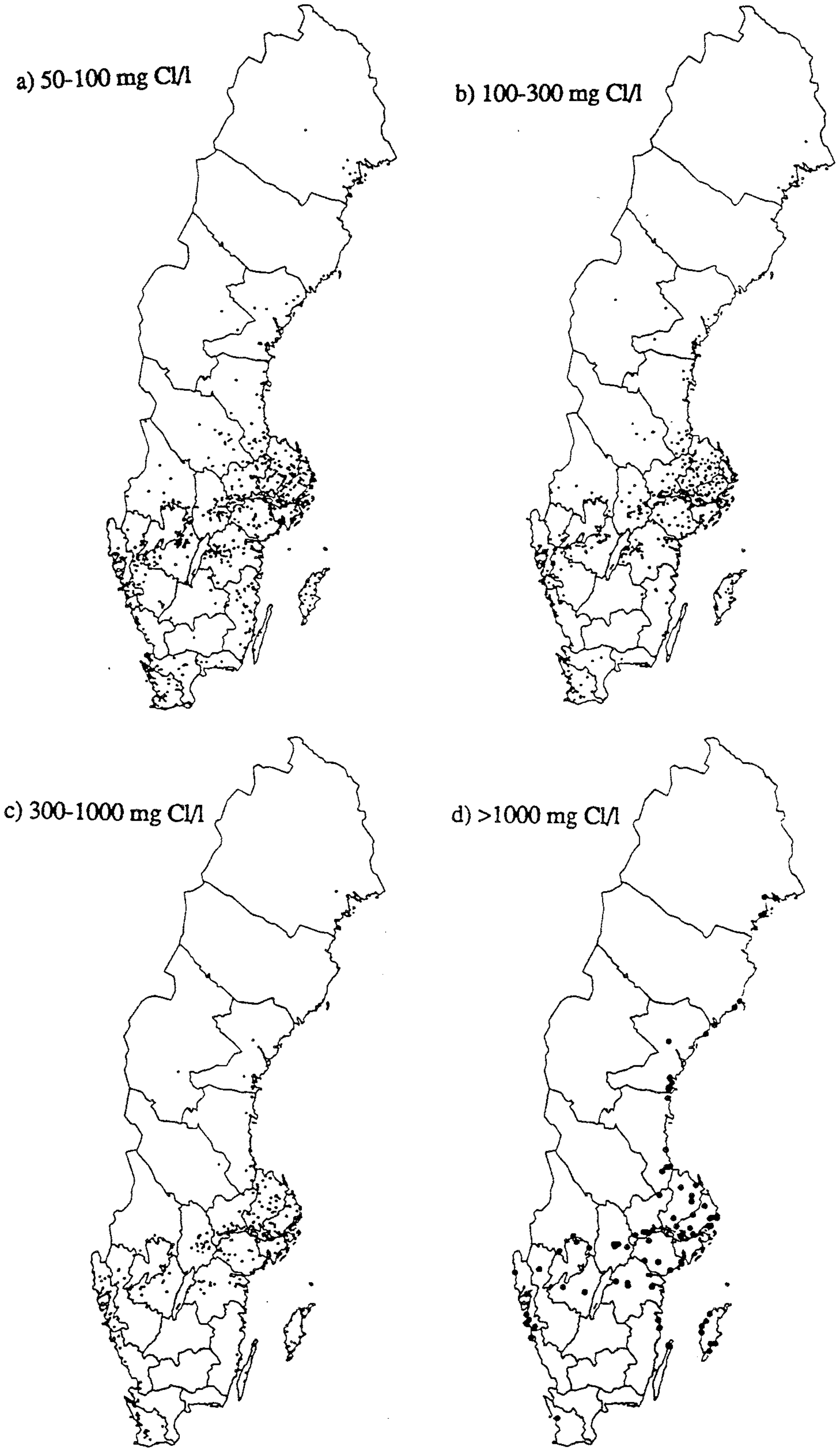

Figure 3-2. *Distriburion of chloride in Swedish wells. After Olofsson, 1994.*

subdivided into six regions, within which the samples have been grouped according to the character of the aquifer, and have been treated in three categories, namely, Quaternary deposits, Precambrian rocks and younger sedimentary rocks. The statistics from these studies show that the chloride concentrations in the material varies between 0.3 and 12 900 mg/L that the usual values of Cl is between 8 and 40 mg/L. The median value is 17 mg/L and the mean value is 66 mg/L. The distribution of the chloride in Swedish wells are seen in Figure 3-1 and 3-2. Deep drillholes (>500 m) which are reported in this study have been performed in Sweden by varies mining companies, Vattenfall (Swedish Power Company) and SKB (Laaksoharju, 1988; Smellie and Laaksoharju, 1992) (Figure 3-3). Other important contributions are made by Wikberg (1987), Olofsson (1994) and Knutson and Morfeldt (1993).

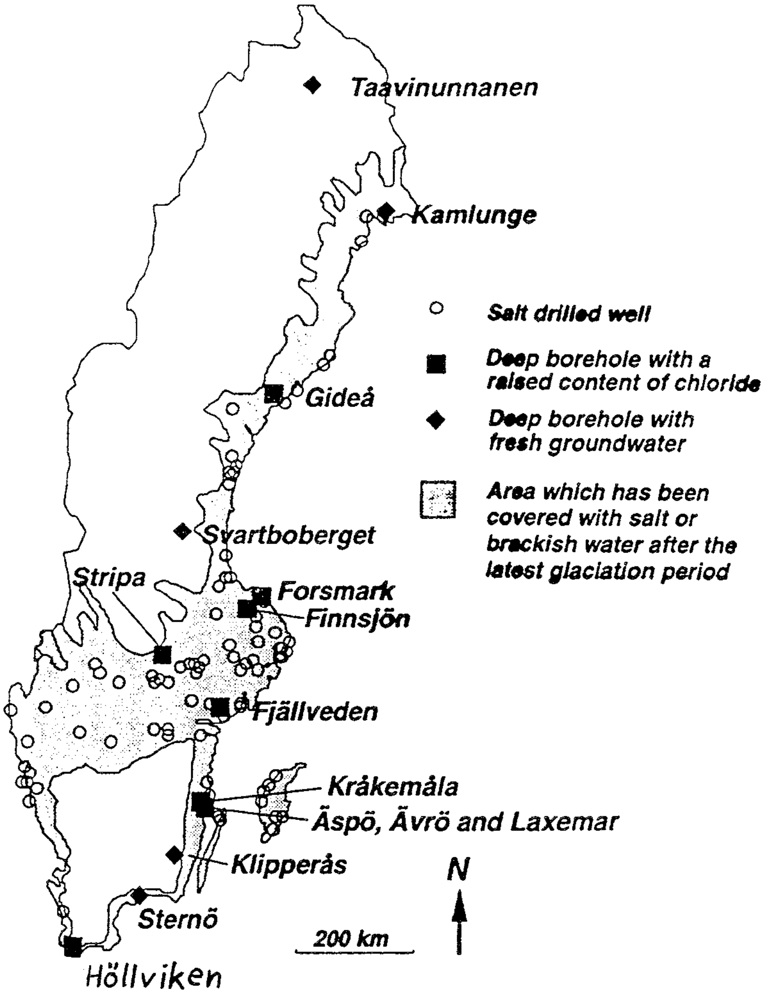

Figure 3-3. *Map showing the sites of deep drilled boreholes performed by SBK within the program for the search of a final nuclear waste repository. The shaded area indicate the highest marine shore line during post-glacial time. Wells with Cl concentrations >300 mg/L are marked by rings.*

3.2 GROUNDWATER WELLS IN FINLAND

In Finland both coastal (Nordstrom, 1986; Kankainen, 1986; Wickström and Lampén, 1986; Nordstrom, 1989; Lampén and Snellman, 1993) and inland groundwater wells (Lahermo and Kankainen, 1986; Lahermo and Lampén, 1987; Lahermo et al., 1991; Mitrega and Lahermo, 1991; Mäkelä and Rönkä, 1994) have been examined. The groundwater wells have generally been treated as brackish or saline wells and divided in two categories; namely those with Cl concentrations between to 170 mg/L and 1000 mg/l those above 1000 mg/L (Figure 3-4).

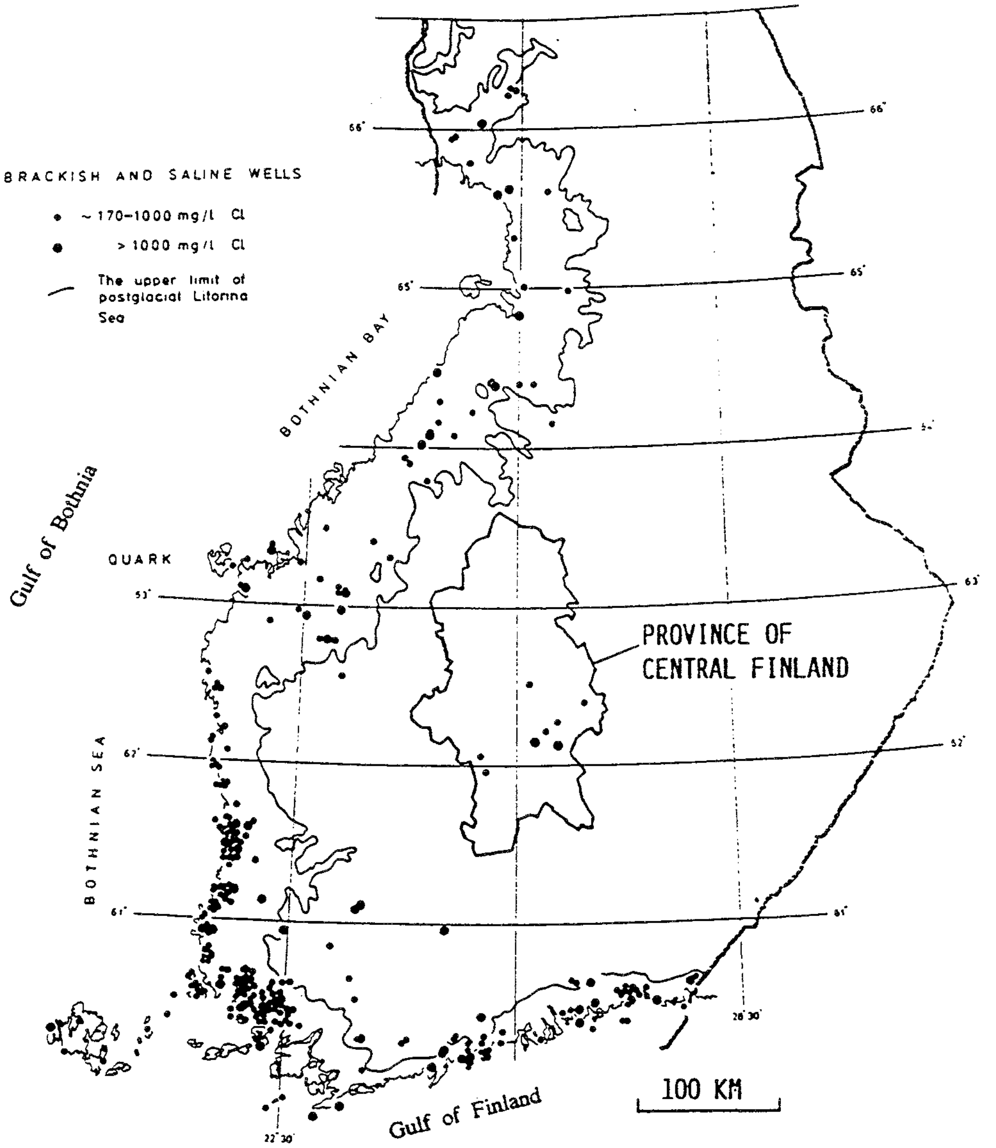

Figure 3-4. *Brackish and saline wells drilled in the coastal areas of Finland and in Central Finland. The drillholes are divided in two groups; namely between 170 mg/L and 1000 mg/L and above 1000 mg/L. After Mitrega and Lahermo, 1991; Mäkelä and Rönka, 1994.*

4 REGIONAL PALAEOHYDROLOGY AND GROUNDWATERS IN THE BALTIC REGION

4.1 GROUNDWATERS IN SWEDEN

Saline groundwaters in Sweden are mainly found below the highest shore line of the Litorina stage of the Baltic Sea. Hence, most of the saline waters are interpreted to originate from marine water intrusion. In the coastal area highly saline waters strongly suggest that there is a marine origin for the aquifers residing at the intermediate depth of about 150 to 500 m depth, such as those at Äspö (Wallin, 1990; Tullborg and Wallin, 1991; Wallin, 1992). In contrast, a few groundwaters are interpreted as being locally derived e.g. through leaching of fluid inclusions due to the water/rock interaction processes, such as those at Stripa (Nordström et al., 1989c). In addition, Smellie and Wikberg (1989) found that the groundwater at Finnsjön, in comparison to other groundwaters in Sweden, is mainly of a marine origin but has undergone changes due to water/rock interaction processes.

4.1.1 Höllviken

Deep boreholes have been drilled in the Precambrian crystalline basement as well as in Palaeozoic/Kenozoic sedimentary terrains. Most of the drilling activity have been performed during prospecting for minerals, oil and gas. The deepest borehole made is in Gravberg, central Sweden (DDP,) reaching 6200 m. The most saline waters recorded in Sweden are reported from Cretaceous and Jurassic sedimentary rocks at Höllviken (Figure 3-4) in south-western Scania (Brotzen, 1944; Brotzen 1949; Lundblad, 1949). Extremely high chloride concentrations of more than 100 000 mg/L and a total salinity of up to 256 000 mg/L were measured at a depth of 1862 m. The rocks are dominated by Jurassic conglomerates, sandstones and shales from Kueper and Muschelkalk. Some of the sandy horizons have dolomitic (20 % $MgCO_3$) layers including gypsum and salt. The relatively high Mg content may indicate a marine or phreatic origin for the carbonates and hence, closely related to the observed salt. Most likely these saline waters or rather brines (Stenhoff, 1944; Assarsson, 1948), can be explained by a leaching of the sediment salts due to the relatively high temperature input which is recorded in the area at these depth. The presence of these salt may also be explained by leaching of the evaporates which are trapped in the sedimentary basins south of Höllviken in the southern part of the Baltic area.

4.1.2 Klipperås

In the drill hole at Klipperås less than 150 km Southwest of Äspö (Figure 3-4), above the highest marine shore level (Smellie et al., 1987a), display a totally different water from that at Äspö. The highest chloride concentration of 60 mg/L is recorded at a depth of 800 m The $\delta^{18}O$ signatures of the groundwater at deeper depth suggest an extensive meteoric water input in the basement rocks. Two groundwater types are distinguished; near surface waters and intermediate waters. The waters are overall of a reducing nature with slightly enhanced Na Cl, Br and F and reduced amounts of Ca and HCO_3 (Smellie et al., 1987b). The geochemical modelling show that the groundwaters are a) nearly saturated with respect to calcite and carbonate minerals and b) both Fe^{2+} and Al^{3+} ions appear to be saturated with their hydroxides.

4.1.3 Fjällveden

At Fjällveden in eastern Sweden south of Stockholm (Figure 3-4) groundwater analyses have been performed in 3 different boreholes FJ2, FJ4 and FJ6 (Allard et al., 1983; Laurent, 1983b). All groundwaters examined show very low concentrations of chloride, with the highest value of 170 mg/L in the FJ2 drillhole. It is interesting to note that this locality is situated below the highest limit of the postglacial Litorina Sea, similarly to Gideå. In clear contrast to the coastal waters in Finland and Äspö these waters seem to have another history. The $\delta^{18}O$ signatures of the groundwater in all drillholes reveal a value of about-11 and -11.5 o/oo PDB, typical meteoric signatures for that area. In one of the drillholes, FJ2, the $\delta^{18}O$ below 500 m depth decreases to -14 o/oo PDB, indicative of a totally different water than above this depth. The low $\delta^{18}O$ signature suggest that this water may be residual meltwaters or any other meteoric water formed from a colder climate. If so, it is interesting to note that in this area as well as in Gideå, as a marked contrast to Äspö and the Finish coastal waters, there may have been formation of groundwaters by meteoric water or possibly postglacial meltwaters.

4.1.4 Gideå

Gideå is situated on the east coast of northern Sweden (Figure 3-4) half way between Kamlunge in the north and Svartoberget in the south. The groundwaters at Gideå, similarly to Fjällveden, have low concentrations of chloride, with the highest observed value of 310 mg/L (Laurent, 1983a). The $\delta^{18}O$ values of the groundwater vary between -12.5 and -13.8 o/oo PDB (Allard et al., 1983) for the water at depth down to 500 m. This is significantly lower than those observed at Fjällveden but coincide with the spread observed in the Äspö groundwaters above 500 m depth. The Gideå groundwaters is totally different from the groundwaters seen at Äspö. The most likely source for these water are meteoric waters and possibly a mixture of meteoric and post-glacial meltwaters. There is no signs of any saline waters residing at Gideå and hence, any marine transgression in the area seem not have played any important role for the waters above 500 m depth.

4.1.5 Finnsjön

In contrast to Gideå and Fjällveden the groundwater at Finnsjön (Figure 3-4) is much more saline, reaching chloride concentrations of 5650 mg/L. Two groups of water are distinguished; one with high HCO_3 concentrations and low Cl, Ca, Na and SO_4 concentrations, and the other which is characterised as a Ca-, Na-, Cl- and SO_4-rich water. These carbonate groundwaters may be explained by an extensive calcite dissolution/precipitation process (Geirnhart, 1972; Deines and Langmuir, 1974; Dienes, 1980; Jones et al., 1987). The aquifers are residing in a granodiorite and granite complex which is foliated and intersected with pegmatites (Ahlbom et al. 1986). $\delta^{18}O$ (-10.9 to -12.0 o/oo) and δD (-83 to -90 o/oo) show very little variation and the water reveal homogeneous isotopic signatures (Hultberg et al., 1981). The $\delta^{18}O$ values are typical of the annual mean value for the meteoric recharge in the area (Burgman et al., 1987; Calles and Westman, 1989). The saline water at Finnsjön may be interpreted to originate from a saline injection into the crystalline basement by any pre-Baltic water, since the location of the site is well below the highest limit of the postglacial Litorina Sea. Smellie and Wikberg (1989) suggest that the groundwater at Finnsjön, in comparison to other groundwaters in Sweden, mainly represent a water of a marine origin but modified by water/rock interaction processes.

4.1.6 Stripa

The chemical analyses of the groundwaters obtained from the Stripa granite (Figure 3-4) different waters are distinguished (Carlsson and Olsson, 1985; Moser et al., 1989; Nordstrom et al., 1989a; Nordstrom et al., 1989b; Andrews et al., 1989a). The surface groundwaters are characterised as Ca-HCO3 type representing dissolution of calcite under typical recharge conditions. The intermediate to deep groundwaters are characterised by a Na-Ca-Cl type groundwater reaching a maximum of about 700 mg/L (Nordstrom et al., 1989a). This is considerably higher Cl concentrations than those observed at Fjällveden and Gideå, but lower than the Finnsjön groundwaters. Further on, the Na-Ca-Cl type groundwaters at Stripa are at or more commonly above saturation with respect to calcite, being driven by high pH values (up to 10) and increased calcium concentrations. The distribution of Cl concentrations is not regular with depth and probably represents a highly variable flow path within the crystalline rock Andrews et al., 1989b). According to Nordstrom et al. (1989c) the source of the saline constituents in the deep groundwater is interpreted to be local, rock-derived salinity, e.g. leakage from fluid inclusions (Kaminemi, 1987; Nordstrom et al., 1989c). This is mainly based on the Br/Cl and I/Cl ratios in the water which are enriched relative to sea water. Although there is not as high Cl readings as at Äspö and Finnsjön a locally derived saline water seem not likely, using the stable isotope data as well.

The plot of $\delta^{18}O$ versus δD (Figure 4-1) show that most of the waters follow the meteoric water line (Moser et al., 1989). The surface waters differ considerably, indicating a depletion in δD. Isotope records in the calcite fissure fillings show interaction between the groundwater and the granite body (Clayton, 1959; Clauer et al., 1989). The δ^{18}O values varies between -9 and -13 o/oo SMOW (Fritz at al., 1989), similar to the Äspö waters.

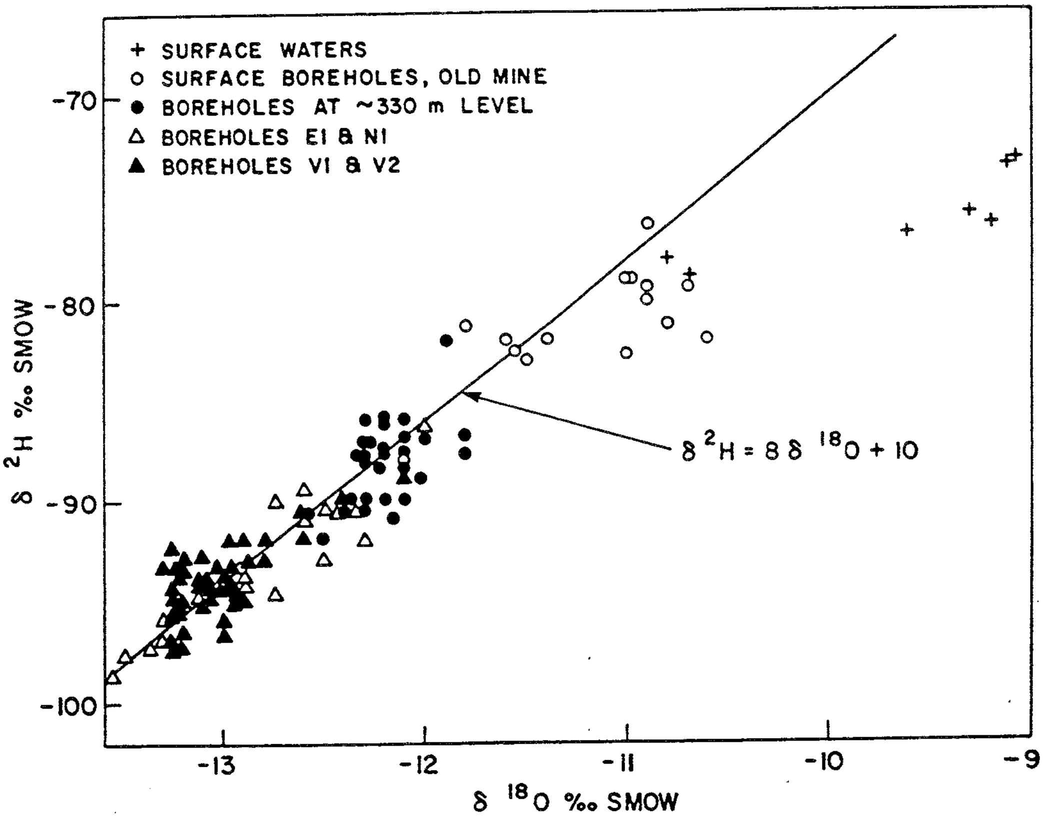

Figure 4-1. *δ^{18}O values plotted versus δD for the groundwater at Stripa. After Moser et al., 1989.*

The δ^{34}S values of the dissolved sulphate in the Stripa groundwaters show a large variation between +27.92 and +2.16 o/oo. The higher readings are according to Fontes et al. (1989) indicative of reduction of deep sulphates and the lower signatures may be a contribution of reduced sulphur due to oxidation of sulphides in the basement rocks (Rees et al., 1978; Claypool et al., 1980). These δ^{34}S values of the dissolved sulphate is considerably higher than those observed at Äspö, supporting a nonmarine origin for this sulphur. In conclusion the sulphate in the Stripa granite clearly reflects multiple sources. In shallow groundwaters atmospheric fallout and oxidation of reduced sulphur species provide most of the sulphate. In deep waters an external source has to be assumed although its origin is not clearly definable. The data obtained from the Stripa study support the interpretation that the chemistry of the deep groundwaters reflects mixing of at least two different waters and/or sources fro the salts (Fabryka-Martin et al., 1989; Loosli et al., 1989; Nordstrom et al., 1989). One end-member is local freshwater, indicated by the typical local meteoric signatures of $\delta^{18}O$, the other according to Fontes et al., (1989) may be a brine. The lower $\delta^{34}S$ values is not incompatible with a sedimentary origin (Michelot et al., 1987) and are similar to what is known about Permian evaporates (Figure 6). This is similar to the $\delta^{34}S$ values observed at larger depth at Äspö, which are typical of Permian evaporates with values around +10 o/oo CDT.

Like the $\delta^{34}S$ values at Äspö, secondary processes seem to be important in the Stripa waters and the isotope data show that bacterial enhanced redox processes play a major role in the control of the concentration of the heavy isotope contents of aqueous sulphate (Figure 4-2) in Stripa groundwaters (Rafter and Mitzutani, 1967).

