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SKB/DOE Hard Rock Laboratory Studies

**Task 3. Geochemical investigations
using stable and radiogenic isotopic
methods**

Bill Wallin¹, Zell Peterman²

1 Geokema AB, Lidingö, Sweden

2 U.S. Geological Survey, Denver, Colorado, USA

January 1994

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SWEDISH NUCLEAR FUEL AND WASTE MANAGEMENT CO

BOX 5864 S-102 40 STOCKHOLM

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SKB/DOE HARD ROCK LABORATORY STUDIES

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**SKB/DOE
HARD ROCK LABORATORY STUDIES**

**TASK 3. GEOCHEMICAL INVESTIGATIONS USING
STABLE AND RADIOGENIC ISOTOPIC METHODS -
FIRST YEAR**

Bill Wallin¹, Zell Peterman²

¹Geokema AB, S-181 46 Lidingö, Sweden

²U.S. Geological Survey, MS 963, Box 25046 DFC,
Denver, Colorado, USA

January 1994

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ABSTRACT

A stable isotope ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $\delta^{34}\text{S}$) study combined with radiogenic ($\delta^{87}\text{Sr}$) isotopes on ground water and calcite fracture fillings at Äspö, southeastern Sweden, suggest that several end-members have been involved in the ground water formation. None of the isotope signatures of the present ground water resemble those of modern Baltic sea water although the possibility of mixing between Baltic sea water and shallow ground waters cannot be excluded. The large range in $\delta^{13}\text{C}$ values in the carbonate system is indicative of multiple sources for the carbon, including atmospheric, organic and methane derived carbon. The $\delta^{18}\text{O}$ signatures in the water as well as in calcite fracture fillings suggest mixing of meteoric and marine waters, but most of the calcites are precipitated from waters with $\delta^{18}\text{O}$ values similar to those of present-day ground water. The $\delta^{34}\text{S}$ values of the dissolved sulphate indicate a multiple sulphur source, including marine, non-marine and bacterially reduced sulphur. The 1.8-Ga host rock at Äspö is characterized by low Rb/Sr ratios, and a calculated mean $\delta^{87}\text{Sr}$ 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. Calcite fracture fillings add further complexity to the Sr-isotope budget. The most significant result of this study is that several waters have been involved in the formation of the calcite fissure fillings at Äspö. This indicates a complex paleohydrology which must be better understood if credible predictions of future hydrology are to be made. Finally, this study demonstrates that a comprehensive isotopic approach to ground water studies utilizing a combination of stable and radiogenic isotopes can yield critical and relevant data for developing an understanding of the origin and evolution of the ground water at Äspö in particular and in the circum-Baltic region in general.

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SUMMARY

This progress report summarizes the results of a comprehensive stable (O, H, S, and C) and radiogenic (Sr) isotopic investigation of ground water and calcite fracture fillings at the SKB's Äspö Hard Rock Laboratory. The integration of these isotopic techniques, along with water quality data, provides a powerful approach for understanding the origin and evolution of the ground water and the hydrogenic minerals deposited in fractures. The fracture fillings mark the pathways of past fluid movement so an understanding of their genesis is particularly important for understanding the paleohydrogeology of the area. The utility in applying the multiple-isotope to ground water and fracture minerals derives from the fact that the different systems represent different processes. Oxygen and hydrogen isotopes in ground water at low temperatures are considered to be conservative with little modification by water-rock interaction. Hence, they reflect the values of water or waters recharged into the system. Dissolved carbon is derived largely through atmospheric input or by solution of CO₂ in the soil zone during infiltration. Among the stable isotopes, sulphur may exhibit the most complex behavior because of its multiple valence states its amenability to bacterial fractionation. Strontium is a dissolved species geochemically analogous to calcium. The variability of strontium in ground water results solely from dissolution of or exchange with minerals during infiltration and along the flow paths. In addition to sourcing the ground water, O, C, and Sr provide important constraints on identifying the water from which the hydrogenic deposits precipitated. Sr isotopes do not fractionation with phases changes, and the fractionation of O isotopes can be readily calculated. If multiple but isotopically distinct waters are present, all of these systems are helpful in identifying mixing.