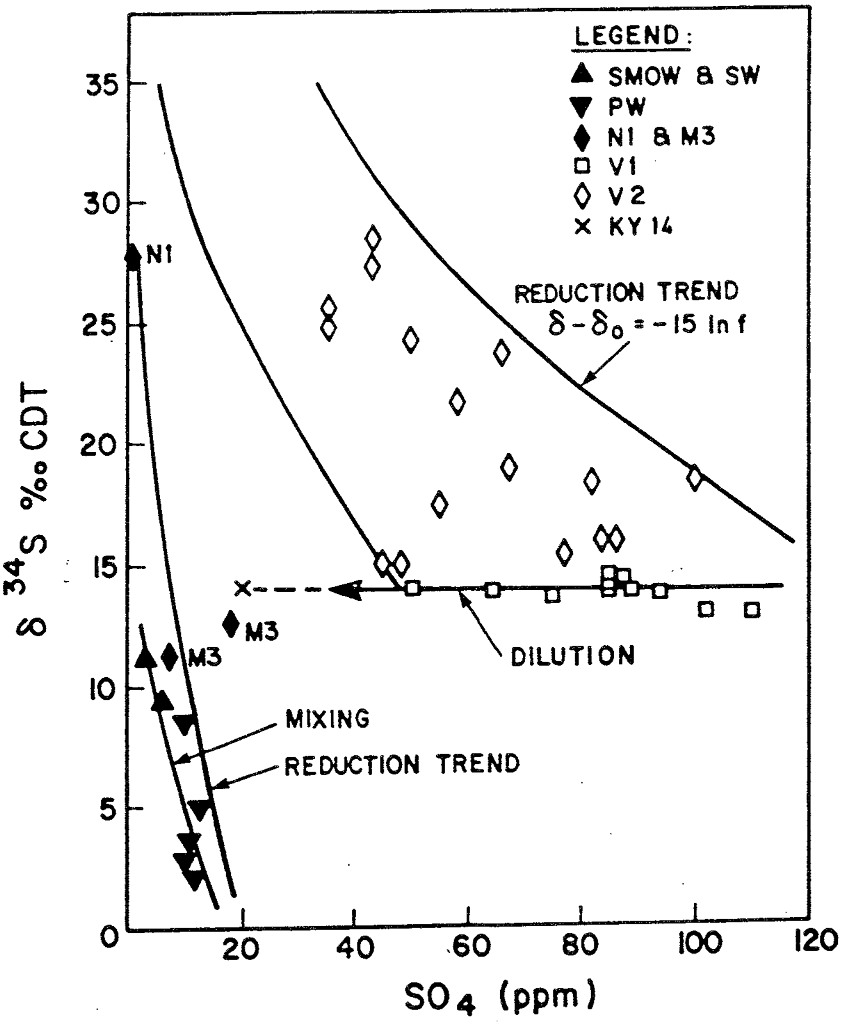

Figure 4-2. *$\delta^{34}S$ values of the dissolved sulphate plotted versus SO_4 in the groundwater at Stripa, after Fotes et al., 1989.*

4.1.7 Äspö

A description of the Äspö groundwater is made here to get a reference to the other described groundwaters in the Baltic region. Groundwater as well as calcite fracture fillings have been analysed in detail at Äspö. None of the isotope signatures resemble those of modern Baltic sea water although the possibility of mixing between Baltic sea water and shallow ground waters cannot be excluded. δD values ranges between -112 to -55 o/oo and $\delta^{18}O$ values range between -7 and -15 o/oo (Figure 4-3).The $\delta^{13}C$ of the bicarbonate range between -16 and -6 o/oo, and decrease systematically with depth suggesting mixing of organic and inorganic carbon (Sackett and Moore, 1966; Pearsson, 1991; Wallin, 1993; Banwart et al., 1994; Wallin et al., 1995). The $\delta^{18}O$ of the bicarbonate is uniform (+18 and +22 o/oo) and in equilibrium with the most of the ground water.

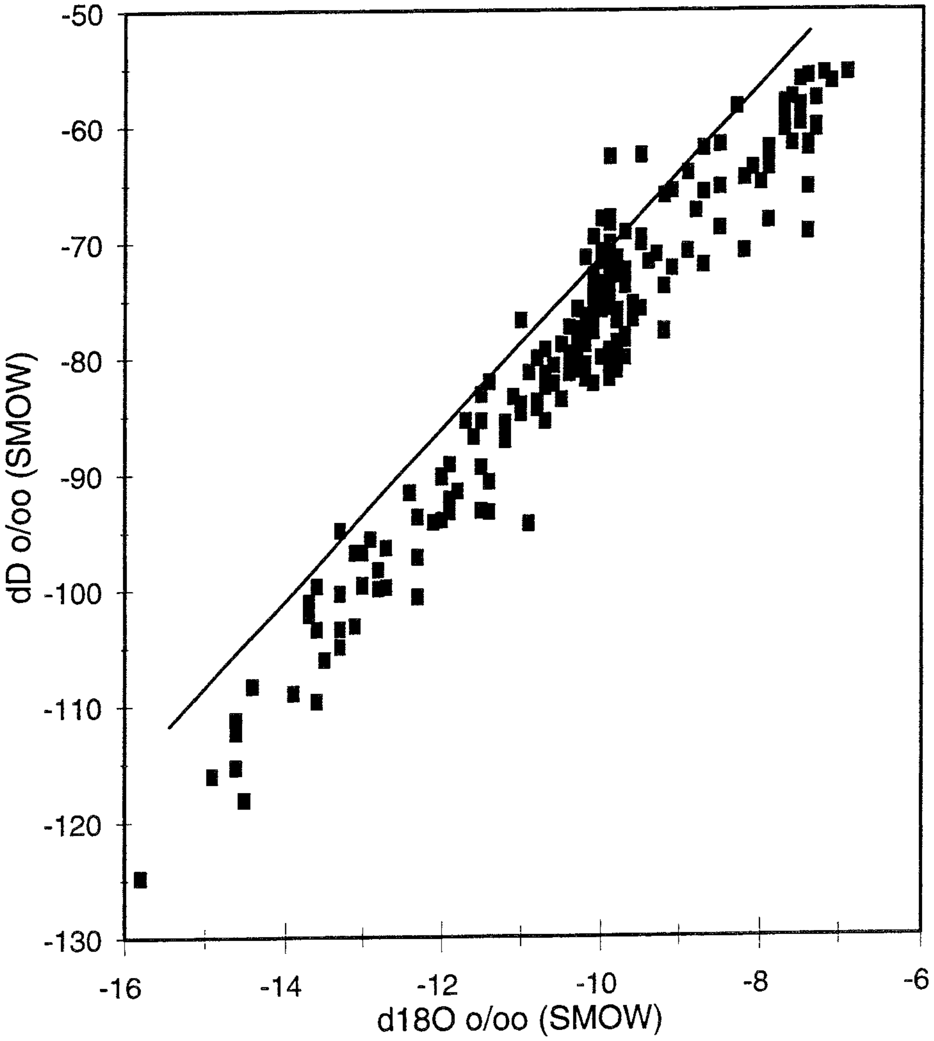

Figure 4-3. *$\delta^{18}O$ values plotted versus δD for the groundwater at Äspö. After Wallin and Peterman, 1994.*

$\delta^{34}S$ values of the dissolved sulphate varies between +9.8 to +21 o/oo (Figure 4-4). More than twenty samples ground water from 15 to 800 m deep have $\delta^{87}Sr$ values between +9.9 and +13.9 o/oo (Figure 4-5) in contrast with five samples of Baltic Sea water collected in the vicinity of Äspö with $\delta^{87}Sr$ values between +0.2 and +0.4 o/oo, only slightly larger than open ocean water ($\delta^{87}Sr = 0$ o/oo). The 1.8-Ga host rock (Johansson, 1988) at Äspö is characterised by low Rb/Sr ratios, and a calculated mean $\delta^{87}Sr$ of approximately +2.5 o/oo demonstrates a lack of isotopic equilibrium between the ground water and the host granite at the bulk rock scale although preferential mineral dissolution is possible.

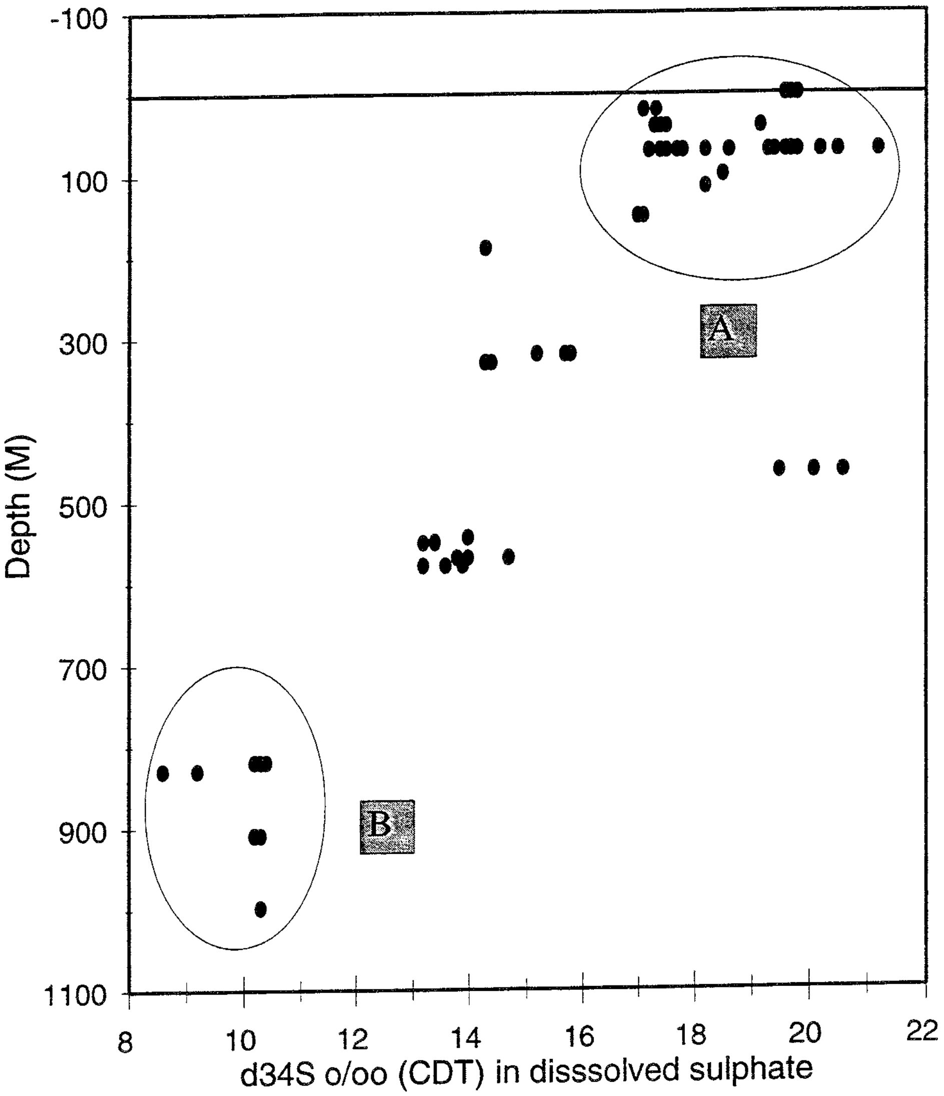

Figure 4-4. *$\delta^{34}S$ values of the dissolved sulphate in the groundwater plotted versus depth at Äspö. After Wallin and Peterman, 1994.*

For example, biotite has extremely large $\delta^{87}Sr$ values, but studies of saline ground water in the Canadian Shield indicate that preferential reaction with plagioclase results in δ^{87}Sr that are typically smaller than the bulk-rock values (McNutt, 1987; Pearsson, 1987; Pekdeger and Balderer, 1987). Calcite fracture fillings add further complexity to the Sr-isotope budget. Calcite fillings from depth between 363 and 612 m have δ^{87}Sr values between +4.7 and +9.9 o/oo (Figure 4-5) whereas deeper samples (815 m) have smaller value of -3.0 to +0.6 o/oo coupled with an order of magnitude larger Sr concentrations.

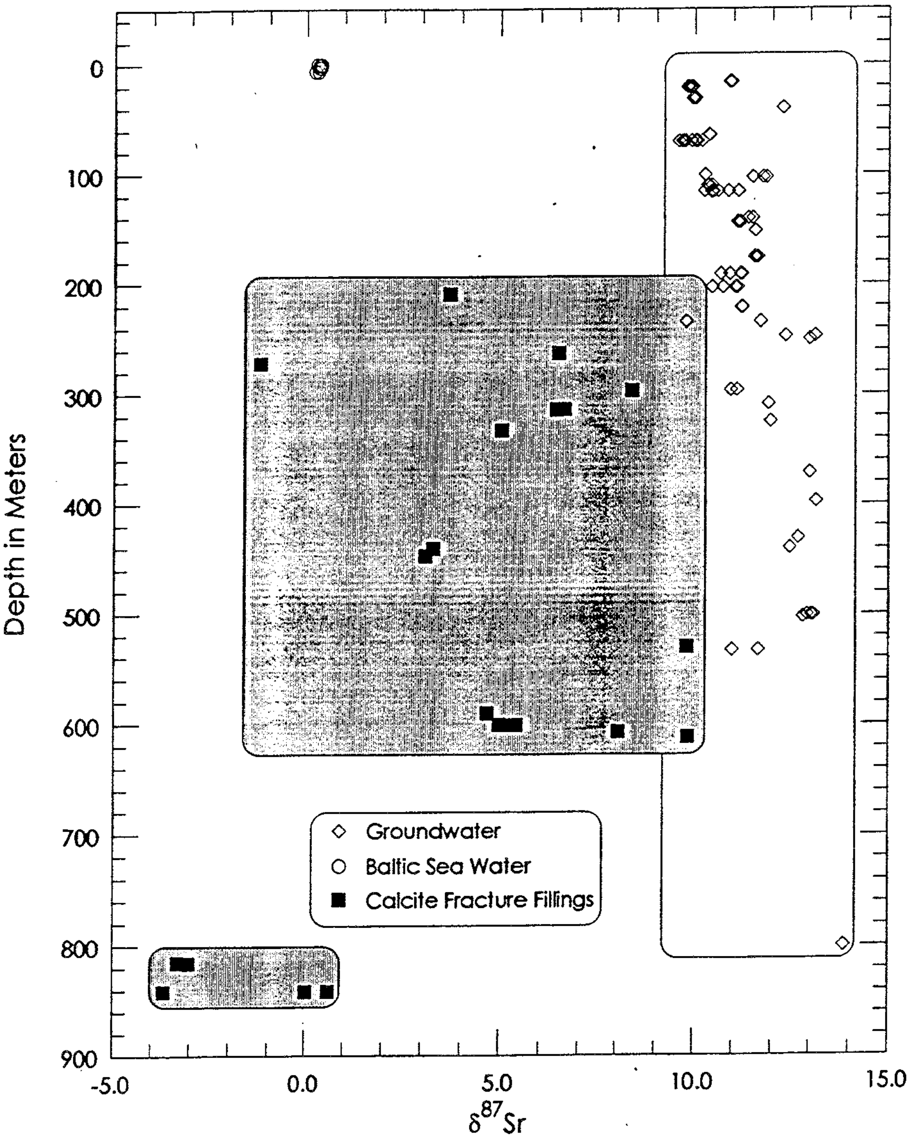

Figure 4-5. *δ^{87}Sr values in calcite fracture fillings as well as in present day groundwater at Äspö and Baltic Sea water plotted versus depth. As can be seen from this plot the two different calcite precipitates did not formed directly from present day groundwater at Äspö. After Wallin and Peterman, 1994.*

δ^{13}C values in the calcite fissure fillings range between -25 and -3 o/oo and the δ^{18}O values range between +15 to +35 o/oo (Figure 4-6). The large range in δ^{13}C values is indicative of multiple sources for the carbon, including atmospheric (Murata et al., 1969), organic (Keith and Weber, 1964; Pearsson and Hanshaw, 1970; Shulz and Calder, 1976; Irwin et al., 1977) and methane derived carbon (Donnovan, 1969; Andrews and Wilson, 1987; Edmonds et al., 1984; Edmonds et al., 1985). The $\delta^{18}O$ signatures suggest mixing of meteoric and marine waters (Hanor, 1978; Hoefs, 1987), but most of the calcites are precipitated from waters with $\delta^{18}O$ values similar to those of present-day ground water.

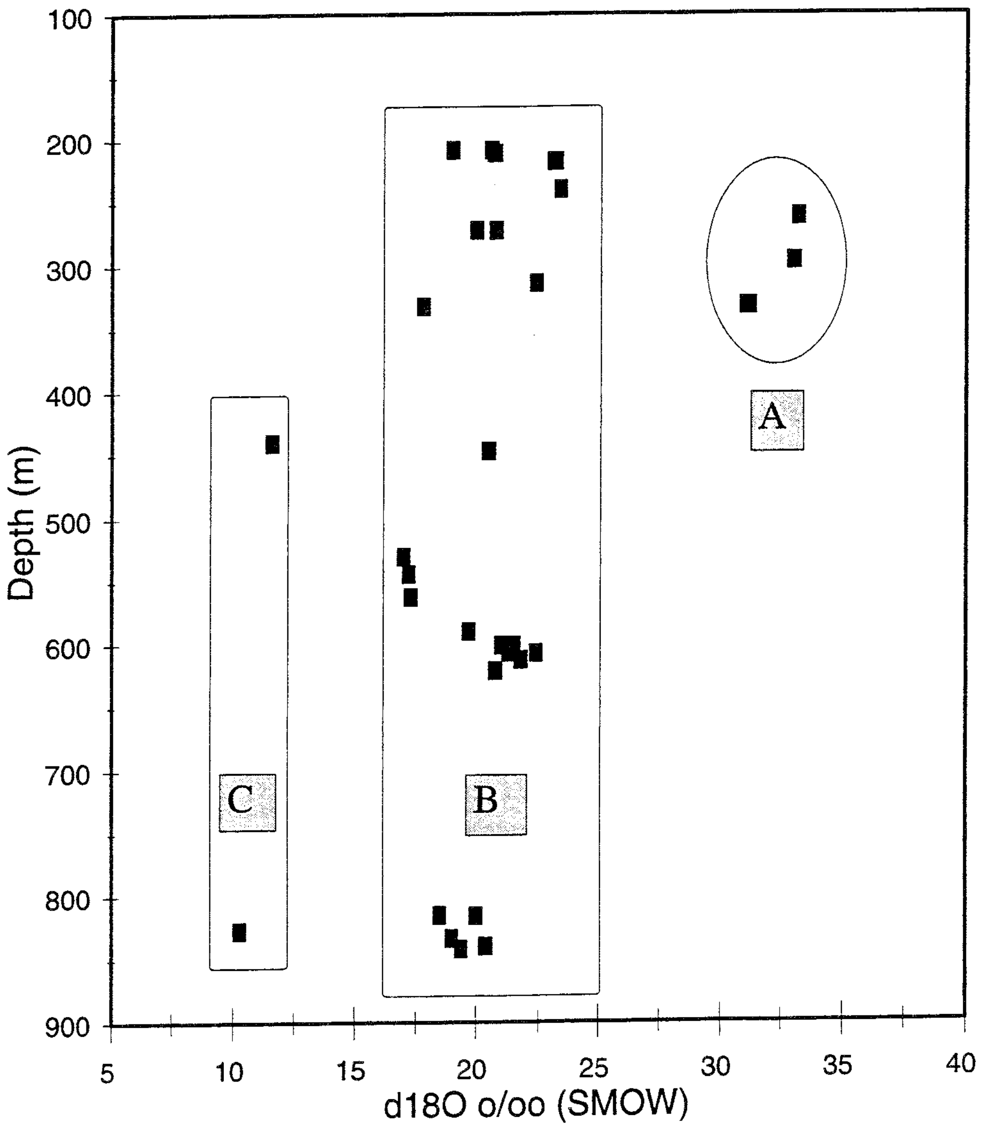

Figure 4-6. *$\delta^{18}O$ in calcite generations plotted versus depth at Äspö. After Wallin and Peterman, 1994.*

The stable isotope data from the calcite fissure fillings and the dissolved species suggest three different water layer at Äspö: (1) a shallow ground water (0-150 m) characterised by a mixture of meteoric water and minor proportions of Baltic Sea water, (2) an intermediate ground water (150 - 500 m) characterised by a mixture of marine and meteoric isotope signatures, and (3) a deep ground water body (>500m) which is highly saline with nonmarine signatures of the dissolved species. According to the seasonal variation of the isotopic signature (D and $\delta^{18}O$) of the rain water the recharge of this water lens takes place during the autumn and the winter. In the intermediate water body, a substantial decrease in the $\delta^{34}S$ values of the dissolved sulphate (Figure 4-5) indicates the addition of a component of a non-marine sulphur that could derive from the oxidation of sulphide minerals such as pyrite (Krause, 1980). Therefore, the sulphur and oxygen isotope data combined for that water suggest that the intermediate groundwater originates from an early injection of a highly oxygenated Baltic seawater after the latest ice recession in the area. The deep ground water body has a stable isotope assembly with overall typically nonmarine signatures which coincidentally correspond to $\delta^{34}S$ signatures found in Permian evaporates (Sakai, 1972), and hence may therefore possibly be sedimentary in origin (Holser, 1966; Hoefs, 1987; Longinelli, 1989). However, the spread in $\delta^{34}S$ values of the dissolved sulphate in combination with the sulphide sulphur signatures (Wallin, 1992) suggest that considerable bacterial sulphate reduction (Bågander, 1977; 1980) takes place in the upper part of this water body.

4.1.8 Laxemar

Highly saline waters are also reported from drill holes in the coastal areas in southeastern Sweden at Äspö and Laxemar which are performed by SKB. At depth of about 800 m the chloride concentrations increases dramatically from 6000 mg/L to 60 000 mg/L at a depth of 1400 m. This is surpassingly high readings for groundwaters in the crystalline basement, represented by granites and granodiorites of Småland type (Johansson, 1988) and no other waters in the crystalline basement (Stanfors, 1988; Stråhle, 1989) have reached these high chloride concentrations (Gascoyne et al., 1987; Vovk, 1987). The stable isotope data from the groundwater at Laxemar support two major groundwater types. The shallow groundwater ($\delta^{18}O$ = -12.1 to -9.9 o/oo; δ^2H = -85.2 to -73 o/oo) project close to the Global Meteoric Water Line (GMWL) whereas, the deep groundwater ($\delta^{18}O$ = -10.4 to -8.9 o/oo; δ^2H = -60.2 to -44.9 o/oo) show significant deviation from the GMWL (Laaksuharjo, 1994). This is in accordance with the deep Canadian brines (Frape and Fritz, 1987) which show similar characteristics. The deep water, below approximately 1000 m depth, at Laxemar show a homogeneous $\delta^{18}O$ value of about -9 o/oo, different from the shallow waters, indicating a more stable water body. The change in the $\delta^{18}O$ signature of the water coincide with the change in chloride concentration, with a depletion in $\delta^{18}O$ with increased chloride concentration. The $\delta^{34}S$ values of the dissolved SO_4 at Laxemar show a wide range between +9.9 to +21 o/oo CDT. The deep groundwater below display a very uniform signature of $\delta^{34}S$ of about +10 o/oo, supporting the idea of having a sedimentary source, presumably leached evaporates as a source for that sulphur (Wallin, 1990; Wallin, 1992).

4.2 GROUNDWATERS IN FINLAND

Brackish to saline groundwaters, in the range of 1000 to 15 000 mg/L total dissolved solids, commonly occur in coastal areas of Finland (Figure 3-3) beginning at depth of 50 - 150 m from the surface (Nordstrom, 1989). Many of these waters are interpreted to originate from seawater transgression into the Baltic during the Litorina period of 7700 to 2500 years B. P. based on the geographic distribution. The major part of the saline water wells are located in the area below the highest limit of the postglacial Litorina Sea (Figure 3-3) . Moreover, the groundwater from the central Finland is dominating by brackish waters. Hence, similarly to what is observed in Sweden as well, the saline wells are typically found in the coastal regions. Chemical analyses from various wells along the coast indicate that numerous upper shallow (< 100 m) and some intermediate groundwaters (100 to 300 m) show a similar chemistry to what should be expected from a marine water. At Hästholem e.g., north-east of Helsinki, (Figure 4-7) a shallow freshwater lens of Ca-HCO3 type water sits above saline groundwater containing about 5000 mg/L of chloride (Kankainen, 1986; Nordstrom, 1989).

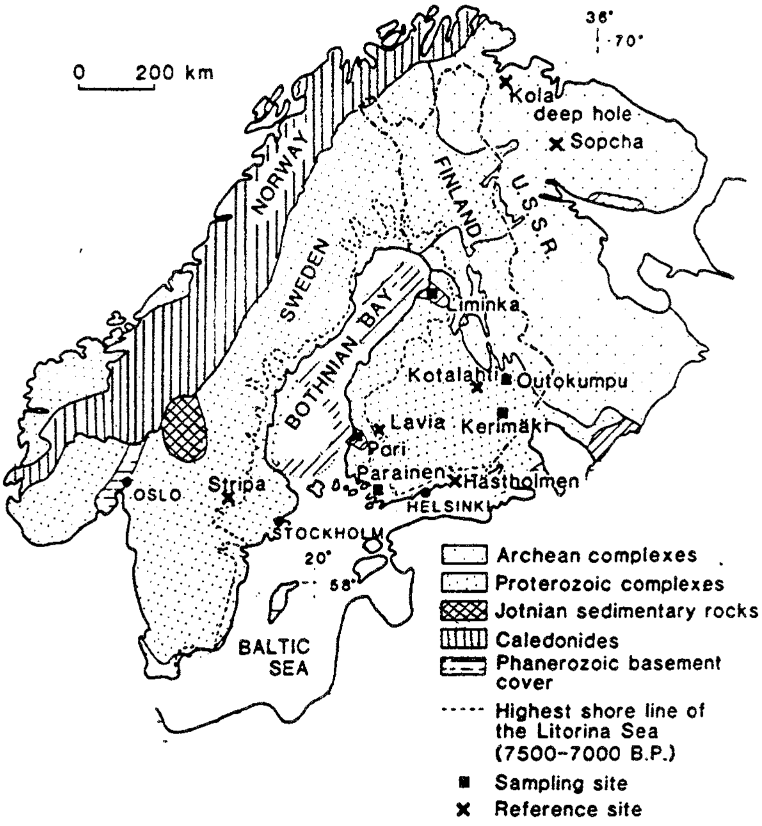

Figure 4-7. *Map showing the geological features of the Fennoscandian Shield, and location of important deep drillholes from Finland. After Nurmi et al., 1988.*

4.2.1 Hästholmen

In the coastal well at Hästholmen (Figure 4-7) in Finland the chemical composition of the saline water which is residing below the freshwater lens, is chemically relatively uniform (Nordstrom, 1989d; Snellman and Helenius, 1992). The $\delta^{18}O$ signatures of this water is also very uniform around -8 o/oo. These values are significantly higher readings than what is observed at Äspö (-11 to -13 o/oo). In addition the higher $\delta^{18}O$ values at Hästholmen coincide very well with the values of the Baltic sea water of today. For example at Äspö the Baltic sea water signatures are about -7 o/oo (Wallin, 1989; Tullborg and Wallin, 1991) and in the southern part of Baltic as high as -6 o/oo. Hence, since the $\delta^{18}O$ isotope analyses of the saline groundwater at Hästholmen display such a uniform quality, the larger part of that water must have derived from one source only (Kankainen, 1986). Estimates made by Kankainen (1986) suggest that if this saline water originated from the marine water of the Litorina Sea, then the residence time for this water is equivalent with a possible infiltration, which roughly refers to about 7000 years. This is also based on the calculations made by Winn et al (1988) which show that the initial stage of the Litorina transgression took place at about 7000 to 8000 years ago in the southern Baltic area. During the Holocene the history of the Baltic sea has had only one marine stage, that of Litorina Sea, which Hästholmen saline groundwater can be attributed. This must be due to the northerly position of Hästholmen.

4.2.2 Outokumpu and Kerimäki

In contrast to the coastal groundwater of Hästholmen, the saline groundwater observed in the Outokumpu (Figure 4-7) have much higher $\delta^{18}O$ signatures between -13 and 14 o/oo. These higher $\delta^{18}O$ values are also commonly observed at Kerimäki (Figure 4-7) in the eastern central Finland. Interestingly the $\delta^{18}O$ signatures at both sites display a very uniform pattern from the surface to the deeper depth at about 1000 m at Outokumpu and 700 m at Kerimäki (Nurmi et al., 1988). These lower values are also seen at Äspö although more uniform at lower depth, approximately 500 m and below. The surface waters at Äspö are more enriched in the ^{18}O isotope than what is seen here. This must be explained by the coastal situation for Äspö in comparison to the inland, continental position of Outokumpu and Kerimäki. Moreover it seem very unlikely that there has been any marine waters residing in these central areas of Finland during the last glaciation. The dramatic increase in the high salinities marked by the sharp transition which are observed at Outokumpu below 600 m (Figure 4-8, 4-9), must hence be attributed to other processes than intruding marine waters (Fyfe, 1987). The brackish and saline groundwaters below the fresh water layer at Outokumpu do not actively participate in the present-day surface water circulation but they may bear fingerprints of an earlier interaction between the deep saline water (or brines, Kholodov, 1973; Gascoyne et al., 1987; Nordstrom et al., 1987), fresh water and bedrock (Nurmi, et al., 1988). It is important to note that the that sharp zones of transition, such as those detected between the fresh and saline water, may exist between successive saline water (e.g. Outokumpu). This is clearly demonstrated in the Kola superdeep drillhole, where several brine layers with different geochemistry and salinity have been detected (Borevsky et al., 1984; Kremenetsky and Ovchinnikov, 1986). These sharp transition zones are clearly developed at both Äspö and in the deep drillhole at Laxemer. At about 500m depth this transition in salinity occur at Äspö, reaching chloride concentrations of about 13000 mg/L. In Laxemar a very sharp transition zone is developed at about 1000 m. The upper 1000 m is characterised by a low saline (< 600 mg/L Cl) and below this depth there is highly saline groundwater reaching a chloride concentration of 46000 mg/L.

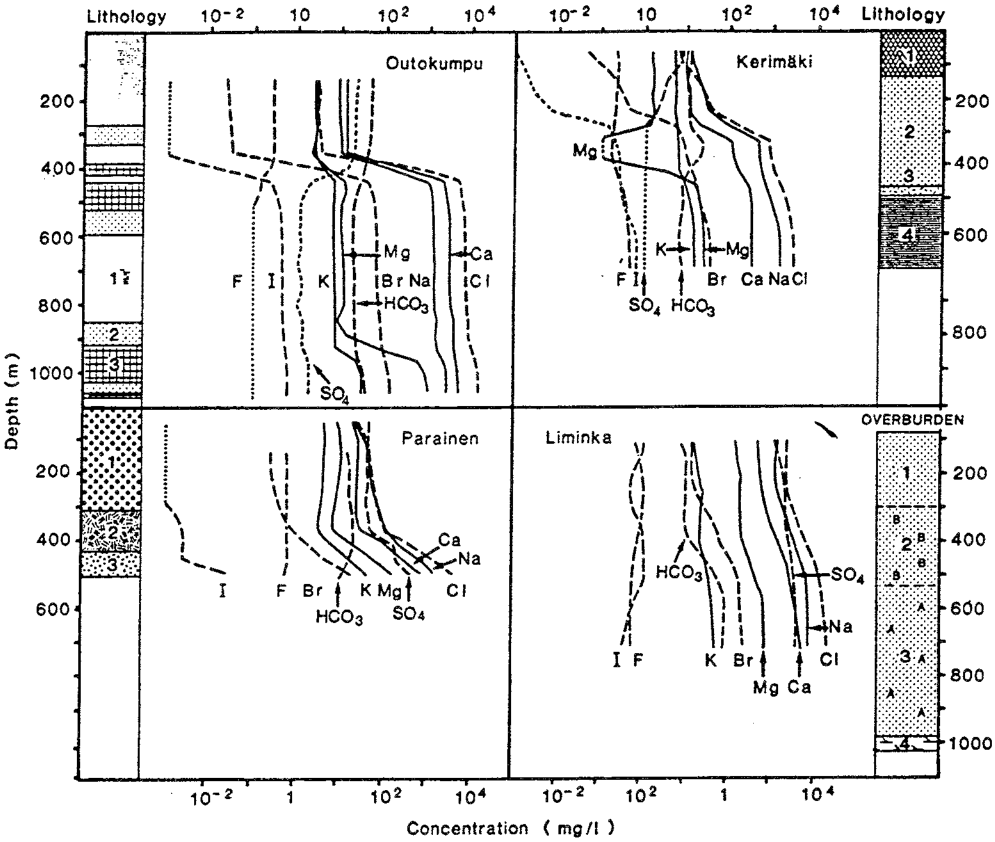

Figure 4-8. *Diagram showing the variation in the chemical composition versus depth at Outokumpo, Kerimäki, Parainen and Liminka. After Murni et al., 1988.*

The $\delta^{18}O$ signatures of the deep water at Laxemar display a relatively homogeneous pattern ranging between -9 to -10 o/oo, slightly higher than the $\delta^{18}O$ values at Outokumpu and Kerimäki. The stable isotope data from the groundwater at Laxemar support two major groundwater types. The shallow groundwater ($\delta^{18}O$ = -12.1 to -9.9 o/oo; δ^2H = -85.2 to -73 o/oo) project close to the Global Meteoric Water Line (GMWL) whereas, the deep groundwater ($\delta^{18}O$ = -10.4 to -8.9 o/oo; δ^2H = -60.2 to -44.9 o/oo) shoe significant deviation from the GMWL (Laaksuharjo, 1994). This is in accordance with the deep Canadian brines (Frape and Fritz, 1987) which show similar characteristics. The characteristics of the dissolved components of the groundwater at Outokumpu (Figure 4-8) support a brine type of water similar to that described on the Canadian Shield (Frape and Fritz, 1982; Fritz and Frape, 1982; Frape at al., 1984). This is especially exemplified when plotting the Ca-Na-Mg fraction distribution in a piper plot (Figure 14). The brine type of water typically show an increase in Ca with a significantly decrease in the Na concentration. Moreover, the increase in temperature versus depth reveal that the geothermal gradient is developed and there is no direct signs of any advective situation (Figure 4-9). The deep saline waters observed at Outokumpu and other inland wells have elemental ratios which for the major part deviate from marine waters (Blomqvist, 1990). Accordingly, the concentrations exceed by far the values in the ocean waters (Blomqvist et al., 1989). There is a close relation between the groundwater appearance and the basement geology, hence these water may partly have originated due to water/rock interaction.

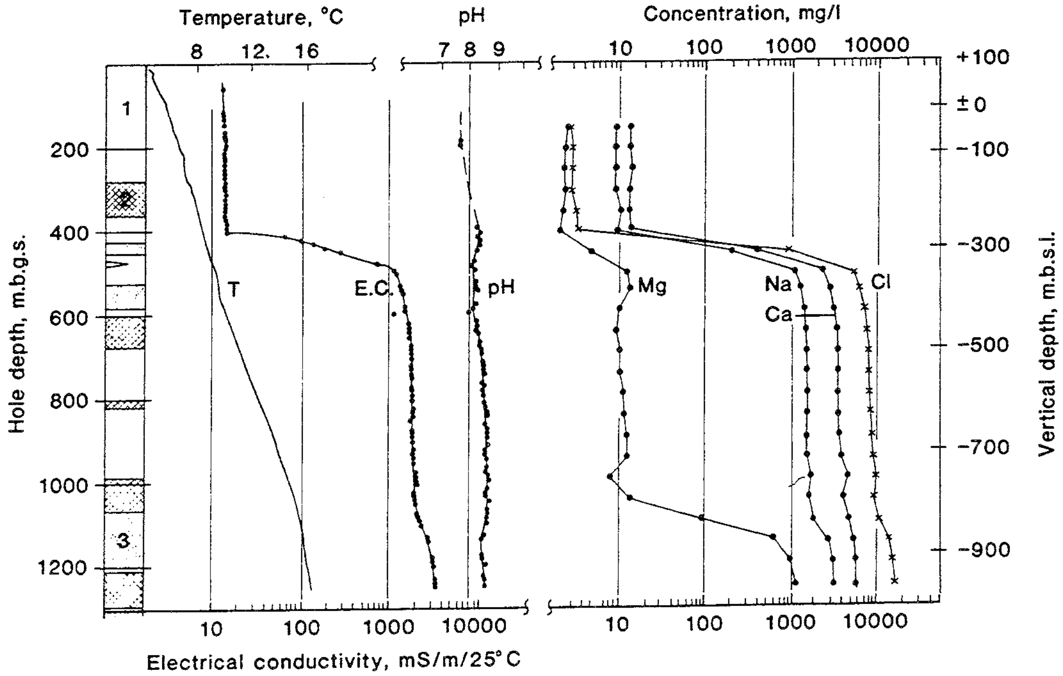

Figure 4-9. *showing the variation in the chemical composition versus depth at Outokumpo including the temperature curve. After Lahermo and Lampén, 1987.*

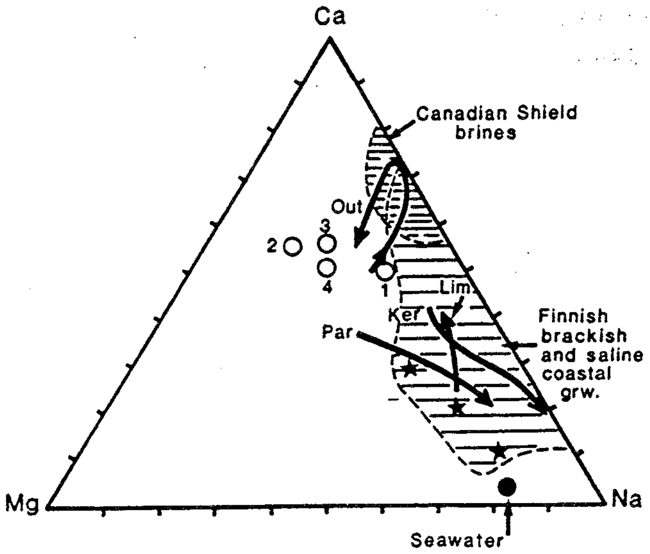

Figure 4-10. *Ca-Mg-Na diagram showing the trends in the groundwater from different sites in Finland. After Nurmi, et al., 1988.*

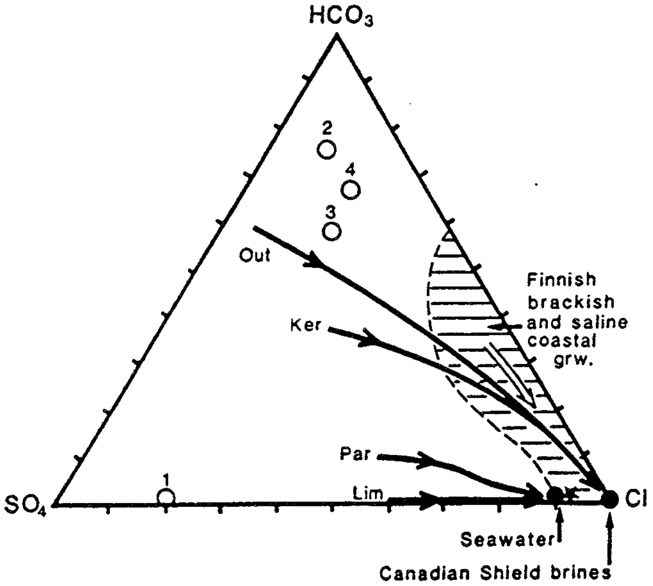

Figure 4-11. *HCO_3-Cl-SO_4 diagram showing the trends in the groundwater from different sites in Finland. After Nurmi, et al., 1988.*

4.2.3 Parainen, Liminka and Lavia

In both Parainen and Liminka (Figure 4-7) which are located in the coastal areas show a deep freshwater with chloride concentrations below 1000 mg/L at depth of 400 m. This is explained by different hydrogeogological conditions and as a result of effective infiltration of fresh water along subvertical fracture zones. Both these two sites are located below the highest limit of the postglacial Litorina Sea. In contrast the Lavia hole (Figure 4-7) which is drilled in a granite pluton adjacent to regional shear zones have a groundwater flow into the basement at low depth and a large freshwater aquifer which is at least 950 m thick (Wickström and Lampén, 1986) Studies in the Kola hole show that freshwater circulation reaches down to 800 m (Borevsky et al., 1984). Hence, it is not unlikely to have a large freshwater layer such as the one developed at Laxemar in Sweden. The chemistry of the groundwater at Parainen and Liminka is characterised by an increase in Na concentrations along with a decrease in Ca (Figure 4-8) typical of the coastal aquifer patterns, totally different from the Outokumpu waters.

4.2.4 Romuvaara, Veitsivaara, Kivetty, Syyri and Olkiluoto

The detailed investigation made by Lampén and Snellman (1993) through TVO of selected sites for safe final disposal of nuclear wastes, provide a lot of data from 5 different sites namely Romuvaara, Veitsivaara, Kivetty, Syyri and Olkiluoto. Roumavaara, Veitsivaara and Kivetty is situated in central and eastern Finland (Figure 4-7) above the highest limit of the postglacial Litorina Sea and Syyry and Olkiluoto are situated in the western Finland (Figure 4-7) below the highest limit of the postglacial Litorina Sea. The inland groundwaters from Roumavaara, Veitsivaara and Kivetty may be characterised as Ca-Na-HCO3 waters (Figure 4-11). The geology in the Roumavaara, Veitsivaara and Kivetty districts are dominated by gneisses and tonalitic rocks of Archean age, although at Kivetty some mafic rocks are seen, mainly as gabbros. In contrast the groundwaters at Syyry and Olkiluoto is characterised by a Ca-Na-Cl waters (Figure 4-10), which is typical of what is observed at other sites in Finland in areas which are located below the highest limit of the postglacial Litorina Sea. The geology at these sites is not much different from the inland sites, Roumavaara, Veitsivaara and Kivetty, which suggests that there has been no or little water/rock interaction for the coastal groundwaters.

In summery we can conclude that two significant groups of groundwaters are observed in the crystalline basement in Finland, similarly to what is seen in Sweden. The first group is typical of a Ca-Na-HCO3 rich waters (Figure 4-10, 4-11) which is located above the highest limit of the postglacial Litorina Sea and the other group of Ca-Na-CL rich water (Figure 4-10) which is found in the coastal areas adjacent to the PaleoBaltic border. In addition, the inland deep waters of Finland is, similarly to the Swedish waters residing in the crystalline basement enriched in Br/Cl ratio in relation to the marine signature (Figure 4-12). Moreover, most of the deep groundwaters from the sites situated above the highest limit of the postglacial Litorina Sea show a major as well as minor element composition which is typical of the basement rock types (Figure 4-13) (Hyyppä, 1984; Hyyppä, 1986; Nurmi et al, 1988). This strongly support that the groundwaters found in the coastal areas of the Baltic region in the crystalline basement may represent relict marine waters which have entered the ground during the post-glacial marine stages, presumably from the Litorina sea. The low saline surface waters at Romuvaara, Veitsivaara, Kivetty, Syyri and Olkiluoto show a variation in Cl concentration depending on inland or near coastal location (Figure 4-14). All other deep saline inland deep waters seem to be originate from water/rock interaction processes or leaching of sediments or deposits by an extensive meteoric influx during long time periods, similar to the groundwaters in the Canadian Shield (Frape et al., 1984; Frape and Fritz, 1987; Fritz et al., 1987).

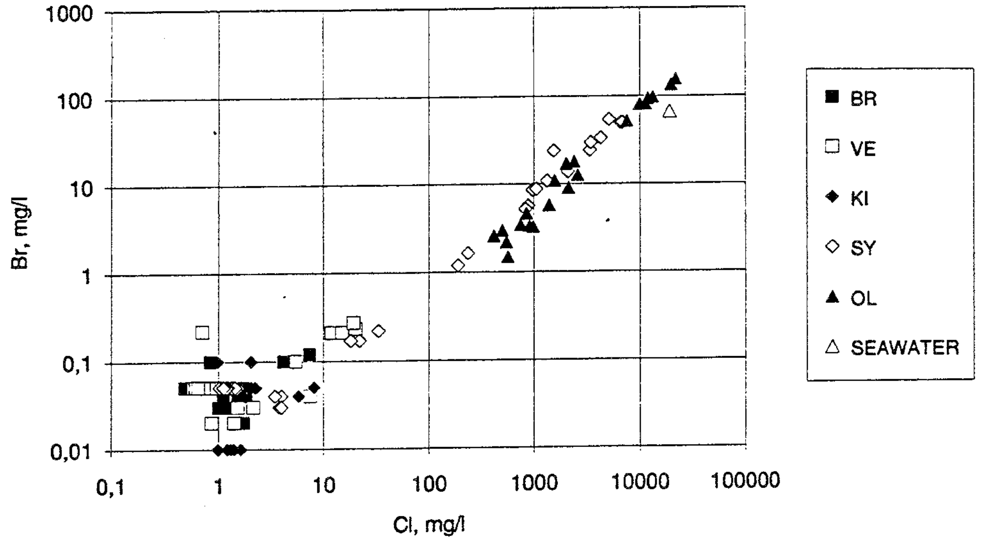

Figure 4-12. *Diagram showing the Br conc. versus Cl conc. of the groundwater from (BR), Veitsivaara (VE), Kivetty (KI), Syyry (SY), Olkiluoto (OL) and Seawater. After Lampén and Snellman, 1993.*

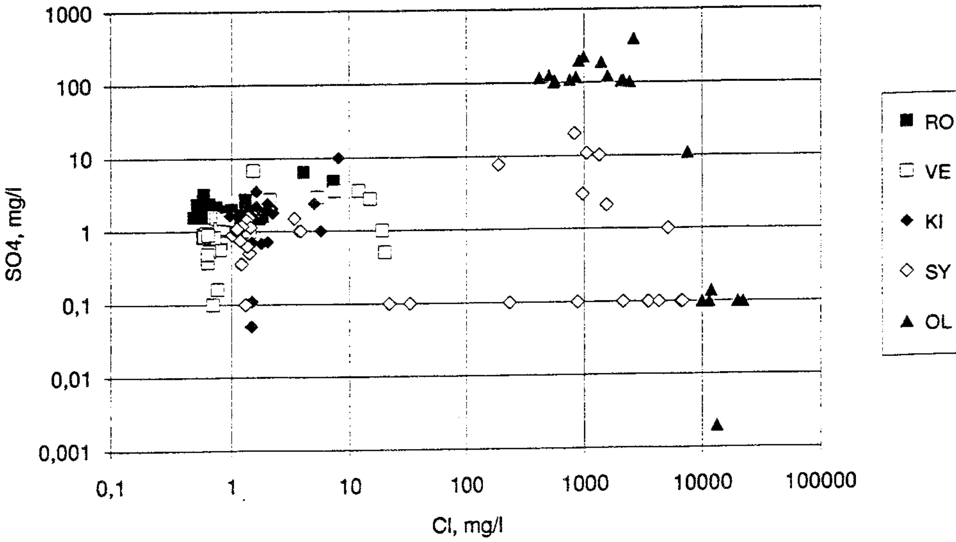

Figure 4-13. *Diagram showing the SO_4 conc. versus Cl conc. of the groundwater from Romuvaara (RO), Veitsivaara (VE), Kivetty (KI), Syyry (SY), Olkiluoto (OL) and Seawater. After Lampén and Snellman, 1993.*

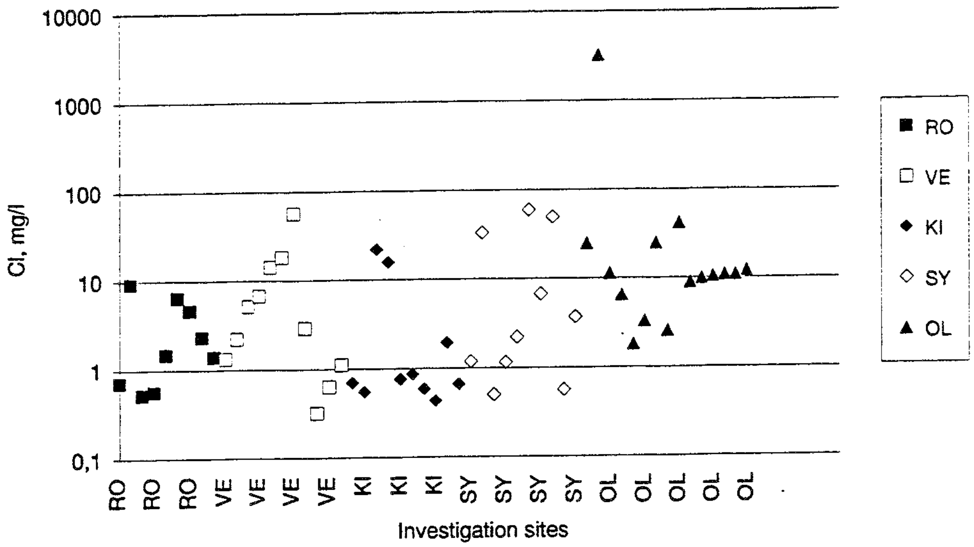

Figure 4-14. *Cl levels of the surficial water samples at Romuvaara (RO), Veitsivaara (VE), Kivetty (KI), Syyry (SY) and Olkiluoto (OL). After Lampén and Snellman, 1993.*

5 STRONTIUM BEHAVIOUR IN SOME FINNISH AND SWEDISH GROUNDWATERS

Strontium isotopes in the Finnish groundwaters show relatively high $^{87}Sr/^{86}Sr$ numbers similar to those observed at Äspö and Laxemar. In the coastal groundwaters at Parainen and Liminka which are situated below the highest limit of the postglacial Litorina Sea the $^{87}Sr/^{86}Sr$ values varies between 0.716618 and 0.71881 ($\delta^{87}Sr$ = +9.9 and +13.5 o/oo). These values coincide very well with the groundwater measurements at Äspö in KAS02, KAS03, KAS06, KAS07, KAS08, KAS09 KAS12 and KAS13. The dissolved solids together with stable isotope evidence from the intermediate (100 to 500m) groundwater at Äspö suggest a possible marine origin for that water. In contrast, the strontium isotope signature show a more terrogene component, totally different from a marine component, suggesting that the higher $\delta^{87}Sr$ signatures indicate a large input of strontium due to the continental runoff in connection with the postglacial ice recession. If this is true then the Litorina sea may have been enriched in strontium ^{87}Sr from the meltwater run-off. Hence, since the same pattern arises both in Finland and Sweden for some of the coastal aquifers then refers to a Litorina intrusion of saline waters with elevated $\delta^{87}Sr$ signatures. Another explanation for the elevated $\delta^{87}Sr$ values may also be a result of a preferential interaction with plagioclase feldspar, a process to explain unradiogenic Sr in deep waters in the Canadian Shield (Frape and Fritz, 1986). The Kerimäki (Figure 4-7) which is located, in the ester central Finland have much less values than those observed in the coastal areas of Sweden and Finland. Possibly these numbers refer to the mean values which are expected from the recharge meteoric water in the area.

In Outokumpu, the $^{87}Sr/^{86}Sr$ signatures of the deep groundwater is much more positive than those reported in Finland as well as Sweden along the Baltic sea margin. A feaseble explanation for this is that these waters, which presumably are very old, has undergone an extensive water/rock interaction. Most likely interaction between fissure clay minerals and the groundwater has developed these high $^{87}Sr/^{86}Sr$ signatures.

6 TEMPERATURE CHANGE AND STABLE ISOTOPE DISTRIBUTION IN ATMOSPHERE AND METEORIC WATER RECHARGE

Due to climatic changes the temperature variation is recorded as a fingerprint in the isotope ratios (Taylor, 1974; Wallin, 1982). This is especially demonstrated in the $\delta^{18}O$ signature in the meteoric water. There is a clear correlation between the isotope variation in the water and the latitude of formation. $\delta^{18}O$ measurements in ice cores (Figure 6-1) from Byrd Station in Antarctica and Camp Century on Greenland show extremely low signatures of about -40 o/oo (SMOW).