Ground water and calcite fracture fillings 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. D values ranges between -112 to -55 o/oo and $\delta^{18}\text{O}$ values range between -7 and -15 o/oo. The $\delta^{13}\text{C}$ of the bicarbonate range between -16 and -6 o/oo, and decrease systematically with depth suggesting mixing of organic and inorganic carbon. The $\delta^{18}\text{O}$ of the bicarbonate is uniform (+18 and +22 o/oo) and in equilibrium with the most of the ground water. $\delta^{34}\text{S}$ values of the dissolved sulphate varies between +9.8 to +21 o/oo. More than twenty samples ground water from 15 to 800 m deep have $\delta^{87}\text{Sr}$ values between +9.9 and +13.9 o/oo in contrast with five samples of Baltic Sea water collected in the vicinity of Äspö with $\delta^{87}\text{Sr}$ values between +0.2 and +0.4 o/oo -- only slightly larger than open ocean water ($\delta^{87}\text{Sr} = 0$ o/oo). The 1.8-Ga host rock at Äspö is characterized by low Rb/Sr ratios, and a calculated mean $\delta^{87}\text{Sr}$ 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. For example, biotite has extremely large $\delta^{87}\text{Sr}$ values, but studies of saline ground water in the Canadian Shield indicate that preferential reaction with plagioclase results in $\delta^{87}\text{Sr}$ that are typically smaller than the bulk-rock values. Calcite fracture fillings add further complexity to the Sr-isotope budget. Calcite fillings from depth between 363 and 612 m have $\delta^{87}\text{Sr}$ values between +4.7 and +9.9 ‰ whereas deeper samples (815 m) have smaller value of -3.0 to +0.6 ‰ coupled with an order of magnitude larger Sr concentrations.

$\delta^{13}\text{C}$ values in the calcite fissure fillings range between -25 and -3 ‰ and the $\delta^{18}\text{O}$ values range between +15 to +35 ‰. The large range in $\delta^{13}\text{C}$ values is indicative of multiple sources for the carbon, including atmospheric, organic and methane derived carbon. The $\delta^{18}\text{O}$ signatures suggest mixing of meteoric and marine waters, but most of the calcites are precipitated from waters with $\delta^{18}\text{O}$ values similar to those of present-day ground water.

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) characterized by a mixture of meteoric water and minor proportions of Baltic Sea water, (2) an intermediate ground water (150 - 500 m) characterized 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 (δD and $\delta^{18}\text{O}$) 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 $\delta^{34}\text{S}$ values of the dissolved sulphate indicates the addition of a component of a non-marine sulphur that could derive from the oxidation of sulphide minerals such as pyrite. Therefore, the sulphur and oxygen isotope data combined for that water suggest that it 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. However, the spread in $\delta^{34}\text{S}$ values of the dissolved sulphate in combination with the sulphide sulphur signatures (Wallin, 1992) suggest that considerable bacterial sulphate reduction takes place in the upper part of this water body.

1. INTRODUCTION

This progress report summarises the results of a comprehensive stable (δD , $\delta^{18}O$, $\delta^{13}C$ and $\delta^{34}S$) and radiogenic (Sr) isotopic investigation of ground water and calcite fracture fillings at the SKB's Äspö Hard Rock Laboratory. The integration of these isotopic techniques, along with water quality data, provides a powerful approach for understanding the origin and evolution of the ground water and the hydrogenic minerals deposited in fractures. The fracture fillings mark the pathways of past fluid movement so an understanding of their genesis is particularly important for understanding the paleohydrogeology of the area. The utility in applying the multiple-isotope to ground water and fracture minerals derives from the fact that the different systems represent different processes. Oxygen and hydrogen isotopes in ground water at low temperatures are considered to be conservative with little modification by water-rock interaction. Hence, they reflect the values of water or waters recharged into the system. Dissolved carbon is derived largely through atmospheric input or by solution of CO_2 in the soil zone during infiltration. Among the stable isotopes, sulphur may exhibit the most complex behaviour because of its multiple valence states its amenability to bacterial fractionation. Strontium is a dissolved species geochemically analogous to calcium. The variability of strontium in ground water results solely from dissolution of or exchange with minerals during infiltration and along the flow paths. In addition to sourcing the ground water, O, C, and Sr provide important constraints on identifying the water from which the hydrogenic deposits precipitated. Sr isotopes do not fractionation with phases changes, and the fractionation of O isotopes can be readily calculated. If multiple but isotopically distinct waters are present, all of these systems are helpful in identifying mixing.

Äspö, an island situated on the Baltic coast in south-eastern Sweden (fig. 1), has been selected as a study site for evaluating the suitability of crystalline rock for hosting a nuclear waste repository. An underground laboratory (Äspö Hard Rock Laboratory--ÄHRL) is now being constructed at Äspö under a program initiated by the SKB (Swedish Nuclear Fuel and Waste Management Company) in 1986. This construction phase was preceded by detailed geologic site characterization studies to evaluate the capabilities of surface and drill-hole investigations to predict subsurface conditions (Wikberg and others, 1991). Extensive hydrologic studies were conducted in the pre-construction phase to establish a baseline for evaluating the impact of tunnelling on the local and regional ground-water systems. The final phase of the program will entail operation of the ÄHRL as an underground laboratory for the next decade.

A large number of scientists and research organisations are involved in this studies centered around the ÄHRL. SKB and DOE (U.S. Department of Energy) have several ongoing co-operative studies of the ground water, hydrogenic deposits, and bedrock at site. One of these studies is entitled "Task 3. Geochemical Investigations Using Stable and Radiogenic Isotopic Methods" (DOE/SKB Agreement, 1993) is focused on stable and radiogenic

isotope studies of the fracture filling minerals and the ground water. The results of investigations carried out during the first year of the program are summarized here. The geohydrologic system of any site being evaluated for a nuclear waste repository must be thoroughly understood.

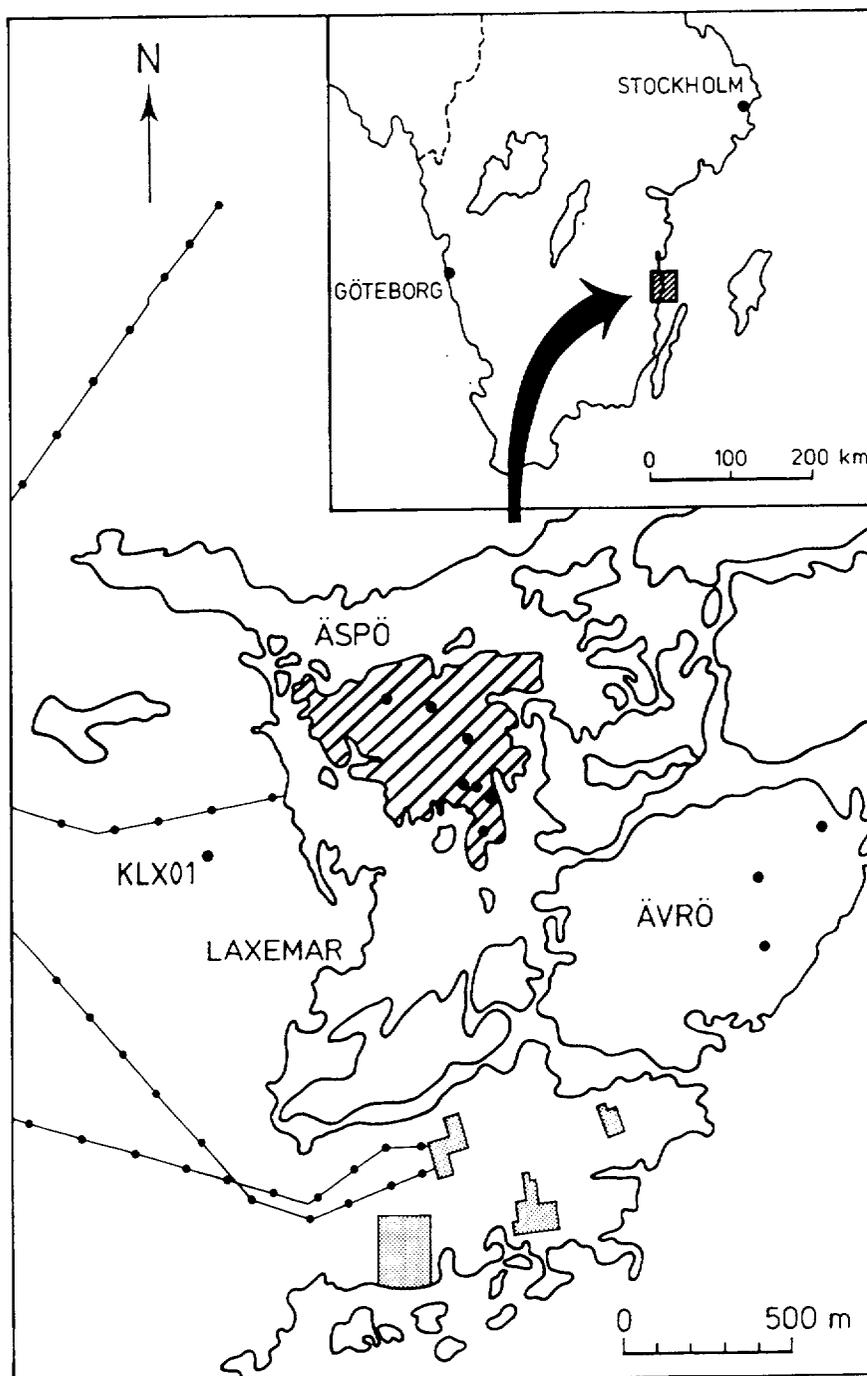


Figure 1. Map showing the location of the Äspö and Laxemar area.