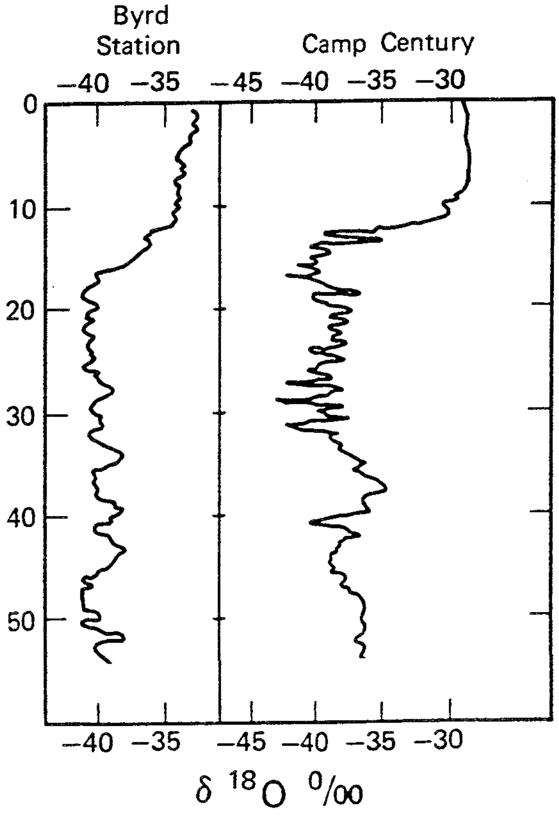

Figure 6-1. *Variation of* $\delta^{18}O$ *in ice cores from Byrd Station, Antarctica and Camp Century, Greenland. The more negative* $\delta^{18}O$ *values in this figure are from about 50000 to 12000 years B. P. in both cores reflect colder climate conditions during the last ice age. Modified after Faure, 1977.*

This depletion in $\delta^{18}O$ signatures is also observed in northern Atlantic surface water with increased latitude. In addition, this depletion in $\delta^{18}O$ signatures is followed by a depletion in salinity in the North Atlantic Ocean (Figure 6-2). The most likely explanation for this is the high input of ice meltwater and heavy negative $\delta^{18}O$ signatures in the higher latitudes. The depletion in $\delta^{18}O$ signatures due to the temperature and latitude effect is clearly observed in the groundwaters in Scandinavia (Figure 6-3).

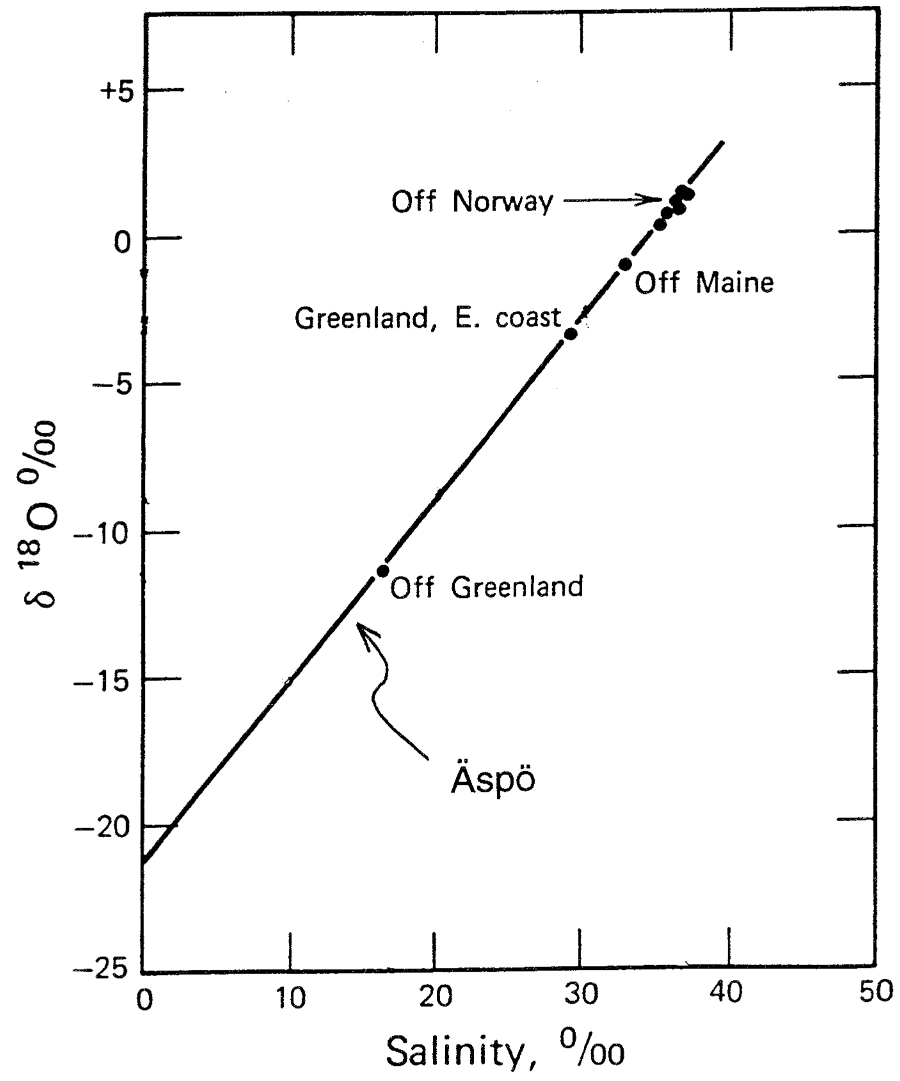

Figure 6-2. *Relationship between $\delta^{18}O$ and salinity surface water from the North Atlantic Ocean. After Faure, 1977.*

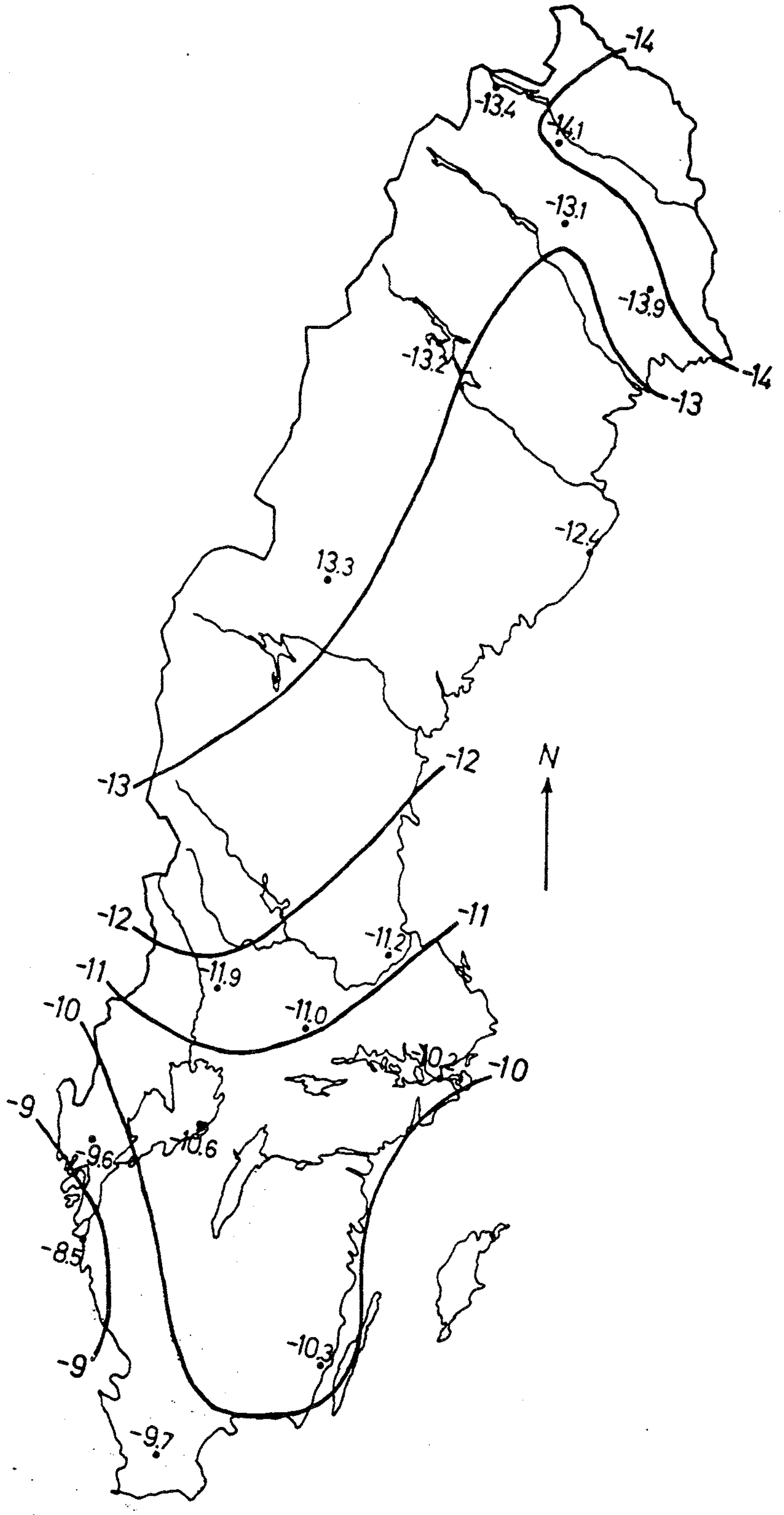

Figure 6-3. *Isoline pattern based on the average $\delta^{18}O$ values in the rainwater precipitation between 1975 and 1980 in Sweden. After Burgman et al., 1983.*

In a smaller scale the seasonal temperature variation has shown to be important to understand fluctuation of the stable isotope signature of δD and $\delta^{18}O$. During a 15 year time period the annual temperature of the surface groundwater was recorded at one station (Figure 6-4) showing an average annual variation of about 6°C. The temperature variation in the atmosphere is also recorded in the δD and $\delta^{18}O$ ratios of precipitate rain fall. This is nicely exemplified from the Smedby meteoric station (Figure 6-5) not far from Äspö, where the $\delta^{18}O$ varied between -8 and -13 o/oo. As another example the annual variation in δD at Kivetty in Finland is shown in Figure 6-6.

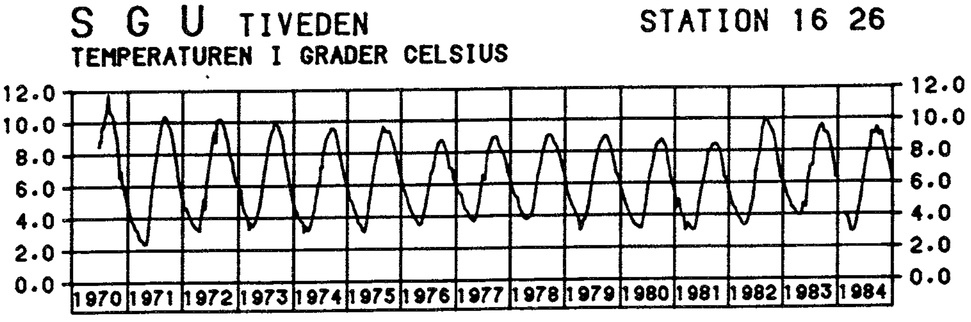

Figure 6-4. *Annual fluctuation of the surface groundwater temperature in a well in central Sweden during a period of 15 years. After Johnsson et al., 1985.*

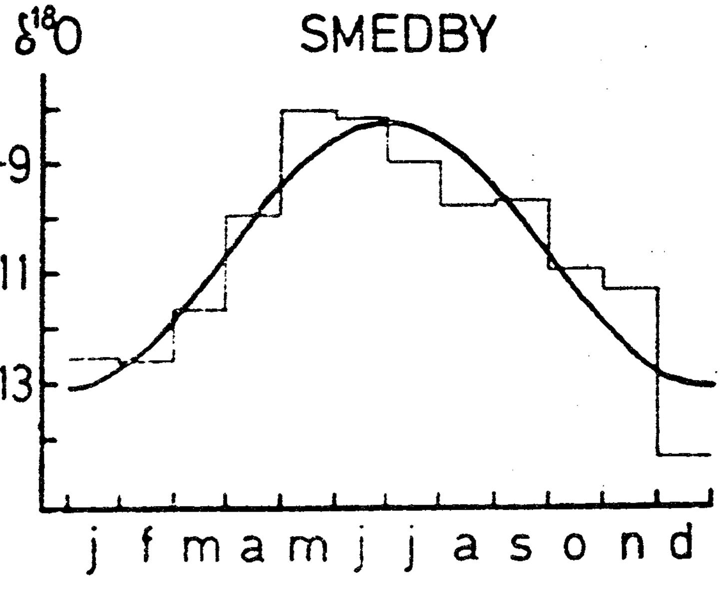

Figure 6-5. *Annual variation in $\delta^{18}O$ in the rainwater precipitation at Smedby southeastern Sweden, close to Äspö. After Burgman et al., 1983.*

In order to compare different the groundwaters from the stable isotope point of view the conventional plot of δD versus $\delta^{18}O$ helps a lot. Normally the average isotopic signatures from the precipitates follow the so called Global Meteoric Water Line (GMWL) which is seen in Figure 6-7. However, there are differences in the ratios between the two stable isotopes which indicate smaller climatic changes as well as ion exchanges processes due to water/rock interaction (Figure 6-7, 6-8). Seawater may be depleted in $\delta^{18}O$ in comparison to δD as seen in both Swedish and Finish waters, caused by evaporation and mixing processes.

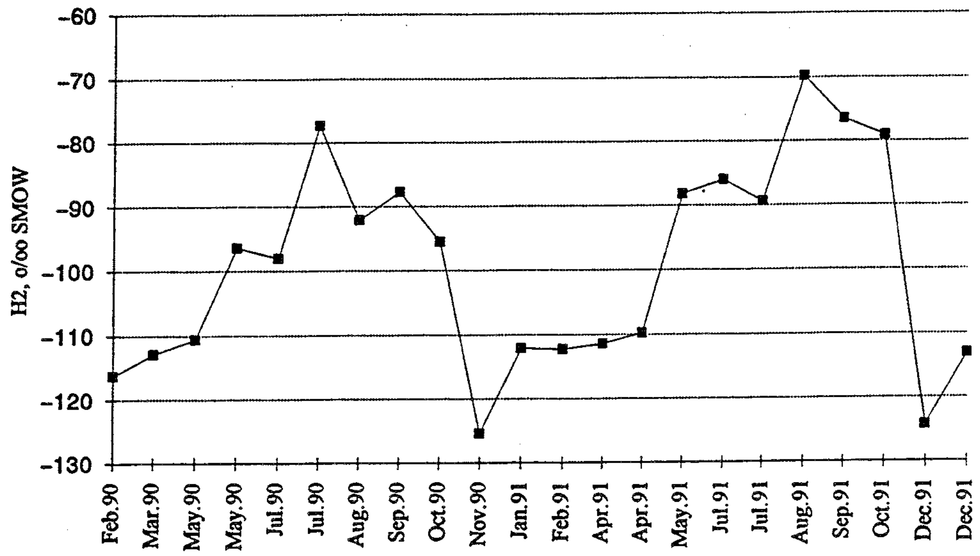

Figure 6-6. *Annual variation in δD in the rainwater precipitation at Kivetty in Finland during a two year period. After Lampén and Snellman, 1993.*

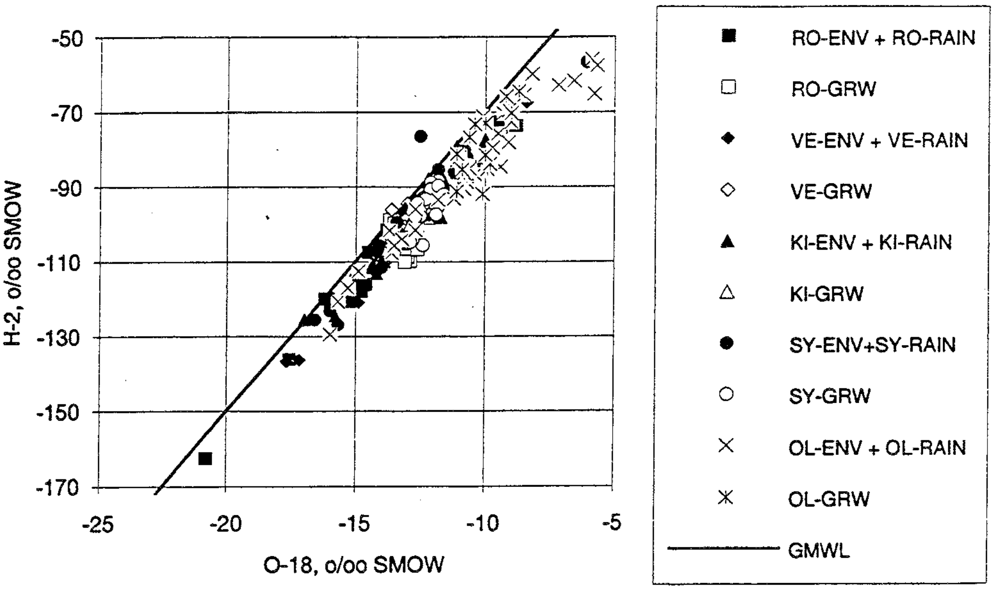

Figure 6-7. *δD plotted versus $\delta^{18}O$ for rainwater at different sites in Finland. After Lampén and Snellman, 1993.*

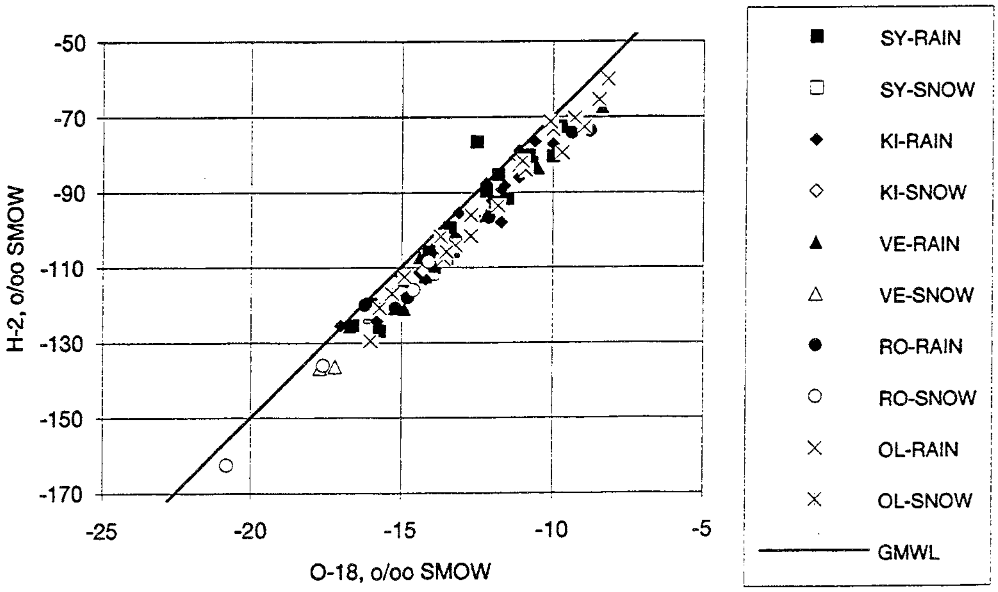

Figure 6-8. *δD plotted versus $\delta^{18}O$ for rainwater and snow at different sites in Finland. After Lampén and Snellman, 1993.*

7 CALCITE FRACTURE FILLINGS AS INDICATORS OF PALAEOHYDROLOGY OF THE DEEP WATER AT ÄSPÖ/LAXEMAR, KLIPPERÅS AND FINSJÖN IN SWEDEN

7.1 ÄSPÖ AND LAXEMAR

Isotopic compositions of carbon (δ^{13}C), oxygen (δ^{18}O) and strontium (δ^{87}Sr) in calcite fracture fillings are being used to reconstruct the palaeohydrology and source and evolution of the groundwater. These calcites precipitated from groundwater in the fractured crystalline rocks at some time in the past, and δ^{13}C, δ^{18}O and δ^{87}Sr values of the calcites reflect those of the source waters. Detailed sampling and analyses of the calcite indicate that they formed from waters that were compositionally distinct from the present day groundwaters (Tullborg, 1989). In contrast with systematic, depth related compositional and isotopic variations in the modern groundwater, none of the isotopic systems in the calcites display well defined depth dependent trends. However, at depth in excess of 900 meters, δ^{87}Sr (-5.6 to +8.4 o/oo) (Figure 7-1) correlates positively with δ^{18}O (+8.8 to +20.5 o/oo) (Figure 7-1, 7-2) and negatively with and δ^{13}C (-0.8 to -7.5 o/oo) (Figure 7-1, 7-3); δ^{87}Sr varies inversely with Sr concentrations (46.8 to 455.6 ppm). The δ^{18}O values (+8.8 to +20.5 o/oo) suggest that most of the calcites have not formed from the present-day groundwater although some of the larger δ^{18}O values could reflect equilibrium with groundwater under current *in-situ* temperature (O'Neil et al., 1969; Taylor, 1974; Arnórsson and Gunnlaugson, 1985).

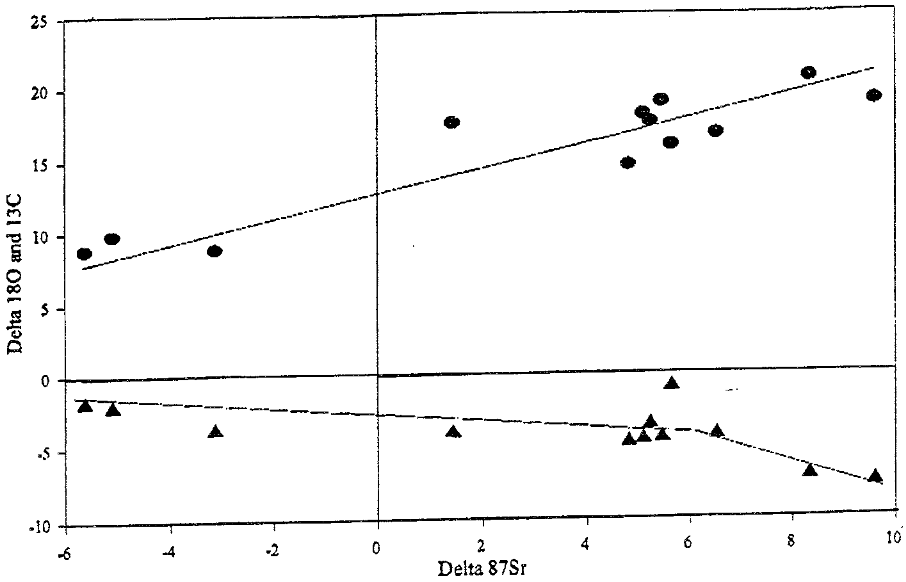

Figure 7-1. *δ^{18}O and δ^{13}C plotted versus δ^{87}Sr in calcite fracture fillings from KLX02 drillhole. Wallin and Peterman, in prep.*

Similarly, the low $\delta^{18}O$ values (+8.8 to 9.8 o/oo) (Figure 7-2) could have formed from groundwaters but at temperatures 30° to 40° higher than ambient (approximately 18°C). There is no correlation of the observed $\delta^{18}O$ values for the calcites with the geothermal gradient. Hence, if the spread in $\delta^{18}O$ values for the calcites were the result of increased temperature, the temperature distribution within the source water was probably strongly advective. $\delta^{87}Sr$ values of the calcites (-5.6 to +9.8 o/oo) do not overlap with those of the present-day groundwaters (+9.9 to +13.9 o/oo).

The order of magnitude difference in Sr concentrations of the calcites suggests large compositional variations in the source waters; samples with negative $\delta^{87}Sr$ values would have precipitated from waters with the largest dissolved load (Wallin and Peterman, 1994).

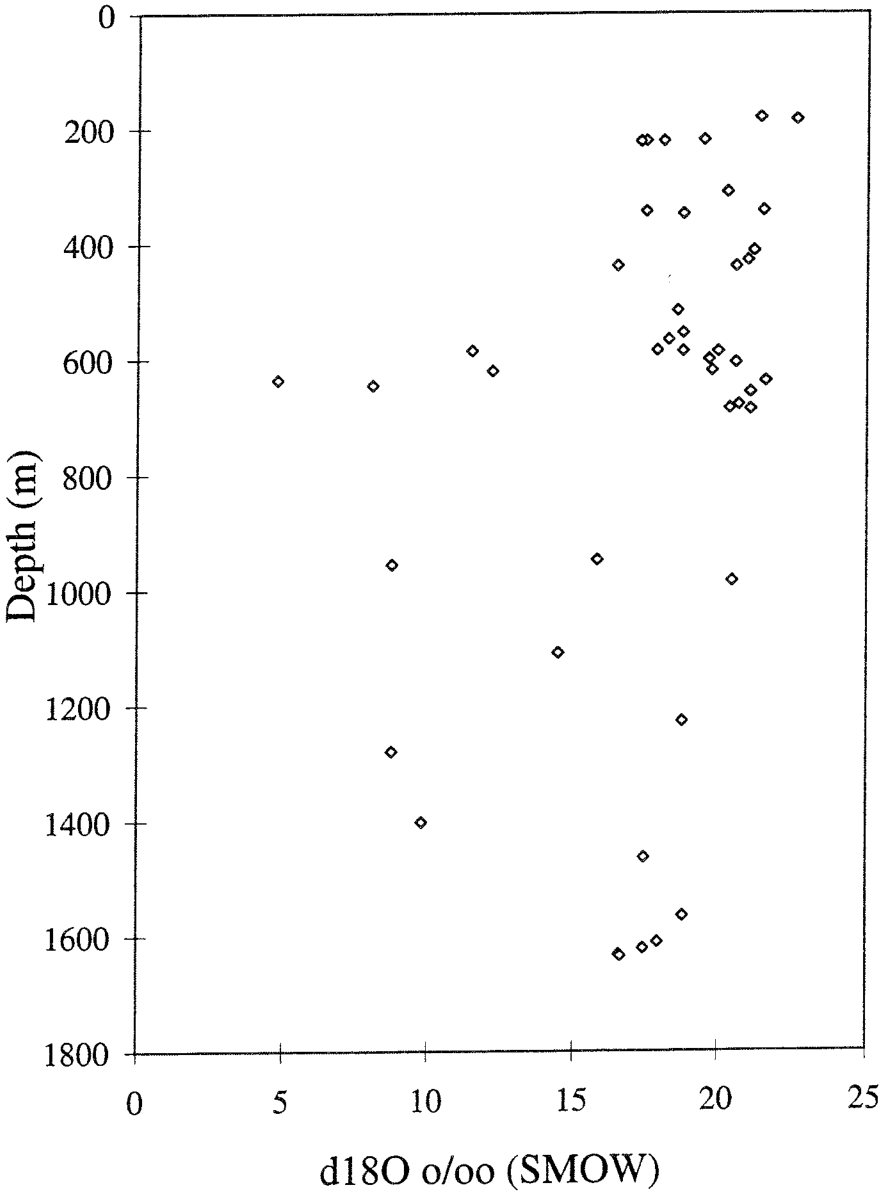

Figure 7-2. *$\delta^{18}O$ values from calcite fracture fillings versus depth in Laxemar (KLX02). Wallin and Peterman, in prep.*

Such waters could derive their dissolved ions in part from water-rock reactions (Edmonds et al., 1987; Paces, 1987). In such a scenario, the small δ^{87}Sr values of some calcites could reflect preferential interaction with plagioclase feldspar, a process suggested to explain unradiogenic Sr in deep saline waters of the Canadian Shield (McNutt, 1987; McNutt et al., 1987; McNutt et al., 1990). Plagioclase from a sample of typical granodiorite at Äspö has a δ^{87}Sr of -6.4 o/oo.The relatively large δ^{13}C values (-0.8 to -7.5 o/oo) for the deep the calcite fracture fillings reflect a nonbiogenic origin, presumably a deep-seated carbon source (Donnovan, 1969; Andrews and Wilson, 1987; Edmonds et al., 1984; Edmonds et al., 1985). The homogeneity of the δ^{13}C values suggests one dominating carbon source (Hathaway and Degens, 1969). An oxidation of a carbon species, such as methane, could explain the δ^{13}C signatures observed in the calcites (Giggenbach, 1980; Wallin, 1980; Welhan et al., 1987; Wallin, 1993; Wallin et al., 1995). This is supported by the δ^{13}C values of -40 o/oo observed for dissolved methane.