Furthermore, the paleohydrology must be established in order to construct credible scenarios of possible future geohydrologic changes that could occur within the time frame of concern. The geohydrologic system at Äspö appears to be representative of crystalline rock terranes in the circum-Baltic region, but the origin and evolution of brackish-to-saline ground waters common to this region and the age and origin of hydrogenic fracture fillings are not yet fully understood. In order to attain a better understanding of the geohydrology at the site, and by inference similar areas in the region, a detailed sampling of fracture minerals as well as ground water has been made on a regular basis since August 1992 for this isotope study. Preliminary studies of the ground water chemistry suggest a very complicated history. However, the isotopic data obtained in this study demonstrate that it is possible to postulate mixing of marine, meteoric and "fossil" ground water end members to explain the complex ground water system at Äspö.

2. GEOLOGICAL SETTING, FRACTURES AND FRACTURE FILLINGS

The Precambrian basement rocks of the Äspö area are variably fractured crystalline rock of granodioritic to granitic composition with sheets or lenses of greenstone and metadacite. The granites are part of the serorogenic Småland-Värmland granites (ca 1.8 Ma) and the metavolcanic rocks are related to the Småland porphyries within the Svekokarelian belt.

The fracture frequency at Äspö is considered to be medium to high, whereas at Laxemar only 7 km towards the east it is low (Strähle, 1989). The greenstones commonly have a higher fracture frequency than the granites. At least two different tectonic phases are recorded in the horizontal and subhorizontal fractures which are developed in the area. The fracture-filling mineralogy, which is similar at both sites (Stanfors, 1988), is dominated by calcite, hematite, Fe-oxyhydrite, chlorite, fluorite and minor proportions of sulphides. Calcite is by far the most common fracture minerals and is more abundant at Laxemar than at Äspö. Fluorite occurs primarily in subhorizontal fractures, which may be related to a specific event (Stanfors, 1988). The sulphides present are pyrite, chalcopyrite, and lesser amounts of galena. Pyrite, commonly present as well crystallised micron sized cubes, is the dominant sulphide. The pyrite cubes are usually found growing preferentially on the calcite in open fractures and appear to occur in greatest abundance between 400 to 500 m depth.

3. HYDROCHEMISTRY

The ground water at Äspö shows systematic compositional changes with depth (Smellie and Laaksoharju, 1992). Cl, Na, K, Ca, SO_4 and Br, increase progressively with depth and HCO_3 , dissolved CO_2 , Mg and Fe decrease with depth. The pH increases slightly with depth. The hydraulic conductivity is lower in the greenstones in comparison to the granite despite the fact that they

have a higher fracture frequency (Stråhle, 1989). The total water chemistry does not correlate with the different rock types that produce the water.

Stable isotopic data coupled with the concentrations of the dissolved components have suggested the presence of three distinct waters. These three water layers are: shallow water (0 - 150 m), intermediate water (150 - 400 m) and deep water (400 - 1000 m). This division is mainly based on the results from this study in combination with the previous isotopic studies at Laxemar (Wallin, 1990) and Äspö (Tullborg and Wallin, 1991).

4. METHODS

4.1. Sample Collections

In September 1992 and again in September 1993 ground water and fracture minerals were sampled. Ground water was collected from various depth in the wells HBH01, HBH02, KAS02, KAS03, KAS06, KAS07, KAS08, KAS09, KAS12, KAS13 as well as from the side wells (SA709 to SA2074) in the ÄHRL tunnel. Total dissolved inorganic carbon (TIC) from the ground water was sampled from filtered water for $\delta^{13}\text{C}$ - and $\delta^{18}\text{O}$ -analyses, and dissolved sulphate was precipitated for $\delta^{34}\text{S}$ -analyses. Raw, unfiltered water samples were collected for $\delta^{87}\text{Sr}$ -analyses and filtered and acidified in the laboratory prior to analysis. Rain water and sea water from the archipelago surrounding the island of Äspö were sampled as reference waters. Calcite fracture fillings were collected from open as well as filled fissures in the drill cores KAS02, KAS03 and KAS06. The granite and additional fracture minerals such as epidote, chlorite, fluorite and pyrite were collected for bulk rock $\delta^{87}\text{Sr}$ and $\delta^{34}\text{S}$ analyses.