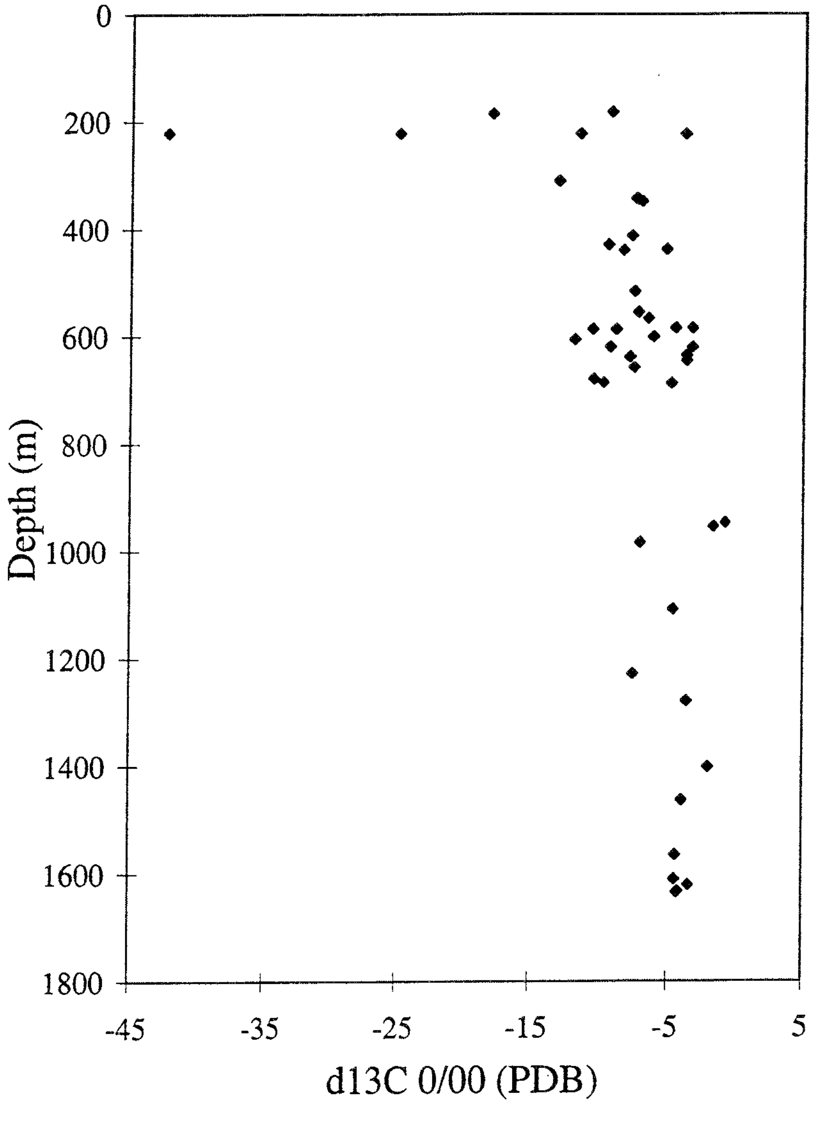

Figure 7-3. *δ^{13}C values from calcite fracture fillings versus depth in Laxemar (KLX02). Wallin and Peterman, in prep.*

7.2 KLIPPERÅS

Only a minor part of the calcite fissure fillings in the conductive fracture zones at Klipperås is suggested to be in chemical equilibrium (Sharma and Clayton, 1965) with the groundwater. $\delta^{13}C$ and $\delta^{18}O$ analyses of calcites from selected conductive zones support this interpretation (Tullborg, 1986). The wide spread $\delta^{18}O$ isotope signatures (-4.0 to -26 o/oo PDB) show that the majority of the assembly is not in equilibrium with the present day groundwater (Figure 7-4). The $\delta^{13}C$ values show a range between -2.0 and -17 o/oo suggestive of an atmospheric origin for the carbon, although some of the lower values may be indicative of organic carbon input (Tullborg, 1986). This is similar to the Äspö calcites although most of the calcite precipitates there seem to be in equilibrium with the present day groundwater. In addition, at Äspö some of the calcites often reveal very low $\delta^{13}C$ signatures (-15 to -40 o/oo) suggestive of a organic source. No direct geothermal gradient can be distinguished from the $\delta^{18}O$ in the Klipperås. According to Possnert and Tullborg (1989) there is a downward percolation of ^{14}C loaded HCO_3-water in the bedrock. However, the ^{14}C content in the groundwater decreases rapidly due to dissolution calcites causing a contribution of "dead" carbon in the near surface leaching zone between calcite dissolution/precipitation. This phenomenon differs in different deep groundwaters in Sweden (Pettersson et al., 1989; Pettersson and Allard, 1991). This explains the very high value of 72.5 pmC at a depth of 125 m and the very low value at 321 m depth of 9.9 pmC.

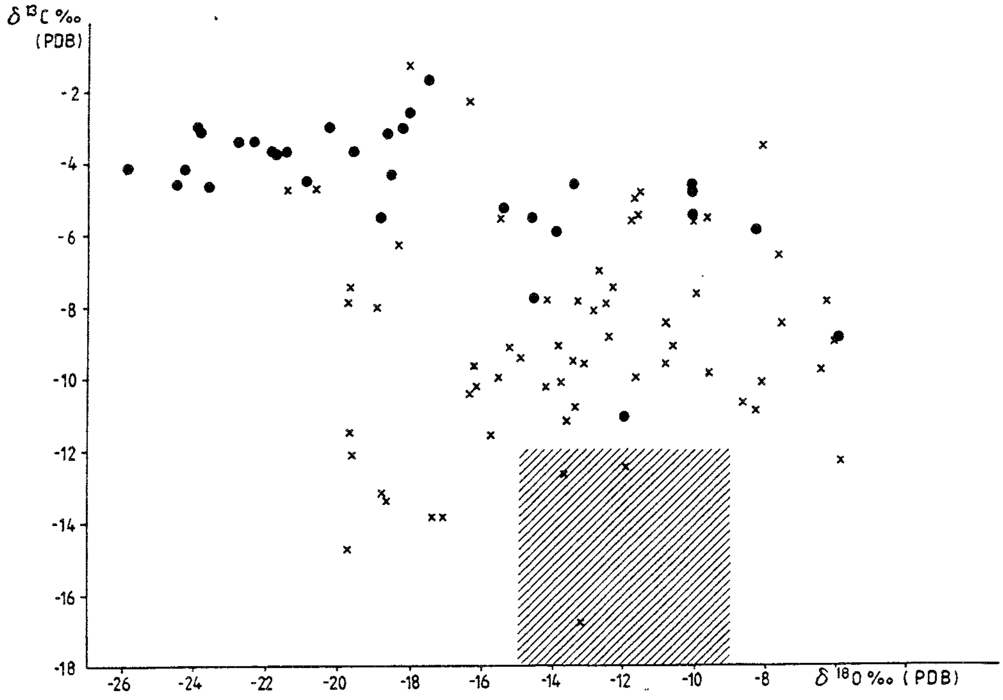

Figure 7-4. $\delta^{18}O$ plotted versus $\delta^{13}C$ for calcite fracture fillings from basite (o) and granite (x) at Klipperås. Stripe area indicate the interval of calcite precipitates from present day groundwater. After Tullborg, 1986.

7.3 FINNSJÖN

Stable $\delta^{13}C$ and $\delta^{18}O$ isotope analyses from open and sealed calcite fracture fillings from Finnsjön show a wide range in spread (Tullborg and Larsson, 1982). $\delta^{18}O$ values in for both open as well as closed fissure fillings decreases with depth (Figure 7-5, 7-6). The degree of redistribution of the isotope signatures are decreasing with depth indicating a preservation of the lower $\delta^{18}O$ signatures at depth (Figure 7-5). The study at Finnsjön show that the spread in $\delta^{18}O$ for calcites in the same depth interval as well as the same fissure, indicate that the sealed fissure fillings contain several calcite generations (Figure 7-5). This is similar to the observations made in the calcite fissure fillings at Äspö (Tullborg and Wallin, 1991). Moreover the $\delta^{18}O$ for calcites from the open fissures show a negative correlation with depth which may indicate a temperature increase with depth, possibly a geothermal gradient (Figure 7-7, 7-8). This has not been recorded at Äspö where the redistribution of the isotopic signatures seem to be more frequent. Even at lower depth such as below 1000 m at Laxemar the geothermal gradient is not developed, since the temperature distribution within the source water was probably strongly advective.

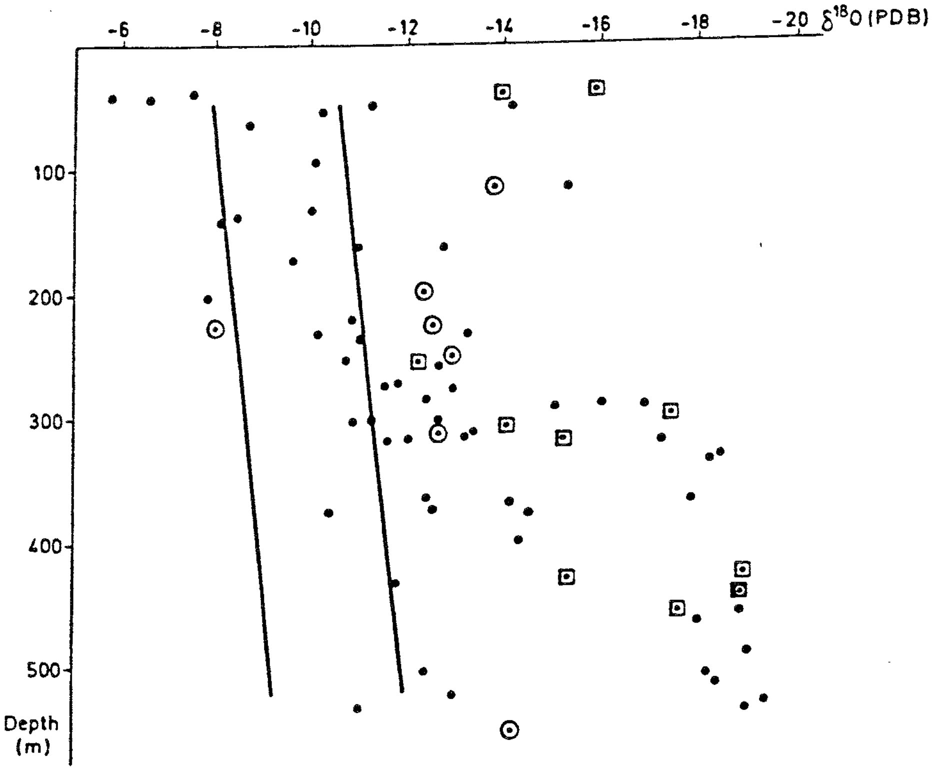

Figure 7-5. *$\delta^{18}O$ values plotted versus depth for sealed calcite fissure fillings at Finnsjön. After Tullborg and Larsson, 1982.*

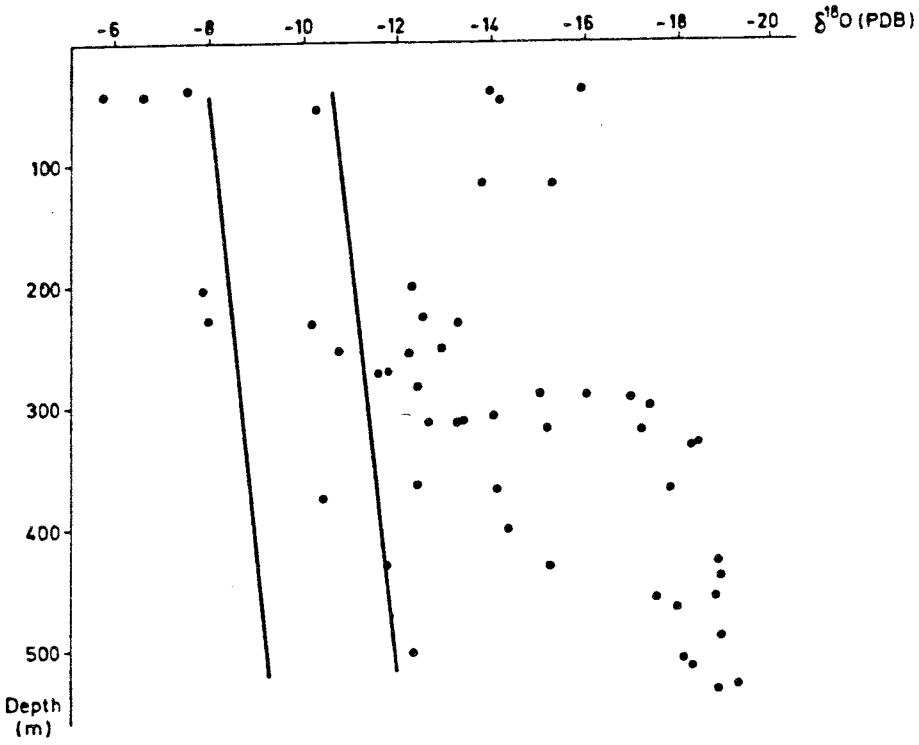

Figure 7-6. *$\delta^{18}O$ values plotted versus depth for open calcite fissure fillings at Finnsjön. After Tullborg and Larsson, 1982.*

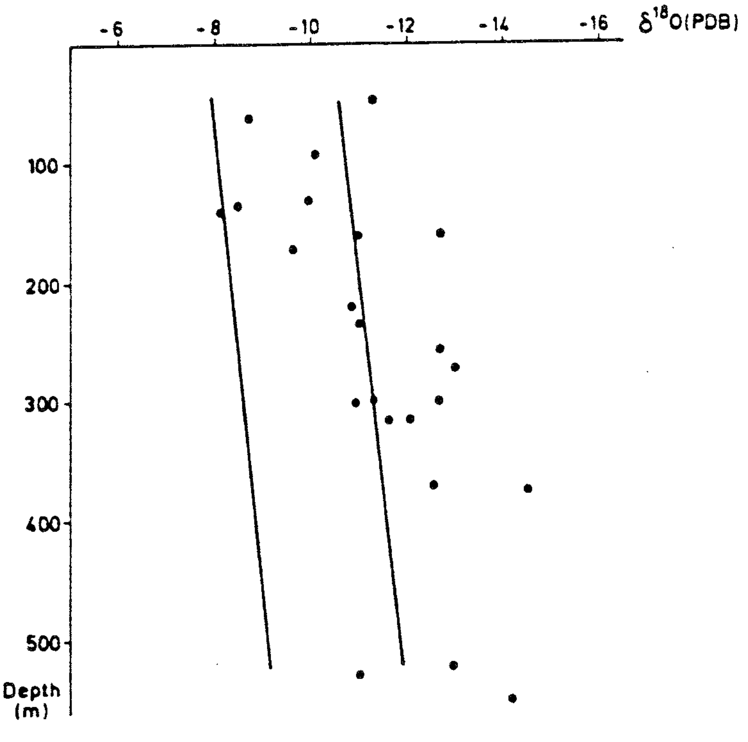

Figure 7-7. *$\delta^{18}O$ values plotted versus depth for open as well as sealed calcite fissure fillings at Finnsjön. After Tullborg and Larsson, 1982.*

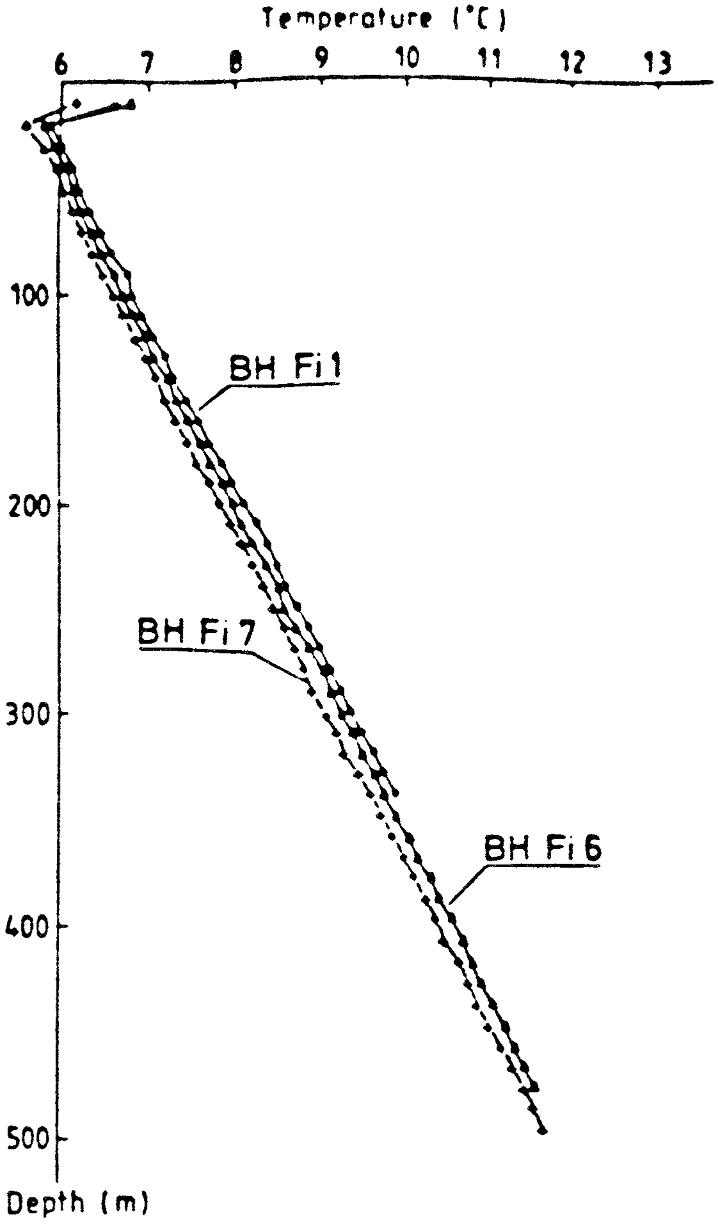

Figure 7-8. *Temperature gradient in some boreholes at Finnsjön. After Tullborg and Larsson, 1982.*

8 GLACIAL AND INTERGLACIAL EVENTS - BACKGROUND AND CONSEQUENCES FOR THE GLOBAL WATER CYCLE AND ÄSPÖ GROUNDWATER ISOTOPE SIGNATURES

The change in the intensity of solar radiation is the driving force for the long-term climatic cycles on Earth and correlate with the variation of the Earth´s orbit in our solar system. The so called Milankovitch variables have a clear origin in the Sun-Earth constellation but still not fully understood mechanisms by which they affect the Earth´s climate (Milankovitch, 1941). Many orbital hypotheses of climatic changes predict that the obliquity of the earth's axis (with a period of about 41,000 years) and the precision of the equinoxes (period of about 21,000 years) are the underlying controlling variables that influence climate through their impact on planetary insolation (Hays et al., 1976; Boulton and Payne, 1992). Paleoclimatological studies on foraminifera from deep sea sediments (Emiliano and Shackleton, 1974) and Greenland ice cores (Johnson et al., 1972) including $\delta^{18}O$ analyses clearly demonstrate the cyclicity of these climatic parameters. Systematic measurements of $\delta^{18}O$ and D have been used to study climatic changes, ice accumulation rates and climatic variations in the past 100 000 years. The fluctuations in the Pleistocene ice sheet has clearly demonstrated that the obliquity of the earth's axis has at least three different defined cycles which influence on the climatic changes (Hays et al., 1976; Boulton and Payne, 1992). Both seawater, atmosphere and consequently the groundwater chemistry is affected by these during a glacial and interglacial period. The changes are seen in a global perspective although local changes may be seen in the groundwater formation. The major parameters which vary directly with the climatic changes are ocean circulation, primary productivity, sedimentation rates, phosphate precipitation, carbonate precipitation, alkalinity, O_2 and lastly PCO_2 in the ocean, ice and atmosphere. Many of these changes can be traced in the groundwater formation during the glacial and interglacial events.

8.1 CHANGES IN P CO_2, OXYGEN AND ALKALINITY IN THE ATMOSPHERE AND SEAWATER AND ITS INFLUENCE ON THE ÄSPÖ GROUNDWATER

There is a dramatic increase in the CO_2 partial pressure in the atmosphere and ocean surface water during a glaciation (see Table 8-1). This change may be caused by the exchange between the ocean and the biomass or "low" (^{12}C) carbon in the shelf sediments. This may be also be due to removal of organic matter deposited along the margins of the sea as they are flooded by water released from melting glaciers (Faure, 1986). This gives an increase in ^{12}C compared to $\delta^{13}C$ in the carbon cycle. Such changes in the $\delta^{13}C$ isotope signature has been observed at Äspö in a shallow calcite fracture fillings. A very large range in $\delta^{13}C$ values from -5 to about -15 o/oo accompanied by the change in $\delta^{18}O$ in these calcite precipitates is recorded (Wallin, 1993) indicating an atmospheric dominating CO_2 source which is changed to an organic dominating carbon source, presumably due to post-glacial increased vegetation. In the marine waters, especially in the oceans, this phenomenon may also be coupled to an increase in the thermohaline "overturning"-effect. If so, the PCO_2 in the ocean surface water will increase in comparison to PCO_2 and alkalinity.

TABLE 8-1.	Begining of glaciation	Glaciation	End of glaciation	Interglacial
PCO2 in atmosphere	decrease	low	increase	high
PCO2 in ocean deepwater	decrease	low	increase	high
δ13C in the CO2 in the atmosphere	increase	high	decrease	low
δ18O in the ocean	increase	high	decrease	low
δ18O of the ice	decrease	low	increase	high
δD in the ocean	decrease	low	increase	high
Methane in the Atmosphere	decrease	low	increase	high
Alkalinity in seawater	decrease	low	increase	high
PO4 in surface seawater	decrease	low	increase	high
PO4 in ocean deepwater	increase	high	decrease	low
O2 in seawater	decrease	low	increase	high
Thermohaline overturning	decrease	low	increase	high
Oceanic circulation	decrease	low	increase	high
High latitude productivity	increase	high	decrease	low
Low latitude productivity	increase	high	decrease	low
Sedimentation rate	increase	high	decrease	low
Carbonate sedimentation rate	decrease	low	increase	high
Phosphate precipitation	increase	high	decrease	low

Table 8-1. *Global changes in PCO_2, PO_2 in atmosphere and seawater and PO_4, alkalinity, productivity, sedimentation rate, carbonate sedimentation, thermohaline overturning and ocean circulation in seawater. Data combined in this table are taken from; Andrews, 1987a; Andrews, 1987b; Backman and Shackleton, 1984/85; Berggen, 1968; Birch et al., 1982; Boström, 1970; Broecker, 1984; Burgman 1983; Burgman 1987; Burnett et al., 1982; Chappellez et al., 1990; Cook and McElhinney, 1979; Craig, 1953; Craig, 1965; Dansgaard, 1964; Emiliano and Shackleton, 1974; Hamza and Broecker, 1974; Hays et al., 1976; Imbrie and Imbrie, 1980; Irwin et al., 1977; Jancke et al., 1983; Malmgren, 1976; McKelvey et al., 1953; Mullins and Rasch, 1985; Pisias and Moore, 1980; Riggs, 1970; Roe and Burnett, 1985; Ruddiman and McIntyre, 1979; Ruddiman et al., 1986; Sarmiente and Toggweiler, 1984; Siegenthaler and Went, 1984; Wallin, 1982.*

Further on, this will lead to a nutrient increase in the high latitude waters at the end of the glaciations. Since Äspö is situated on the higher latitudes this nutrient rich waters may very well affect some of the marine stages of the Baltic Sea which are observed during the post-glacial period. This is also confirmed by dated fossils which indicate a high organic activity in the near vicinity of the ice front in northern Sweden (Mörner, 1994). The high production of clastic material as clay, sand and moraine hence increases the "continental" signature of the sediments and the chemistry of the meltwater.

8.2 ISOTOPE (δ^{13}C AND δ^{18}O) SHIFT OF THE LOW AND HIGH LATITUDE SEA WATER AS WELL AS MELT WATERS AND ITS INFLUENCE ON THE ÄSPÖ GROUNDWATER

During a glaciation the δ^{13}C variation in the deep ocean is very little. However, the differences between warm surface water, deep ocean water and high latitude cold waters during a glaciation is much larger (Broecker, 1984). According to Siegenthaler and Wenk (1984) the carbon isotope signature changes in CO_2 is due to the change in ocean circulation. Further on, a decrease in PCO_2 in the atmosphere and low PCO_2 in the deep ocean water is a consequence of the oceanic circulation e.g. the change in the thermohaline "overturning"-effect (Sarmiente and Toggweiler, 1984). This phenomenon may partly be one of the observations in the wide range in δ^{13}C which is observed in some carbonates in a shallow calcite fracture filling mentioned above.

In the North Atlantic δ^{18}O -values of the arctic seawater show a decrease in δ^{18}O with a decrease in salinity (Tongiorgi, 1965). This decrease in the isotopic signature is also attributed to the high latitude and consequently colder climate. Values of around -10 to -15 o/oo is not unusual in arctic marine waters outside Greenland (Figure 6-2). At Äspö similar low temperature and low salinity marine environments may have developed in the Baltic region during the last glacial or postglacial period. If so, a marine water with such a characteristic features, may give rise to low $\delta^{18}O$ signatures and a saline water similar to that now found at Äspö. A mixture of marine and meteoric water could have taken place contemporaneous to the groundwater formation, giving rise to the wide scatter in $\delta^{18}O$ of the calcite fissure fillings at Äspö. Thus, this mixing could have been very rapid and the saline water injected the basement rocks was most likely due to the isostatic movements of the Baltic Shield after in the postglacial period.

There is a considerable increase in chloride concentration with depth to a maximum reading of 12300 mg/l at 1000m in KAS03 (Laaksoharju and Nilsson, 1989; Nilsson, 1989). This situation with high salinity waters strongly support a possible input of a marine component for that higher $\delta^{18}O$ values observed in the calcite fissure fillings at Äspö. However, it must be kept in mind that this is only true if the groundwater present is in equilibrium with at least some of the calcite fissures. In the Figure 4-8, $\delta^{18}O$ values observed in the water at Äspö are plotted versus depth, a uniform picture of $\delta^{18}O$ values between -15 and -11 o/oo with a calculated average of -12.4 o/oo is found. A calcite in equilibrium with such a water and with the temperatures observed at Äspö would give a $\delta^{18}O$ value for the calcite fissure filling of +18 o/oo, which is very close to the average value for the $\delta^{18}O$ values observed (Tullborg and Wallin, 1990; Banwart et al., 1993; Banwart et al., 1994). This means that at least some of the calcite fissure fillings observed at Äspö is in equilibrium with the groundwater. The slight indication of a marine component indicated by the higher $\delta^{18}O$ values of the calcite fissure fillings in the upper part of the borehole support such situation. A subsequent input of meteoric water from above is also supported by the $\delta^{18}O$ values in the different generations of precipitates found. This would also explain the meteoric signature (average of -12.4 o/oo) at all depth of the water at Äspö.

Large scale production of saline brines due to seawater freezing in connection with the last glacial period is reported from the Canadian Shield (Fritz and Frape, 1982; Herut et al., 1990). The $\delta^{18}O$ isotope fractionation factor for ice in equilibrium with water is only 1.002, which means that the $\delta^{18}O$ value of sea ice is about +2 o/oo relative to the sea water from which it is formed. Therefore, the formation of sea ice leaves the $\delta^{18}O$ value of the water essentially unchanged, but causes a significant increase in its salinity. As a result, the density increases of such water increases causing it to sink (Bein and Arad, 1992). However the observed water at Äspö is much more negative in $\delta^{18}O$ than would be expected from a normal seawater freezing. In order to explain such a phenomenon, we need to consider the variation in $\delta^{18}O$ of high latitude ocean water or cold diluted seawater of high latitudes (Dansgaard, 1964; Dansgaard et al., 1969; Taylor, 1974). It is clearly seen that the $\delta^{18}O$ becomes more and more negative with a decrease in salinity. This effect may be due to a successively depletion in $\delta^{18}O$ in comparison to ^{16}O in the residual seawater due to the effect of freezing and mixing with meteoric water. The Baltic sea precursors in connection with the latest glacial period may accordingly been very negative in $\delta^{18}O$ similar to what we observe in the north Atlantic today.

8.3 MELTWATER AND CONTINENTAL RUNOFF AND ITS INFLUENCE ON THE BALTIC SEA AND THE ÄSPÖ GROUNDWATER

This continental runoff may be an explanation of the positive $\delta^{87}Sr$ signatures of the intermediate to deep waters at Äspö today. The low $\delta^{18}O$ values of the water support a cold water supply. However, the calcite fracture show a wide scatter in $\delta^{18}O$, suggesting a precipitation from both meteoric and saline (marine) waters. The first meltwater to be formed has the most negative value. A solution to the contradiction between the strontium and stable isotope ($\delta^{13}C$ and $\delta^{18}O$) signatures of the ground water and some of the calcite fracture fillings is attained if it is assumed that the strontium in Baltic Sea water has undergone a significant decrease in $\delta^{87}Sr$ since the last glaciation. The intermediate ground water at Äspö is suggested to be as old as 3500 years on the basis of the development of the sea-level and of radiocarbon analyses. A scenario can be constructed to suggest that the Baltic Sea 3500 years ago contained strontium with much larger $\delta^{87}Sr$ values. Strontium in the modern Baltic is derived from Precambrian terranes on the north and Phanerozoic sedimentary terranes on the south, and perhaps some influx of sea water strontium from the North Sea. Runoff from the Precambrian terranes has a mean $\delta^{87}Sr$ of about +29‰ whereas runoff from the south (Löfvendahl et al., 1990; Andersson et al., 1992) has a value of about +1.2. Because of much higher strontium contents of rivers draining the Phanerozoic terrane, this runoff contributes about 88 percent of the total strontium budget to the Baltic.

As the ice sheet retreated northward during the last glaciation, glacial rock debris, including much fine-grained material such as rock flour, would have been exposed to weathering, erosion, and transport into the Baltic Basin. The fine-grained material would have large $\delta^{87}Sr$ values like the modern runoff from the Precambrian terrane. Accordingly, the hypothesis proposed by Wallin and Peterman (1994) that increased influx of Precambrian strontium overwhelmed the runoff from the Phanerozoic terrane to the south to the extent that the $\delta^{87}Sr$ value for the Baltic was increased to at least the levels of Äspö ground water. This process may have continued during the isolated stages of the Baltic where no communication took place with the marine water in the west. Using the mean runoff $\delta^{87}Sr$ values of Lövendahl et al. (1990) an increase of the contribution strontium through runoff from the north to 42 percent (compared with a present-day estimate of 12 percent) could have increased the $\delta^{87}Sr$ value of the Baltic to +13‰.

The discrepancy of the observed $\delta^{18}O$ values as well as the $\delta^{87}Sr$ values may therefore solely be due to the accumulation of post-glacial runoff waters which are extremely negative in $\delta^{18}O$ as well. In addition, the sulphate $\delta^{34}S$ values (about +14 to +15‰) which are observed at intermediate depth at

Äspö are significantly lower that those of modern marine water sulphates. This is interpreted as being a contribution of reduced sulphur due to water/rock interaction of the marine or brackish waters in the area. It may, in concert with the model to explain the large $\delta^{87}Sr$ values by runoff waters from the shield, be due to extensive load of reduced sulphur from the melt water in the recession stage of the ice cover.

On the other hand, during a glaciation the high latitude productivity is increased. This will undoubtedly lead to a contribution to the increase in sedimentation rate observed during the glaciation. One may also expect anoxic conditions in those areas which generally are depleted in oxygen, such as the oxygen minimum zones. The phosphate concentration in the deep ocean water is increased leading to abundant authigenic phosphate formation. This have been observed in some of the central Baltic sediments suggesting a rapidly increase in the organic productivity. However, the organic content of the Äspö groundwater is mainly dominating by fulvic acids which are 14C-dated to about 3500 years, indicative of a later input of organic matter.

All these parameters such as sedimentation rate, sediment type and organic productivity will of coarse affect the type of water and its trace metal content which is residing in the vicinity of the ice front. Hence, from this evidence the phosphates are very interesting candidates to examine with respect to e.g. REE and transitional element content, as environmental indicators.

9 THE LAST GLACIATIONS AND THEIR EXTENSION IN THE BALTIC REGION

The early geological studies by Pencks and Bruckners from the Alps during the beginning of this century has shown that least four major glaciations are recorded during the Pleistocene in Europe (Kominz and Pisias, 1979). Later works in the northern Europe and Scandinavia reveal that at least three of these glaciations took place during the latest 500.000 years. At about 400.000 to 500. 000 years ago the so called Elster (Mindel glaciation in the Alps, Zeuner, 1945) glaciation is documented from northern Europe and Scandinavia.. Later on the Saale glaciation (Riss glaciation in the Alps, Zeuner, 1945) followed, which most likely had its maximum at about 200.000 years ago. After that glaciation started the last interglacial period, in the Baltic region, which is equivalent to the Sengomon interglacial in the North America (Judge, 1973). This was followed by the last glaciation (Lagerbäck, 1988), known as the Weichsel (Wurm glaciation in the Alps, Zeuner, 1945), which started at about 100.000 years ago (Labeyrie et al., 1987; Mangerud, 1991). Glacial deposits in the middle and eastern Europe indicate that the second last glaciation, the Saale glaciation, was much larger than the last, Weichel glaciation, although it did not lasted as long as the last one. A reconstruction of the extension of the Saale glaciation (Figure

34)show that the ice reached the British Isles including the North Sea and the most part of the northern and eastern Europe (Ljungner, 1943; Ljungner, 1945; Lundqvist, 1958a; Lundqvist 1958b; Lehman et al., 1991; Mörner, 1971; Mörner, 1976; Lindén, 1984; Liedberg-Jönsson, 1988). The Alps were covered by ice and several geological deposits indicate that several isolated glaciers resided on the continent.

10 THE EVOLUTION OF THE BALTIC SEA AND RELATION TO THE GROUNDWATER FORMATION IN THE CIRCUM BALTIC

The evolution of the Baltic Sea during the postglacial period is characterised by a series of events of freshwater and saline stages (Figure 10-1). When the ice started to move back from its maximum the first stage of the Baltic Sea is known as the Baltic Ice Lake. It started to form at about 14000 years ago when during the Older Dryas period (Mörner, 1969). The first water to be formed after the ice recession was the Baltic Ice Lake which is characterised as a freshwater lake, then followed the Yoldia Sea, which is mainly marine water (Lindström 1898; Lindén, 1984). Another fresh water stage, the Ancylus Lake, followed and finally the second marine stages of Litorina and Limnea took over.

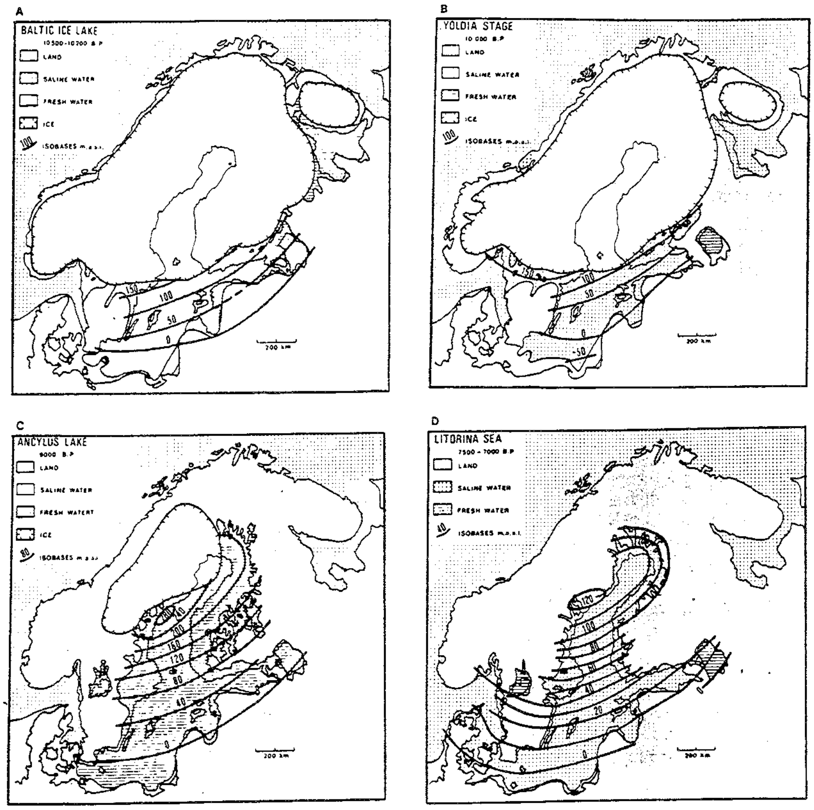

Figure 10-1. *The major Baltic stages during the Late Weichselian and early Holocene. After Eronen, 1983.*

10.1 THE BALTIC ICE SEA

The Baltic Ice Lake (Figure 10-1a) was the first stage to be formed after the ice recession and started to develop about 13000 to 14000 years ago, in the Oldest Dryas during the Late Weichselian (Pleistocene) (Lundqvist, 1959; Lundqvist, 1981; Lundqvist, 1986; Svensson, 1991). The climate during this period is characterised as still being cold (Fromm, 1969; Karlén, 1973). Then followed the Bölling stage which approximately lasted during 1000 years and is characterised as being warm in relation the Oldest Dryas (Gavelin and Högbom, 1910; Björcksjö, 1949; Exon, 1972; Erlenkeuser, 1985). In southern Sweden transgressions are observed during this time although there is no evidence of any marine marine conditions and water intrusions from the west (Svensson, 1989). However, Donner (1969), Björck (1979) and Björck and Digerfeldt (1984, 1986) proposed a westward strait between the Baltic and the North Sea during the latest part of Alleröd has been proposed by A short cold stage during the Older Dryas at about 12 000 years ago slightly changed the conditions for the ice recession. Authers (Kolstrup, 1982; Lemdahl, 1988; Liedberg and Jönsson, 1988) have proposed that the Older Dryas was dry rather than cold. Björck and Möller (1987), however, believe that the conditions during the Older Dryas was both dry and cold in Blekinge, Skåne (Möller, 1959) and Southern Småland (cf Svensson, 1989) not far from Äspö, especially during the winter.

Another warm time period followed, known as the Alleröd stage, which lasted during a 1000 year old period and ended at about 11000 years ago. During this stage the Baltic Ice Lake probably grow very fast and covered most of the Baltic Sea area south of a line between Stockholm in Sweden and Helsinki in Finland. Estimations suggest that the Lake reached depth exceeding 100 m in the northern border close to the ice front (Figure 10-1a). After the Alleröd time the Younger Dryas followed. Reconstruction of paleotemperatures for the Late Weichselian made by Iversen (1954, 1973) and Berglund (1966) show that the characteristic feature for this time is the cooling of the climate (cf Svensson, 1989). Avery rapid increase in temperature was then observed at about 10200 to 10100 years ago (Lemdahl, 1988) which is indicated by both fossil insects and fossil pollen from the region (Berglund, 1966; Björck, 1979, 1981; Påhlsson, 1977; Björck and Möller, 1987). This climatic changes is the end of the Younger Dryas and The Baltic Ice Lake (Lundqvist, 1965). The end of the Baltic Ice Lake is marked by the final drainage north of Mt Billingen. The lowering of the Baltic Ice Lake down to the sea-level was first mentioned by Munthe (1902) but has been discussed by many other since then. The most recent work in the Billingen area by Strömberg (1974; 1977; 1984 and 1986) has led to different views of the final drainage. In any case the final drainage is estimated to be 26 m in south and central Sweden, 26-28 m in Finland and al least 26 m in Blekinge (Björck, 1979, 1981) not far from Äspö.

Most likely no signs from this Baltic Ice Lake are seen in the groundwater at Äspö today. Certainly the $\delta^{18}O$ signatures of the meltwater was very low (-13 to -18 o/oo) in the meltwater from the ice. Moreover, the continental drainage provided a freshwater supply with high $\delta^{87}Sr$ values, according to the hypothesis proposed by Wallin and Peterman (1994).

10.2 THE YOLDIA SEA

According to De Geer (1940), saline water arrived in the Baltic region immediately after the drainage of the Baltic Ice Lake. On the other hand, Caldenius (1944), Nilsson (1968), Perhans (1981) and Strömberg (1986) all argued that the saline water ingression was delayed c. 200 - 250 varve years. Most likely there was a mixed fresh/saline water stage developed in the beginning of the Yoldia stage (Figure 10-1b) (Sandegren, 1939) which followed after the Baltic Ice Lake (pers. comm. Mörner 1994). The Yoldia stage, which was developed during the Preboreal time, is named after the marine bivalve (Portlandia arctica Yoldia arctica), shells of which are present in varved clay in the Stockholm region (Svensson, 1989). This post-glacial stage of the Baltic lasted less than 1000 years and ended at about 9500 years ago.

10.3 THE ANCYLUS SEA

The Yoldia stage followed by the Ancylus Lake (Figure 10-1c) which was formed when the thresholds of the straits in south-central Sweden were raised above sea level by glacio-isostatic uplift (Munthe,1887, 1892, 1902, 1910; Nilsson, 1959; Svensson, 1989). This caused the Ancylus Lake to rise south of the thresholds until new outlets were reached through the Danish Straits, where the uplift was less rapid. Beach ridges from the Ancylus stage show the transgressive nature of the stage as the ridge often overlies terrestrial or limnic organic deposits. Those sequences normally show transition from terrestrial deposits to limnic sediments (Lundqvist, 1928, 1965; Königson, 1968; Persson, 1978). Large logs of *Pinus* are often found well preserved and buried beneath the beach ridge or corresponding minerogenic deposits at Gotland (cf Svensson, 1989). Organic deposits buried during the Ancylus transgression, were studied by Lundqvist (1965) and dated the transgression to C. 8500 BP. On similar material the Litorina-transgression maximum in the southern Baltic was dated to c. 6500 BP and a second transgression approximately 500 years later. During this time Äspö was still below the water level. These transgression are most likely due to the irregular isostatic movements of the Baltic during the post-glacial period. When the shoreline moved back after the maximum transgression of the Ancylus Lake possibly some of the freshwater entered the basement rocks. If so, this water probably left a very low $\delta^{18}O$ isotope signature of the water since most of the water mass build up during this stage was due to the continental runoff of the meltwater. Moreover, a positive strontium isotope signature of the water is expected for the same reason. According to Mörner (pers. comm.) the Ancylus Lake may have been partly saline during a short time period. This may refer to the transgression stage as well which is noted about 8500 years ago.

Svensson (1989) describes the Mastogloia stage as a transitional stage between the Ancylus Lake and the Litorina Sea. After the Ancylus transgression , and after a short time later saline water penetrated through the Danish-Swedish strait. This event marks the beginning of this transitional stage, that was characterised by the common occurrence of *Mastogloia*, a diatom that indicates slightly brackish water (c.f. Svensson, 1989).

The model for groundwater formation at the intermediate depth at Äspö which is presented by Wallin and Peterman (1994) suggests that the PaleoBaltic sea water had elevated $\delta^{87}Sr$ values. We also know that several waters have been involved in the precipitation of calcite fissure fillings, other than present-day water at Äspö. The isotopes δD, $\delta^{18}O$, and $\delta^{87}Sr$ evidence of meteoric waters and/or glacial melt waters as well as fossil marine waters with depleted $\delta^{18}O$ signatures and high Cl concentrations. This mixture observed in the Äspö groundwater may partly be due to the mixing stage described here as well as later transgression stages during the Litorina Sea.

10.4 THE LITORINA SEA

The transgressive nature of the PaleoBaltic Sea continued and during the Litorina stage (Figure 10-1d) which followed after the Ancylus Lake and Mastogloia Sea. The Litorina Sea, which is characterised as being the maximum saline stage during the post-glacial period, covered much more areas than the present Baltic sea (Arnitz et al., 1976; Fredén, 1986) (Figure 10-2, 10-3). Äspö was covered by the saline water and as can be seen in Figure 10-2 a large part of Uppland, Södermanland as well as the eastern Småland was covered by the Litorina Sea. A large part of the west coast of Finland was totally covered by the highest limit of the postglacial Litorina Sea. Isotope studies of Ammonia beccarii (dextral) and A. Beccarii (sinistral) in the southern Baltic sediments reveal details of changes in salinity from the brackish water in the initial stage of the Litorina transgression (7000 to 8000 years ago) to marine conditions (24 + 2 o/oo) during the salinity maximum which exceeds present day salinities by c. 4 o/oo (Winn et al., 1988). During this transgression the isotopic composition of the total organic carbon indicates a gradual change in the nature of the sedimentary organic material from initially terrogenous provenance towards a higher marine contribution (Winn, 1988). This is analogues to the observations made of the change of $\delta^{13}C$ isotope signature observed at Tinstäde Träsk (Mörner and Wallin, 1977) and in fracture filling calcites at Äspö (Wallin, 1993).

The transgressions observed during the Litorina stage is almost all related to eustatic movements of the Baltic shield. This support the idea of a "pumping" of Litorina sea water into the basement.

Figure 10-2. *Figure showing the highest marine shore line during the Holocene in Sweden. After Lundegård, Lundqvist and Lindström, 1978; Knutsson and Morfeldt, 1993.*

10.5 THE LIMNEA STAGE

The salinity increased after the last transgressive stages of the Litorina is dated to about 3000 -3500 B.P. by Liljegren (1982). This last substage of the Baltic is characterised by the snail *Limnea ovata* and named the Limnea stage (Lindström, 1886). It is interesting to note that this last transgressive stage coincide with the time when the Island of Äspö is rising above the water level due to the eustatic movements in the area.

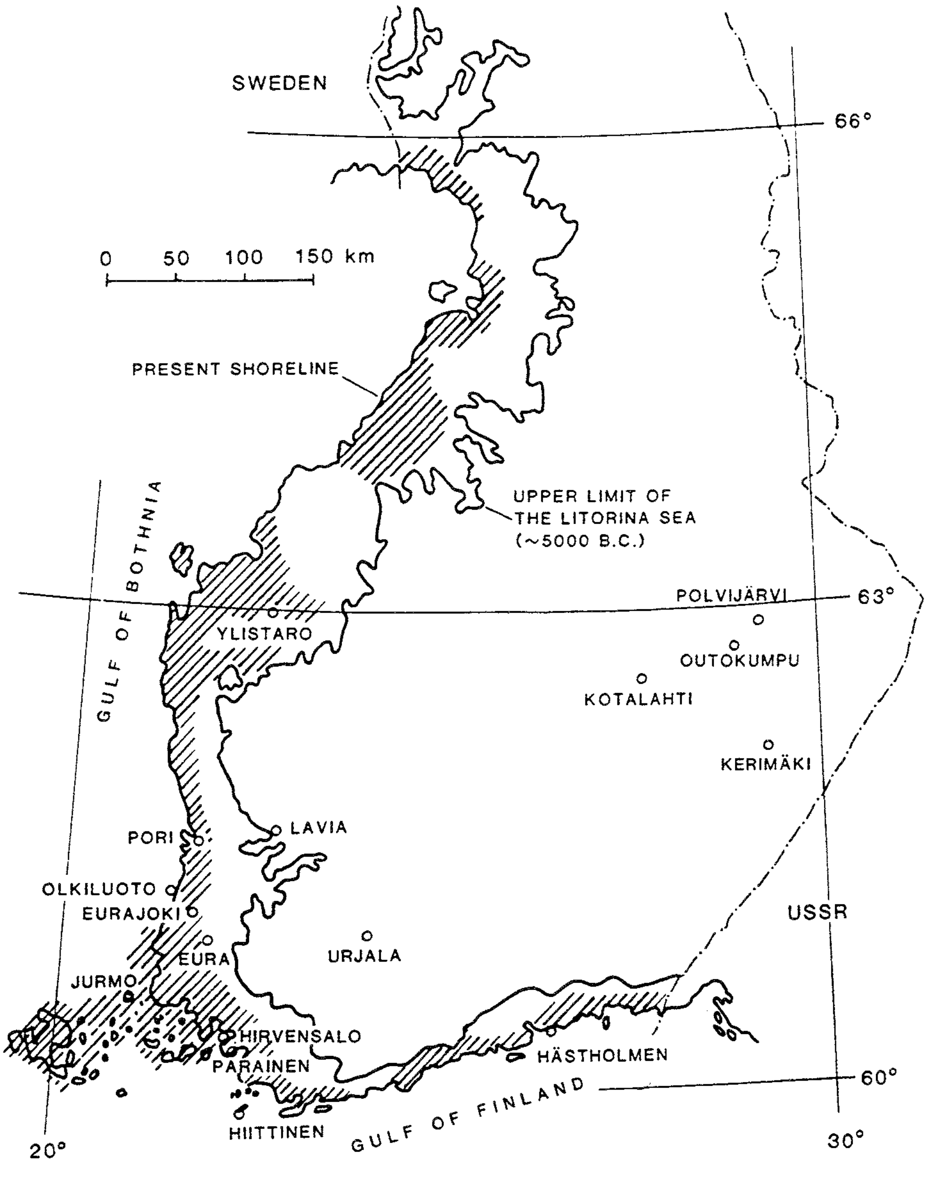

Figure 10-3. *Figure showing the highest marine shore line during the Litorina stage in Finland.Modified after Lahermo and Lampén, 1987.*

11 CONCLUSIONS

Examinations in a large number of groundwater wells in Finland and Sweden suggest a multiple source for the saline waters in the circum-Baltic area. However, most the groundwaters found in the coastal areas below the highest marine transgressions during the Holocene, strongly suggest that saline water intrusions have been responsible for the groundwater formation at intermediate depth, between 150 and 500 m. The saline groundwaters have most likely been formed at different times at different sites due to the prograding isostatic movement during the post-glacial period. Early transgressions (8000 Y, B.P.) during the Litorina stage as well as later transgressions (3000 - 3500 Y, B.P.) during the Limnea stage seem to be important events in the groundwater formation. Moreover, this literature study has shown that there is an extensive ongoing recharge of meteoric water in most of the wells in the circum-Baltic area. Mixing processes between saline groundwaters and the ambient meteoric recharge produces waters of different salinities.

Isotope signatures from the coastal areas reveal a pattern supporting the hypothesis that continental runoff of meltwaters have been in-mixed with the saline waters of the pre-Baltic stages. The discrepancies between $\delta^{18}O$, and $\delta^{87}Sr$ from several groundwaters support this idea. It therefore, seem to be extremely important to understand the interaction between the melt water runoff and mixing with the saline waters during the Yoldia and Litorina stages of the Baltic Sea, in order to interpret the origin of the saline coastal groundwaters.

12 ACKNOWLEDGEMENTS

The auther is indepted to MARGIT SNELLMAN, NILS-OLOF SVENSSON and BO OLOFSSON for their important assistance with litterature in this investigation. Thanks goes to NILS-AXEL MÖRNER for helpful discussions. Most of the publications referred to in this work was provided by DAG ERICSSON at the library at Department of Geology and Geochemistry at Stockholm University.

13 REFERENCES

Ahlbom, K. Gustavsson, E., and Tullborg, E.-L., 1986. Preliminary investigations of fracture zones in the Brändan area, Finnsjön study site. *SKB TR*, 86-05.

Allard, B., Larsson, S.-Å., Tullborg, E.-L. and Wikberg, P., 1983. Chemistry of deep groundwaters from granitic bedrock. *SKBF/KBS, TR*, 83-59.

Andersson, P., Wasserburg, G., and Ingri, J., (1992) The sources and transport of Sr and Nd isotopes in the Baltic Sea. *Earth and Planetary Sciences Letters*, 113:459-472.

Andrews, J. N., 1987. Noble gases in groundwaters from the crystalline rocks. In: Fritz, P. and Frape, S. K., Saline water and gases in crystalline rocks. *Geol. Assoc. of Canada Spec. Pap.*, 33:235-244.

Andrews, J. N. and Wilson, G. B., 1987. The composition of dissolved gases in deep groundwaters and groundwater degassing. In: Fritz, P. and Frape, S. K., Saline water and gases in crystalline rocks. *Geol. Assoc. of Canada Spec. Pap.*, 33:245-252.

Andrews, J. N., Ford, D. J., Hussain, N. Trivedi, D., Youngman, J., 1989. Natural radioelement solution by circulating groundwaters in the Stripa granite. *Geochim. et Cosmochim. Acta,* 53:1791-1802.

Andrews, J. N., Davis, S. N., Fabryka-Martin, J., Fontes, J-Ch., Lehmann, B. E., Loosli, H. H., Michelot, J-L., Moser, H. Smith, B. and Wolf, M. 1989. The in-situ production of radioisotopes in rock matrices with particular reference to the Stripa granite. *Geochim. et Cosmochim. Acta,* 53:1803-1815.

Arnitz, W. E., Brunswig, D. and Sarnthein, M., 1976. Zonierung von Mollusken und Schill im Rinnersystem der Kieler Bucht (Westlische Ostsee). *Senckenbergiana marit.,* 8:189-129.

Arnórsson, S. and Gunnlaugsson, E., 1985. New geothermometers for geothermal exploration-calibration and application. *Geochim. et Cosmochim. Acta,* 49:1307-1325.

Asklund, B., 1936. Den marina skalbärande faunan och de senglaciala nivåförändringarna med särskild hänsyn till den gotiglaciala avsmältningszonen i Halland. *SGU,*C-393:1-103.

Backman, J. and Shackleton, N. J., 1984/85. Quantitative biochronology of Pliocene and early Pleistocene calcareous nannofossil from the Atlantic, Indian and Pacific Oceans. *Mar. Micropal.,* (:141-170.

Banwart, S., Gustavsson, E., Laaksoharju, M., Nilsson, A.-C., Tullborg, E.-L. and Wallin, B.,1994. Large scale intrusion of shallow water into a vertical fracture zone in crystalline bedrock: Initial hydrochemical perturbation during tunnel construction at the Äspö Hard Rock Laboratory, south-eastern Sweden. *Water Resources Research,* 30, No. 6, 1747-1763.

Banwart, S., Tullborg, E.-L., Pedersen, K., Gustafsson, E., Laaksoharju, M., Nilsson, and Wallin, B. (1993) Organic carbon oxidation induced by large-scale shallow water intrusion into a vertical fracture zone at the Äspö Hard Rock Laboratory. *Conference Proceedings, Migration 93.*

Bein, A. and Arad, A., 1992. Formation of saline groundwaters in the Baltic region through freezing of seawater during glacial periods. *Jour. of Hydr.*, 140:75-87.

Berglund, B. E., 1966. Late Quaternary vegetation in eastern Blekinge, southeastern Sweden. A pollenanalytical study. II. Post-Glacial time. *Opera Botanica* 12:, 190 pp.

Blomquist, 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.) Garland, G. D., *Ontario Geological Survey, Special Volume* 3:746-757.

Blomqvist, R. G., 1990. Deep groundwaters in the crystalline basement of Finland, with implications for nuclear waste disposal studies. *Geol. Fören. Stockh. Förh.*, 112:369.

Berggren, W. A., 1968. Micropaleontology and the Pliocene/Pleistocene boundary in a deep-sea core from south central North Atlantic. *Jour. Geol.*, 35:291-312.

Birch, G. F., 1979. Phosporite pellets and rocks from the western continental margin and adjacent coastal terrace of South Africa. *Mar Geol.*, 33:91-116.

Birch, G. F., 1982.

Björck, S.,1979. Late Weichselian stratigraphy of Blekinge, Se Sweden, and water level changes in the Baltic Ice Lake. *Univ. of Lund, Dep. of Quaternary Geology, Thesis* 7, 248 pp.

Björck, S.,1981. A stratigraphic study of Late Weichselian deglaciation, shore displacement and vegetation history in sout-heatern Sweden. *Fossils and Strata,* 14, 93 pp.

Björck, S., and Digerfeldt, G. 1984. Climatic changes at Pleistocene/Holocene boundary in the Middle Swedish endmoraine zone, mainly inferred from stratigraphic indications. In N.-A., Mörner, W. Karlén (Eds.) Climatic changes on a Yearly to Millennial Basis. Reidel Publ. Company, 37-56 pp.

Björck, S., and Digerfeldt, G. 1986. Late Weichselian-Early Holocene shore displacement west of Mt. Billingen, within the Middle Swedish end-morraine zone. *Boreas,* **15**:1-18.

Björck, S. and Möller, P., 1987. Late Weichselian environment history in southeastern Sweden during the deglaciation of the Scandinavian ice-sheet. *Quaternary Research,* **28**:1-37.

Björksjö, N., 1949. Israndstudier i södra Bohuslän. *SGU, Ser. C,* N:o 504:1-321.

Borevsky, L. V., Vartanyan, G. S., Kulikov, T. B., 1984. Hydrogeological essay. In, Kozlovky, Y. A., (Ed.) The superdeep well of the Kola Peninsula, Springer-Verlag, New York, pp. 271.

Boström, K., 1970. Deposition of Mangane rich sediments during glacial periods. *Nature,* 226:629-630.

Boulton, G. S. and Payne, A., 1992. Simulation of the European ice sheet through the last glacial cycle and prediction of future glaciation. *SKB TR* 93-14.

Broecker, W. S., 1984. Carbon dioxide circulation through ocean and atmosphere. *Nature,* 308:602.

Brotzen, F., 1944. De geologiska resultaten från Borrningarna vid Höllviken. Del I: Kritan. *SGU,* Ser. C, N:o 464:1-62.

Brotzen, F., 1944. De geologiska resultaten från Borrningarna vid Höllviken. Del II: Undre Kritan och Trias. *SGU,* Ser. C, N:o 505:1-48.

Burgman, J. O., Eriksson, E. and Westman, F., 1983. A study of oxygen-18 variations in river waters and monthly precipitation in Sweden and determination of mean residence times. *Laboratory of mass spectrometry, Hydrology devision, University of Uppsala.* Pp. 1-19.

Burgman, J. O., Calles, B. and Westman, F., 1987. Conclusions from a ten year study of oxygen-18 in precipitation and runoff in Sweden. In Proceedings of an international symposium on the use of isotope techniques in water resources development. *IAEA-SM*-299/107.

Bågander, L.-E. (1977) In-situ studies of bacterial sulfate reduction at the sediment-water interface. *Ambio Special Report,* **5**,147-155.

Bågander, L.-E., 1980. Bacterial cycling in a Baltic Sediment: An in situ Study in Closed Systems. *Geomicrobial Journal,* **2**:141-159.

Caldenius, C., 1944. Baltiska issjöns sänkning till Västerhavet. En kronologisk studie. *Geol. För. Stockh. Förh.,* 66:366-382.

Calles, B. and Westman, F., 1989. Oxygen-18 and Deuterium in precipitation in Sweden. *University of Uppsala, Department of Physical Geography, Hydrology devision Report Series A,* No 47, pp. 1-20.

Chappellaz, J., Barnola, J. M., Raymond, D., Korotkevich, Y. S. and Lorius, C., 1990. Ice core record of atmospheric methane over the past 160,000 years. *Nature,* 345:127-131.

Cheney, E. S. and Jensen, M. L., (1965) Stable carbon isotopic composition of biogenic carbonates. *Geochimica et Cosmochica Acta,* 29,1331-1346.

Clauer, N., Frape, S. K. and Fritz, B., 1989. Calicte veins of the Stripa granite (Sweden) as records of the origin of the groundwaters and their interactions with the granite body. *Geochim. et Cosmochim. Acta,* 53:1777-1781.

Claypool, G. E., Holser, W. T., Kaplan, I. R. and Sakai, H. (1980) The age of sulfur and oxygen isotopes in marine sulfate. *Chemical Geology,* **28**,199-260.

Clayton, R. N., 1959. Oxygen fractionation in system calcium carbonate-water. *Chemical physics,* 30:1246-1250.

Cook, P. J., and McElhinney, W. M., 1979. A reevaluation of the spatial and temporal distribution of sedimentary phosphate deposits in the light of plate tectonics. *Econ. Geol.,* 74:315-330.

Craig, H. 1953. The geochemistry of stable isotopes. *Geochim. et Cosmochim. Acta,* 3:53-92.

Craig, h., 1965. The measurement of oxygen isotope paleotemperatures. In: Tongiorgi, E. (Ed.), Stable isotopes in Oceanographic studies and paleotemperatures. Pisa, 337p.

Dansgaard, W., 1964. Stable isotopes in precipitation. *Tellus,* 16:436-468.

Dansgaard, W., Johnsen, S. J., Möller, J. and Langway, C. C., 1969. One thousand centuries of climatic record from Camp Century on the Greenland Ice-sheet. *Science,* 166:378-381.

Degens, E. T, and Epstein, S., 1964. Oxygen and carbon isotope ratios in coexisting calcites and dolomites from recent and ancient sediments. *Geochim. et Cosmochim. Acta,* 28:23-44.

De Geer, G. 1940. Geochronologia suecica principles. Kungl. Vetensk. Akad. handlingar, Ser III, Bd 18:6, 360 pp.

Deines, P. and Langmuir, D., 1974. Stable isotope ratios and the existence of a gas phase in the evolution of carbonate ground waters. Geochim. et Cosmochim Acta, 38:1147-1164.

Dienes, P. , 1980. The isotopic composition of reduced organic carbon", In: Fritz, P. Fritz, and J. Ch. Fontes, (eds) Handbook of environmental isotope geochemistry, Volume 1, The terrestrial environment, A: Amsterdam, Elsevier, 329-406.

Donner, J. J., 1969. A profile across Fennoscandia of Late Weichselian and Flandrian shore-lines. *Societas Scientiarum Fennica Commentationes Physico-Mathematicae* 36:1-23.

Donnovan, T. J., 1974. Petroleum microseepage at Cement field, Oklahoma - Evidence and mechanism. *Bull. Am. Assoc. Petr. Geol.,* 58:429-446.

Edmunds, W. M., Andrews, J. N., Burgess, W. G., Kay, R. L. F. and Lee, D. J., 1984. The evolution of saline and thermal groundwaters in the Carnmenellis granite. *Miner. Mag.,* 48:407-.

Edmonds, W. M., Kay, R. L. F. and McCartney, R. A., 1985. Origin of saline groundwaters in the Carnmellis granite: Natural processes and reaction during hot dry rock reservoir insulation. *Chem. geol.,* 49:287.

Edmonds, W. M., Kay, R. L. F, Miles, D. L. and Cook, J. M., 1987. The origin of saline groundwaters in the Carnmellis granite, Cornwall (U.K.): Further evidence from minor and trace elements. In: Fritz, P. and Frape, S. K., Saline water and gases in crystalline rocks. *Geol. Assoc. of Canada Spec. Pap.,* 33:127-143.

Emiliano and Shackleton, 1974. The Bruhnes epoch: isotopic paleotemperatures and geochronology, *Science,* 183:511-514.

Emrich, K, Enhalt, D. H. and Vogel, J C., 1969. Carbon isotope fractionation during precipitation of calcium carbonate. *Earth Planet. Sci. Let.,* 8:363-371.

Enquist, F., 1918. Die Glaziale Entwicklungsgeschichte Nordscandinaviens. *SGU,* Ser. C, N:o, 285:1-143.

Enqvist, P., Fagerlind, T., Lundström, A. and Sandström, 1985. Svenskt vattenarkiv, grundvattenkvalitet. *SGU* Rapporter och meddelanden nr 44:1-113.

Erlenkeuser, H., 1985. Stable isotopes in benthic foraminifers of Skagerak core GIK 15530-4: High resolution of the Younger Dryas and the Holocene. *Norsk geolog. Tidskr.,* 65:49-57.

Eronen, M., 1983. Late Weichselian and Holocene shore displacements in Finland. In: Smith, D. E. and Dawson, G. A. (Eds.). Shorelines and Isostasy. *Institute of British Geographers, Special Publication* 16:183-206.

Exon, N. F., 1972 Sedimentation in the outer Flensburg Fjord Area (Baltic Sae) since the last glaciation. *Meyniana,* 22:5-62.

Faure, G., (1986) Principles of isotope geology. John Wiley & Sons. New York, 464 p.

Fabryka-Martin, J. T., Davis, S. N., Elmore, D. Kubik, P. W., 1989. *In-situ* production and migration of ^{129}I in the Stripa granite, Sweden. *Geochim. et Cosmochim. Acta,* 53:1817-1823.

Fontes, J-Ch., Fritz, P., Louvat, D. and Michelot, J-L., 1989 Aqueous sulphates from the Stripa groundwater system. *Geochim. et Cosmochim. Acta,* 53:1783-1789.

Frape, S. K., Fritz. P. and McNutt, R. H., 1984. The role of water-rock interaction in the chemical evolution of groundwaters from the Canadian shield. *Geochim. et Cosmochim. Acta,* 48:1617-.

Frape, S. K. and Fritz, 1987. Geochemical trends for groundwaters from the Canadian shield. In: Fritz, P. and Frape, S. K., Saline water and gases in crystalline rocks. *Geol. Assoc. of Canada Spec. Pap.*, 33:19-38.

Fredén, C., 1986. Quaternary marine shell deposits in the region of Uddevalla and Lake Vänern. *SGU,* Rapporter och meddelanden nr 46.

Fritz, P. and Frape, S. K, 1982. Saline groundwater's in the Canadian Shield - a first review. *Chem. Geol.,* 36:179-190.

Fritz, P., Frape, S. K. and Miles, M., 1987. Methane in the crystalline rocks of the Canadian shield. In: Fritz, P. and Frape, S. K., Saline water and gases in crystalline rocks. *Geol. Assoc. of Canada Spec. Pap.,* 33:211-223.

Fritz, P., Fontes, J-Ch., Frape, S. K., Luovat, D., Michelot, J-L. and Balderer, W., 1989. The isotope geochemistry of carbon in the groundwater at Stripa. *Geochim. et Cosmochim. Acta,* 53:1765-1775.

Fromm, E., 1969. An interglacial peat at Ale near Luleå, northern Sweden. *SGU,* Ser. C, N:o 574:1-14.

Fyfe, W. S., 1987. The fluid inventory of the crust and its influences on crustal dynamics. In: Fritz, P. and Frape, S. K., Saline water and gases in crystalline rocks. *Geol. Assoc. of Canada Spec. Pap.,* 33:1-4.

Gavelin, A. and Högbom, A. G., 1910. Norra Sveriges Issjöar. I. De isdämnda sjöarna i Lappland och Nordligaste Jämtland (Gavelin, A.). *SGU,* Ser. Ca, N:o 7:1-112. II. De centrala jämtlänska issjöarna (Högbom, A. G.). *SGU,* Ser. C, N:o 7:1-45.

Gascoyne, M., Davison, C. C., Ross, J. D. and Pearson, R., 1987. Saline groundwaters and brines in plutons in the Canadian shield. In: Fritz, P. and Frape, S. K., Saline water and gases in crystalline rocks. *Geol. Assoc. of Canada Spec. Pap.*, 33:53-68.

Geirnhaert, W., 1972. The hydrogeology and hydrochemistry of the Lower Rhine fluvial plain. Leid. Geol. Med., 49:59-84.

Giggenbach, W. F., 1980. Geothermal gas equilibria. *Geochim. et Cosmochim. Acta*, 3:53-92.

Gustavsson, O., Johansson, S. A:, Magnusson, E. and Andersson, E., 1988. Grundvattenundersökningar på Kristanstadsslätten 1976-1987. *SGU*, pp. 91.

Hamza, M. S. and Broecker, W. S, 1974. Surface effect on the isotopic fractionation between CO_2 and some carbonate minerals. *Geochim. et Cosmochim. Acta*, 38:669-681.

Hathaway, J. C. and Degens, E. T, (1969) Methane derived marine carbonates of Pleistocene age. *Science*, 165, 690-692.

Hanor, J. S., 1978. Precipitation of beachrock cements: Mixing of marine and meteoric waters vs. CO_2-degassing. *Jour. Sed. Petrol.,* 48:489-501.

Hays, J. D., Imbrie, J. and Shackleton, 1976. Variation in the Eart's Orbit: Pacemaker of the Ice Ages. *Science,* 194:1121-1132.

Herut, B, Starinsky, A., Katz, A. and Bein, A., 1990. The role of seawater freezing in the formation of subsurface brines. *Geochim. et Cosmochim. Acta*, 54:13-21.

Hoefs, J., 1987. Stable Isotope Geochemistry. Springer-Verlag, 241 p.

Holser , W.T. and Kaplan, I. R., 1966. Isotope geochemistry of sedimentary sulfates. *Chem. Geol.,* 1:93-135.

Hultberg, B., Larsson, S.-Å. and Tullborg, E.-L., 1981. Grundvatten i kristallin berggrund. *SGU*, Projekt Kärnbränslesäkerhet, *KBS*.

Hyyppä, J., 1984. Geochemistry of the groundwaters of the bedrock on Hästholmen, Loviisa. *Nucl. Waste Comm. Finn. Power Comp., Rept* YJT-86-05.

Hyyppä, J., 1986. The composition of the ground water in the bedrock i the Precambrian shield areas of Finland and other countries. *Nucl. Waste Comm. Finn. Power Comp., Rept* YJT-86-30.

Högbom, A. G., 1889. Om relationen mellan kalcium- och magnesiumkarbonat i qvartära aflagringar. (Translated in Mörner 1976) *Geol. För. Stockh. Förh.*, 11:263-273.

Imbrie, J. and Imbrie, J. Z., 1980. Modelling the Climate Response to Orbital Variations. *Science,* 207:943-952.

Irwin, H., Curtis, C. and Coleman, M., 1977. Isotopic evidence for source of diagenetic carbonates formed during burial of organic-rich sediments. *Nature,* 269:209-213.

Iversen, J., 1954. The development of Denmark's nature since the Last Glacial. Late-Glacial flora of Denmark and its relation to climate and soil. *Danmarks Geologiske Undersøgelse* V:8C, 126 pp.

Iversen, J., 1973. The Late-Glacial flora of Denmark and its relation to climate and soil. *Danmarks Geologiske Undersøgelse* II:80:87-119.

Jancke, R. A., Emersson, S. R., Roe, K. K. and Burnett, W. C., 1983. The present day formation of apatite in Mexican continental margin sediments. *Geochim et Cosmochim. Acta,* 48:259-266.

Johansson, Å. (1988) The age and geotectonic setting of the Småland-Värmland granite-porhpyry belt. *Geol. För. i Stockh. Förh.*, **110**,105-110.

Johnson, J. Aastrup, M. Aneblom, T. Johnasson, O., Särnblad, L., Aastrup, B. and Henriksson, B., 1985. *SGU* Rapporter och meddelanden nr 43:1-115.

Jones, B. F. and Bodine, M. W. Jr., 1987. Normative salt characterisation of natural waters. In: Fritz, P. and Frape, S. K., Saline water and gases in crystalline rocks. *Geol. Assoc. of Canada Spe. Pap.,* 33:5-18.

Judge A. S., 1973. Deep temperature observations in the Canadian North. *Permafrost, 2nd Int. Conf., Nat. Acad. Sci.*, Washington, DC, pp 35-40.

Jörgensen, B. B. and Fenchel, T. (1974) The sulfur cycle of a Marine Sediment Model System. *Marine Biology,* 24, 189-201.

Kaminemi, D. C., 1987. Halogen-bearing minerals in plutonic rocks: A possible source of chlorine in saline groundwater in the Canadian shield. In: Fritz, P. and Frape, S. K., Saline water and gases in crystalline rocks. *Geol. Assoc. of Canada Spec. Pap.*, 33:69-79.

Karlén, W., 1973. Holocene glacier and climatic variations, Kebenekaise Mountains, Swedish Lappland. *Geogr. Ann.*, 55:A:29-63.

Kholodov, V. M. 1973. Trace element distribution in the Kurumsak-Chulaktua deposits of Karatua. English translation: *Geoch. Intern.*, 10:796-802.

Kieth, M. L. and Weber, J. N., 1964. Carbon and oxygen isotope composition of selected limestones and fossils. *Geochim. et Cosmochim. Acta*, 24:277-298.

Knutsson, G and Fagerlind, T, 1977. Grundvattentillgångar i Sverige. *SGU* Rapporter och meddelanden, nr 9.

Knutsson, G and Morfeldt, C.-O., 1993. Grundvatten - Teori & tillämpning. Svenskt Tryck AB, Stockholm, pp. 304.

Kolstrup, E., 1982. Late glacial pollen diagrams from Hjelm and Draved Mose (Denmark) with a suggestion of the possibility of draught during the Earlier Dryas. *Review of Palaeontology and Palynology* 36:205-230.

Kominz, M, A, and Pisias, N. G., 1979. Pleistocene Climate: Deterministic or Stochastic?. *Science*, 206:171-172.

Krouse, H. R. (1980) Sulphur isotopes in our environment. In: Fritz, P. and Fontes, J.-Ch., (Eds.), *Handbook of environmental isotope geochemistry*. pp. 435-472. Elsevier, Amsterdam.

Königson, L. K., 1968 The Ancylus transgression in the Skede mosse area, Öland. *Geol. För. Stockh. Förh.*, 90:5-36.

Labeyrie, L. D., Duplessy, J. C. and Blanc, P. L., 1987. Variations in mode of formation and temperature of oceanic deep waters over the past 125,000 years. *Nature,* 327:477-482.

Lagerbäck, R., 1988. The Veiki moraines in northern Sweden - widespread evidence of an early Weichselian deglaciation. *Boreas*, 17:469-486.

Lahermo, P. W. and Lampén, P. H., 1987. Brackish and saline groundwaters in Finland. In: Fritz, P. and Frape, S. K., Saline water and gases in crystalline rocks. *Geol. Assoc. of Canada Spec. Pap.*, 33:103-109.

Lahermo, P. W., and Kankainen, T., 1986. Elemental and isotopic geochemistry of brackish and saline groundwater in coastal areas of Finland. In: Fifth int. Symp. on Water-Rock interaction, Extended abstracts, Raykjavik, Iceland. Int. Assoc. *Geochim. et Cosmochim Acta,* pp. 341-344.

Laurent, S., 1983a. Analysis of groundwater from deep boreholes in Gideå. *SKBF/KBS, TR*, 83-17.

Laurent, S., 1983b. Analysis of groundwater from deep boreholes in Fjällveden. *SKBF/KBS, TR*, 83-19.

Lemdahl, G. 1988. Paleoclimatic and palaeoecological studies based on subfossil insects from Late Weichselian sediments in southern Sweden. *Lundqua Thesis*, 22, 12 pp.

Lehman, S. J., Jones, G. A., Keigwin, L. D., Andersson, E. S., Butenko, G. and Ostmo, S.-R., 1991. Initiation of Fennoscandian ice-sheet retreat during the last glaciation. *Nature,* 349:513-516.

Liedberg-Jönsson, B. 1988. The Late Weichselian microfossil flora in Western Skåne. *Lundqua Thesis* 24, 11 pp.

Lijegren, R. 1982. Paleoekologi och strandförskjutning i en Littorinavik vid Spjälkö i mellersta Blekinge. *Univ. of Lund, Dep. of Quaternary Geology, Thesis* 11, 95 pp.

Lindeén, A. G., 1984. Some ice-marginal deposits in the east-central part of the south Swedish Upland. *SGU,* Ser. C, N:o 805:1-35.

Lindström, G., 1886. Om postglaciala sänkningar af Gotland. *Geol. För. Stockh. Förh.,* 102 Bd. VIII. Häft. 4, 251-281.

Lindström, A., 1898. Några allmänna upplysningar till Översiktskarta angifvande de kvartära havsaflagringarnas område samt kalkstens- och mergelförekomstens utbredning i Sverige. *SGU,* Ser. Ba , N:o 5:1-80.

Lindewald, H., 1981. Saline groundwater in Sweden (Saline groundwater in Sweden). *SGU* Rapporter och meddelanden, nr 27:27-32.

Lindewald, H., 1985. Salt grundvatten i Sverige. Salt water intrusion Meeting (SWIM-81). *SGU* Rapporter och meddelanden, nr 39.

Ljungner, E., 1943. Isdelarstudier vid polcirkeln. *Geol. Fören. Stockh. Förh.,* 65:.

Ljungner, E., 1945. Den sista nordiska nedisningens förlopp. *Geol. Fören. Förh. Stockh.*, 67:.

Loosli, H. H., Lehmann, B. E. and Balderer, W., 1989. Argon-39, argon-37 and krypton-85 isotopes in Stripa groundwaters. *Geochim. et Cosmochim. Acta*, 53:1825-1829.

Laaksoharju, M., 1988. Shallow groundwater chemistry at Laxemar, Äspö and Avrö. *SKB PR* 25-88-04.

Laaksoharju, M, and Nilsson, A.-C., 1989. Chemical characterisation and modelling of deep groundwater at Äspö and Laxemar. *SKB PR* 25-89-04.

Longinelli, A., 1989. Oxygen-18 and sulfur-34 in dissolved oceanic sulphate and phosphate. In: Handbook of environmental isotope geochemistry, 3:(Eds.) Fritz, P. and Fontes, J-Ch., Elsivier, Amsterdam (in press.).

Lundqvist, G., 1928. Studier över Ölands myrmarker. *SGU*, Ser. C, 353, 177 pp.

Lundqvist, G., 1958a. Kvartärgeologisk forskning i Sverige under ett sekel. *SGU*, Ser. C, N:o 561:1-57.

Lundqvist, G., 1958b. Interglacial ooze at Porsi in Lapland. *SGU*, Ser. C, N:o 575:1-26.

Lundqvist, G., 1965. C 14-dateringar från Gotland. *SGU*, Ser. C, 602, 94 pp.

Lundqvist, J., 1959. Issjöar och isavsmältning i Östra Jämtland. *SGU*, Ser. C, N:o 573:1-29.

Lundqvist, J. 1981. Weichselian in Sweden before 15,000 B.P..*Boreas*, 10:395-402.

Lundqvist, J. 1986. Late Weichselian glaciation and deglaciation in Scandinavia. In Sibriva, V (Ed.) Quaternary glaciations in the northern hemisphere. Qutern. Sci. Revs., 5:269-292.in Sweden before 15,000 B.P..*Boreas*, 10:395-402.

Löfvendahl, R., Åberg, G., and Hamilton, P. J., (1990) Strontium in rivers of the Baltic Basin: *Aquatic Sciences*, 52/4, 315-329.

Malmgren, B. A., 1976 Sex and shape variation in the planktonic foraminifer Heterohelix striata (Late Cretaceous, southern Sweden): *Mathimatical Geology* 8:165-182.

Mangerud, J., 1991. The s´Scandinavian ice sheet through the last interglacial/glacial cycle. In Frenzel, B. (Ed.) Kklimageschichtliche Probleme der Letzten 130,000 Jahre. G. Fischer, Stuttgart, pp. 307-330.

McNutt, R. H., Gascoyne, M. and Kamineni, D. C., 1987. $^{87}Sr/^{86}Sr$ values in groundwaters of the east Bull Lake pluton, Superior Province, Ontario, *Canada. Appl. Geochem.*, 2:93.

McNutt, R. H., 1987. $^{87}Sr/^{86}Sr$ ratios as indicators of water/rock interactions: Application to brines found in Precambrian Age Rocks from Canada. In: Fritz, P. and Frape, S. K., Saline water and gases in crystalline rocks. *Geol. Assoc. of Canada Spec. Pap.*, 33:81-101.

McNutt, R. H., Frape, S. K., Fritz, P., Jones, M. G. and McDonald, I. M., 1990. The $^{87}Sr/^{86}Sr$ values of Canadian shield brines and fracture minerals with applications to groundwater mixing, fracture history and geochronology. *Geochim. et Cosmochim. Acta*, 54:205.

McKelvey, V. E., Swanson, R. W. and Shelton, R. P., 1953. The Permian phophorite deposits of Western United States. In: *Congr. Geol. Int. Compt. Rend., 19th, Algiers, 1953, X(II),* pp. 45-64.

Michelot, J.-L., Bently, H. W., Brissaud, J., Elmore, D. and Fontes, J.-Ch., 1987. Progress in environmental isotope studies (^{36}Cl, δ^{34}S, δ^{18}O) at the Stripa site. Isotope hydrology, 1983, *IAEA,* p. 207.

Milankovitch, M. 1941. Canon of insolation and the ice age problem. K. *Serb. Acad. Beorg. Spec. Publö.* 132.

Moser, H., Wolf, M. Fritz, P. Fontes, J-Ch., Florkowski, T. and Payne B. R., 1989. Deuterium, oxygen-18 and tritium in Stripa groundwater. *Geochim. et Cosmochim. Acta*, 53:1757-1763.

Mullins, H. T. and Rasch, R. F., 1985. Sea-Floor Phosphorites along the central California Continental margin. *Econ. Geol.*, 80:696-715.

Munthe, H., 1887. Om postglacial aflagringar med Ancylus fluviatilis på Gotland. *Öfversikt av Kungl. Vetensk. Akad. Förh.,* 10:719-732.

Munthe, H., 1892. Studier öfver Baltiska Hafvets Qvartära historia. *Bihang till Kungl. Vetensk. Akad. Handl.,* Bd 18 Afd. II N:o 1, 120 pp.

Munthe, H., 1902. Beskrivning av kartbladet Kalmar. *SGU,* Ac 6, 119 pp.

Munthe, H., 1910. Studier öfver Gotlands senkvartära historia. *SGU,* Ca-4, pp. 213.

Murata, K. J., Friedman, I. and Madsen, B. M., 1969. Isotopic composition of diagenetic carbonates in marine Miocene formations of California and Oregon. *Am. Geol. Serv. Prof. Paper,* 614-B:B1-B24.

Mäkelä, J. and Rönkä, e., 1994. Chloride concentration and electrical conductivity of groundwaters in the Precambrian crystalline bedrock of central Finland. In: Olofsson B. (Ed.) Salt groundwaters in the Nordic countries. Proceedings of a workshop, Saltsjöbaden, Sweden. *Res. Counc. of Norway Sci and Techn., NHP Report,* 35:63-70.

Möller, H., 1959. Från Nordostis till Lågbaltisk is - En glacialgeologisk studie i Sydvästra Skåne. *SGU,* Ser. C, N:o 566:1-133.

Mörner, N.-A., 1969. The Late Quaternary history of the Kattegatt and the Swedish west coast. Deglaciation, shorelevel displacement, chronology, isostasy and eustasy. *SGU,* Ser. C, N:o 440:1-487.

Mörner, N.-A., 1971. Eustatic changes during the last 20,000 years and a method of separating the isostatic and eustatic factors in an uplifted area. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 9:153-181.

Mörner, N.-A., 1976. Eustatic changes during the last 8000 years in view of radiocarbon calibration and new information from the Kategatt region and other northwestern European coastal areas. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 19:63-85.

Mörner, N.-A. and Wallin, B., 1976. A 10.000 year temperature record from Gotland, Sweden. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 21:113-138.

Mörner, N.-A., 1994. (pers. comm.)

Nilsson, E., 1968. Södra Sveriges Senkvartära historia. Geokronologi, issjöar och landhöjning. *Kungl. Vetensk. Handl., Serie* 4, Bd 12, No. 1, 117 pp.

Nilsson, K., 1959. Isströmmar och isavsmältning i sydvästra Skånes Backlandskap. *SGU*, Ser. C., N:o 567:1-94.

Nilsson, A.-C., 1989. Chemical characterisation of deep groundwater at Äspö. *SKB PR* 25-89-14.

Nordstrom, D. K., 1986. Hydrochemical interpretation of the groundwater at the Hästholmen site, Finland. Nucl. *Waste Comm. Finn. Power Comp., Rept* YJT-86-32.

Nordstrom, D. K. and Olsson, T., 1987. Fluid inclusions as a source of dissolved salts in deep granite groundwaters. In: Fritz, P. and Frape, S. K., Saline water and gases in crystalline rocks. *Geol. Assoc. of Canada Spec. Pap.,* 33:111-126.

Nordstrom, D. K., Olsson, T., Carlsson, L. and Fritz, P., 1989. Introduction to the hydrogeochemical investigations within the international Stripa Project. *Geochim. et Cosmochim. Acta*, 53:1717-1726.

Nordstrom, D. K., Ball, J. W., Donahoe, R. J. and Whittemore, D., , 1989. Groundwater chemistry and water-rock interactions at Stripa. *Geochim. et Cosmochim. Acta*, 53:1727-1740.

Nordstrom, D. K., Lindblom, S., Donahoe, R. J. and Barton, C. C., , 1989. Fluid inclusions in the Stripa granite and their possible influence on the groundwater chemistry. *Geochim. et Cosmochim. Acta*, 53:1741-1755.

Nordstrom, D. K., 1989. Application of a cation exchange mass-balance model to the interpretation of saline groundwater chemistry evolved from

Holocene seawater entrapped in rapakivi granite at Hästholmen, Finland. Water Rock interaction, Miles (Ed.), Balkena, Rotterdam, pp. 521-523.

Nurmi, P. A., Kukkonen, I. T. and Lahermo, P. W., 1988. Geochemistry of saline groundwaters in the Fennoscandian Shield. *Applied Geochemistry,* 3:185-203.

Olofsson, B., 1994. Salt groundwater in Sweden. In: Olofsson B. (Ed.) Salt groundwaters in the Nordic countrys. Proceedings of a workshop, Saltsjöbaden, Sweden. *Res. Counc. of Norway Sci and Techn., NHP Report,* 35:19-35.

O'Neil, J. R., Clayton, R. N. and Mayeda T. K., 1969. Oxygen isotope fractionation in divalent metal carbonates. *Jour. Chem. Phys.*, 51:5547.

Paces, T., 1987. Hydrochemical evolution of saline waters from crystalline rocks of the Bohemian Massif (Czechoslovakia). In: Fritz, P. and Frape, S. K., Saline water and gases in crystalline rocks. *Geol. Assoc. of Canada Spec. Pap.*, 33:145-156.

Pearson, F. J. Jr and Hanshaw, B. B., 1970. Sources of dissolved carbonate species in groundwater and their effects on carbon-14, In: Isotope Hydrology, 1970 Proceedings of a symposium, Vienna, 9-13 March 1970: Vienna, International atomic energy agency, 217-286.

Pearson, F. J. Jr., 1987. Model of mineral controls on the composition of saline groundwaters of the Canadian shield. In: Fritz, P. and Frape, S. K., Saline water and gases in crystalline rocks. *Geol. Assoc. of Canada Spec. Pap.,* 33:39-51.

Pearson, F. J. Jr, 1991. Carbonate isotopes, In: F. J. PEARSON, Jr, (eds) Applied isotope hydrogeology a case study in northern Switzerland. *Nagra, technical report* 88-01.

Pekdeger, A. and Balderer, W., 1987. The occurrence of saline groundwaters and gases in the crystalline rocks of northern Switzerland. In: Fritz, P. and Frape, S. K., Saline water and gases in crystalline rocks. *Geol. Assoc. of Canada Spec. Pap.*, 33:157-195.

Perhans, K.-E., 1981. Lervarvskronologin mellan Borensberg och Vingåker. In: "Den senaste nedisningens förlopp med särskild hänsyn till deglaciationen i Sverige. Sammanfattningar av föredragen". Symposie volym för IGCP projekt, 73:1:24, Stockholm, 66-68.

Persson, C., 1978. Datering av Ancylus- och Littorinatransgressionerna på södra Gotland. *SGU,* Serie C, 745, 34 pp.

Pettersson, C., Arenie, I., Ephraim, J., Borén, H. and Allard, B., 1989. Properties of fulvic acids from deep groundwaters. *Sci. Tot. Environ.*, 81/82:287-296.

Pettersson, C. and Allard, B., (1991) Dating of Groundwaters by 14C-analyses of Dissolved Humic substances. In: Allard, B. Borén, H. and Grimvell, A. (Eds), Humic Substances in the Aquatic and Terrestrial Environment, 136 - 141, Springer Verlag.

Pisias, N. G. and Moore, T. C., 1980. The evolution of Pleistocene Climate: a time series approach. *Earth. Planet. Sci. Let.*, 52:450-458.

Possnert, G. and Tullborg, E.-L., 1989. 14C Analyses of calcite coatings in open fractures from the Klipperås study site, Southern Sweden. *SKB TR*, 89-36.

Påhlsson, I., 1977. A Standard Pollen Diagram from the Lojsta area of central Gotland. *Striae,* 3, 40 pp.

Rafter, T. A. and Mitzutani, Y. (1967) Oxygen isotope composition of sulphates, 2. Preliminary results on oxygen isotopic variation in sulphates and their relationship of their environment and to their $\delta^{34}S$ values. *New Zeeland Journal of Science*, **10**, 1141-1162.

Rees, C. E., Jenkins, W. J. and Monster, J., 1978. The sulfur isotopic composition of ocean water sulphate. *Geochim. et Cosmochim. Acta*, 42:377-381.

Riggs, S., 1979. Phosphorite sedimentation in Florida - A model phosphogenic system. *Econ. Geol.*, 74:285-315.

Roe, K. K. and Burnett, W. C., 1983. Uranium disequilibrium dating of phosphate deposits from the Lau Group, Fiji, *Nature*, 302:603-606.

Ruddiman, W. F. and McIntyre, A., 1981. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 35:145-214.

Ruddiman, W. F., Shackleton, N. J. and McIntyre, A., 1986. North Atlantic seasurface temperatures for the last 1.1 million years. In Summerhayes, C.P. and Shckleton, N. J. North Atlantic Paleooceanography. *Geol. Soc. Special Publ.*, 21:155-173.

Sackett, W. M. and Moore, W. S., 1966. Isotopic variations of dissolved organic carbon. *Chemical geology*, 1:323-328.

Sakai, H. (1972) Oxygen isotope ratios of some evaporates from Precambrian to Recent ages. *Earth and Planetary Sciences Letter*, **15**, 201-205.

Sandegren, R., 1939. Nedre Klarälvsdalens postglaciala utvecklingshistoria. *SGU*, Ser. C, N:o 422:1-38.

Sarmiente, J. L. and Toggweiler, J. R., 1984. A new model for the role of the oceans in determining atmospheric P CO_2. *Nature*, 308:621-624.

Siegenthaler, U. and Wenk, Th., 1984. Rapid atmospheric CO_2 variations in the ocean circulation. *Nature*, 308:624-626.

Sharma, T. and Clayton, R. N., 1965. Measurement of $^{18}O/^{16}O$ ratios of total oxygen of carbonates. *Geochim. et Cosmochim. Acta*, 29:1347-1353.

Shultz, D. J. and Calder, J. A., 1976. Organic carbon $^{13}C/^{12}C$ variations in estuarine sediments. *Gochim. et Cosmochim. Acta*, 40:381-385.

Smellie, J. A, Larsson, N.-Å., Wikberg, P. and Carlsson, L., 1987. Hydrochemical investigations in crystalline bedrock in relation to existing hydraulic conditions: Experience from the SKB test-sites in Sweden. *SKB TR*, 85-11.

Smellie, J. A, Larsson, N.-Å., Wikberg, P., Puigdoménech, I. and Tullborg, E.-L., 1987. Hydrochemical investigations in crystalline bedrock in relation to existing hydraulic conditions: Klipperås test-site, Småland, Southern Sweden. *SKB TR*, 87-21.

Smellie J. A. T., and Wikberg, P., 1991. Hydrochemical investigations at Finnsjön. *SKB, TR*, 89-19.

Smellie, J. A. T and Laaksoharju, M., 1992. The Äspö Hard Rock Laboratory: Final evaluation of the hydrogeochemical pre-investigations in relation to existing geologic and hydraulic conditions: *SKB TR*, 92-31.

Snellman, M. and Helenius, J., 1992. Groundwater chemistry at Hästholmen, Loviisa - Summary of investigations in 1980-1992. (Loviisan Hästholmenin Pohjavesikemia-yhteenveto Vousien 1980-1992 Tutkimuksista). *Nucl. Waste Comm. Finn. Power Comp., Rept* YJT-92-27.

Shultz, D. J. and Calder, J. A., (1976) Organic carbon $^{13}C/^{12}C$ variations in estuarine sediments. *Geochimica et Cosmochica Acta*, **40**, 381-385.

Stanfors, R. (1988) SKB hard rock laboratory, Geological borehole description, KAS02, KAS03, KAS04, KLX01. *SKB PR* 25-88-18.

Stråhle, A. (1989) Drillcore investigation in the Simpevarp Area, Boreholes KAS02, KAS03, KAS04 and KLX01. *SKB PR* 25-88-17.

Strömberg, B., 1974. Billingenområdet vid slutet av den senaste istiden. *Skaraborgsnatur* 11:1-16.

Strömberg, B., 1977. Deglaciation vid Billingen och Baltiska issjöns tappning. Geol. För. i Stockh. Förh., 99:1:92-95.

Strömberg, B., 1984. Nya data rörande Baltiska Issjön vid Billingen, Västergötland. *Abstarcts 16e, Nordiska Geologmötet* 1984, p. 217.

Strömberg, B., 1986. Om anknytningen mellan de Svenska och Finska lervarvskronologierna. *Abstarcts 17e, Nordiska Geologmötet* 1986, p. 193.

Svensson, N. O., 1989. Late Weichselian and Early Holocene shore displacement in the central Baltic, based on stratigraphical and morphological records from eastern Småland and Gotland, Sweden. *Lundqua*, 25:1-195.

Svensson, N. O., 1991. Late Weichselian and Early Holocene shore displacement in the central Baltic Sea. Quaternary International, 9:7-26.

Taylor, H. P., 1974. Oxygen and hydrogen isotope evidence for large-scale circulation and interaction between groundwaters and igneous intrusions with particular reference to the San Juan volcanic field, Colorado. In: geochemical transport and kinetics. *Carnegie Inst. Washington*, 634:299-323.

Tongiorgi, E., 1965. Stable isotopes in Oceanographic studies and paleotemperatures. Pisa, 337p.

Tullborg, E-L. and Larsson, S-Å., 1982. Fissure fillings from Finnsjön and Studsvik Sweden. Identification, chemistry and dating. *SKBF/KBS TR*, 82-20.

Tullborg, E-L., 1986. Fissure fillings from the Klipperås study site. *SKB TR* 86-10.

Tullborg, E-L., 1989. Fracture fillings in the drillcores KAS05-KAS08 from Äspö, southestern Sweden.

Tullborg, E.-L. and Wallin, B. (1991) Stable isotope studies of calcite fracture fillings (^{18}O, ^{13}C and groundwaters (^{18}O, D). In: Tullborg, E-L., Wallin, B., and Landström, O., Hydrogeochemical studies of fracture minerals from water conducting fractures and deep groundwaters at Äspö. *SKB PR* 25-90-01, 1-24.

Valley, J.W., Komor, S., Baker, K., Jeffrey, A. W., Kaplan, I. R. and Råheim, A., 1988. Calcite crack cements in granite from the Siljan Ring, Sweden: Stable isotope results. *Intern. Report, Djupgasprojektet*, Vattenfall.

Vovk, I. F., 1987. Radiolytic salt enrichment and brines in the crystalline basement of the east European platform. In: Fritz, P. and Frape, S. K., Saline water and gases in crystalline rocks. *Geol. Assoc. of Canada Spec. Pap.*, 33:197-210.

Wallin, B., 1980. Hydrocarbon derived hydrothermal carbon in carbonates from the ore-bearing sandstone at Vassbo, Sweden. In: Annual Report of the Ore Research Group, Stockholm University, (Ed.) Rickard, D., *ORG* 80:112-137.

Wallin, B., 1982. Sedimentology of the Lower Cambrian sequence at Vassbo, Sweden. *Stockh. Contr. Geol.*, 39:1-111.

Wallin, B. 1989. Origin of the Lower Cambrian phosphatic bed at Vassbo, Sweden. *Terra Nova*, 1:274-279.

Wallin, B. 1990. Carbon, oxygen and sulfur isotope signatures for groundwater classification at Laxemar, southeastern Sweden. *SKB PR* 25-90-12, 1-23.

Wallin, B., 1992. Sulphur and oxygen isotope evidence from dissolved sulphates in groundwater and sulphide sulphur in fissure fillings at Äspö, southeastern Sweden, *SKB PR* 25-92-08, 1-44.

Wallin, B., 1993. Organic carbon input in shallow groundwater at Äspö, southeastern Sweden. Proceedings of the Fourth Annual International Conference, Las Vegas, Nevada, April 26-30, 1993. *American Nuclear Society.*

Wallin, B., and Peterman, Z., 1994. Isotope systematics in ground water and hydrogenic deposits at Äspö, Sweden. Proceedings of the Fourth Annual International Conference, Las Vegas, Nevada, May 22-26, 1993. *American Nuclear Society*, 4:2692-2701.

Wallin, B. Tullborg, E.-L. and Pettersson, C., 1995. Carbon cycling in the shallow water intrusion into a vertical fracture zone at the Äspö Hard Rock Laboratory. In press. *SKB PR, (in press.)*

Welhan, J. A., 1987. Characteristics of abiotic methane in rocks. In: Fritz, P. and Frape, S. K., Saline water and gases in crystalline rocks. *Geol. Assoc. of Canada Spec. Pap.,* 33:225-233.

Wikberg, P., 1987. The chemistry of deep groundwaters in crystalline rocks. *Royal institute of Technology,* 111 p.

Wikberg, P., Gustavsson, G., Rhén, I. and Stanfors, R., 1991. Hydrogeochemical investigations in relation to existing geologic and hydraulic conditions. *SKB TR*, 92-31.

Wickström, P. and Lampén, P., 1986. Lavian Koereikä - Yhteenveto pohjavesitutkimuksista 1984-1985. *Nucl. Waste Comm. Finn. Power Comp., Rept* YJT-86-11.

Winn, K., Werner, F. and Erlenkeuser, H., 1988. Hydrography of the Kiel Bay, Western Baltic during the Littorina Transgression. *Meyniana*, 40:31-46.

List of SKB reports

Annual Reports

1977-78
TR 121
KBS Technical Reports 1 – 120
Summaries
Stockholm, May 1979

1979
TR 79-28
The KBS Annual Report 1979
KBS Technical Reports 79-01 – 79-27
Summaries
Stockholm, March 1980

1980
TR 80-26
The KBS Annual Report 1980
KBS Technical Reports 80-01 – 80-25
Summaries
Stockholm, March 1981

1981
TR 81-17
The KBS Annual Report 1981
KBS Technical Reports 81-01 – 81-16
Summaries
Stockholm, April 1982

1982
TR 82-28
The KBS Annual Report 1982
KBS Technical Reports 82-01 – 82-27
Summaries
Stockholm, July 1983

1983
TR 83-77
The KBS Annual Report 1983
KBS Technical Reports 83-01 – 83-76
Summaries
Stockholm, June 1984

1984
TR 85-01
Annual Research and Development Report 1984
Including Summaries of Technical Reports Issued during 1984. (Technical Reports 84-01 – 84-19)
Stockholm, June 1985

1985
TR 85-20
Annual Research and Development Report 1985
Including Summaries of Technical Reports Issued during 1985. (Technical Reports 85-01 – 85-19)
Stockholm, May 1986

1986
TR 86-31
SKB Annual Report 1986
Including Summaries of Technical Reports Issued during 1986
Stockholm, May 1987

1987
TR 87-33
SKB Annual Report 1987
Including Summaries of Technical Reports Issued during 1987
Stockholm, May 1988

1988
TR 88-32
SKB Annual Report 1988
Including Summaries of Technical Reports Issued during 1988
Stockholm, May 1989

1989
TR 89-40
SKB Annual Report 1989
Including Summaries of Technical Reports Issued during 1989
Stockholm, May 1990

1990
TR 90-46
SKB Annual Report 1990
Including Summaries of Technical Reports Issued during 1990
Stockholm, May 1991

1991
TR 91-64
SKB Annual Report 1991
Including Summaries of Technical Reports Issued during 1991
Stockholm, April 1992

1992
TR 92-46
SKB Annual Report 1992
Including Summaries of Technical Reports Issued during 1992
Stockholm, May 1993

1993
TR 93-34
SKB Annual Report 1993
Including Summaries of Technical Reports Issued during 1993
Stockholm, May 1994

List of SKB Technical Reports 1995

TR 95-01

Biotite and chlorite weathering at 25°C. The dependence of pH and (bi) carbonate on weathering kinetics, dissolution stoichiometry, and solubility; and the relation to redox conditions in granitic aquifers

Maria Malmström[1], Steven Banwart[1], Lara Duro[2],
Paul Wersin[3], Jordi Bruno[3]
[1] Royal Institute of Technology, Department of Inorganic Chemistry, Stockholm, Sweden
[2] Universidad Politécnica de Cataluña, Departmento de Inginería Química, Barcelona, Spain
[3] MBT Tecnología Ambiental, Cerdanyola, Spain
January 1995

TR 95-02

Copper canister with cast inner component. Amendment to project on Alternative Systems Study (PASS), SKB TR 93-04

Lars Werme, Joachim Eriksson
Swedish Nuclear Fuel and Waste Management Co,
Stockholm, Sweden
March 1995

TR 95-03

Prestudy of final disposal of long-lived low and intermediate level waste

Marie Wiborgh (ed.)
Kemakta Konsult AB, Stockholm, Sweden
January 1995

TR 95-04

Spent nuclear fuel corrosion: The application of ICP-MS to direct actinide analysis

R S Forsyth[1], U-B Eklund[2]
[1] Caledon-Consult AB, Nyköping, Sweden
[2] Studsvik Nuclear AB, Nyköping, Sweden
March 1995

TR 95-05

Groundwater sampling and chemical characterisation of the Laxemar deep borehole KLX02

Marcus Laaksoharju[1], John Smellie[2]
Ann-Chatrin Nilsson[3], Christina Skårman[1]
[1] GeoPoint AB, Sollentuna, Sweden
[2] Conterra AB, Uppsala, Sweden
[3] KTH, Stockholm, Sweden
February 1995