4.2. Analytical Work

4.2.1. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ analyses

The calcite cement was extracted from the drill cores by use of a dental drill. The carbonate samples were reacted with 100% phosphoric acid in evacuated reaction vessels for 12 hours. Equilibrium of the reaction was made at a temperature of 25°C. Collection of CO_2 was done in a preparation line using liquid nitrogen to trap the gas. Excess water and other impurities was removed by freezing with a mixture of ethanol and dry ice. Cleaning with PbAc was used for some samples to free the CO_2 gas from any traces of H_2S gas generated from coexisting sulphides in the sample. A Finnigan MAT Delta E double inlet system mass spectrometer was used for the analyses. The analyses was performed at the Section of Biogeochemistry at the Department of Geology and Geochemistry at Stockholm University.

4.2.2. $\delta^{34}\text{S}$ analyses

Ground water was collected in acid-washed plastic containers. The samples were filtered and dissolved sulphate was precipitated as barium sulphate, carefully washed in distilled water, removed by decanting and dried. The preparation for the sulphur isotope analyses was made according to a technique proposed by (Sakai, 1982), where the sulphate was mixed with vanadium pentoxide (P_2O_5), silica (only small samples, pers com. Krouse, 1993) and pure copper and placed in a quartz glass boat and preheated in an oven at 450°C for 30 minutes. Then the sample was burned in an oven at 900°C for another 30 minutes. The SO_2 gas generated was collected in a pentane trap using liquid nitrogen to remove excess CO_2 gas. The SO_2 gas was transferred to a sample vessel for analyses.

The extraction of the oxygen isotopes from the sulphate was made by the conventional reduction technique described by Rafter (1967), Mizutani, (1971) and Claypool (1980). The sample was mixed with graphite (C). The mixture was preheated for 10 minutes at 400°C to give a complete dehydration. The mixture was reduced at 1100°C and the CO_2 produced was then trapped by liquid nitrogen. Carbon monoxide gas (CO) formed during the reduction stage was converted by sparkling to CO_2 .

Sulphur isotopes were determined with a Finnigan Mat Delta E, double inlet mass spectrometer at the Department of Geology and Geochemistry, Stockholm University, and at Energiteknikk at Kjeller, Oslo, Norway. The oxygen isotopes were run at the Laboratoire d'Hydrologie at de Geochimie isotopique at Universitee de Paris-Sud in Paris.

4.2.3 $\delta^{87}\text{Sr}$ Analyses

Strontium isotope analyses were completed in the laboratory of U.S. Geological Survey, Yucca Mountain Project Branch, Isotope and Geochemistry Section in Denver, Colorado. Water and carbonate samples were analysed on either a VG Isomass 54E or Finnigan MAT 262 mass spectrometer. The relative accuracy of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios is equal to or better than 0.01 percent of the values. This correspond to a 0.1 per mil in $\delta^{87}\text{Sr}$

5. RESULTS

The results from the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotope analyses of the calcite fissure fillings and the $\delta^{34}\text{S}$ ground water isotope are presented in several plots. The strontium isotope analyses of the calcite fracture fillings and the analyses of the ground water are combined and presented in one figure. The $\delta^{13}\text{C}$ values are referenced to PDB (Pee Dee Formation Belemnite) standard, $\delta^{18}\text{O}$ to SMOW (Standard Mean Ocean Water), $\delta^{34}\text{S}$ to CDT (Canyon Diablo Troilite), and $\delta^{87}\text{Sr}$ to the value for modern sea water using USGS standard

EN-1 which is a *Tridacna* shell collected from Enewetok Lagoon in the western Pacific Ocean. Isotopic analyses of the water and the calcite fissure infillings are expressed in per mil (o/oo) deviations (δ values) from the appropriate standards listed above, where δ is defined as:

$$\delta R_{\text{sample}} = [(R_{\text{sample}}/R_{\text{standard}}) - 1] * 1000$$

and R is either $^{13}\text{C}/^{12}\text{C}$, $^{18}\text{O}/^{16}\text{O}$, $^{34}\text{S}/^{32}\text{S}$, or $^{87}\text{Sr}/^{86}\text{Sr}$.

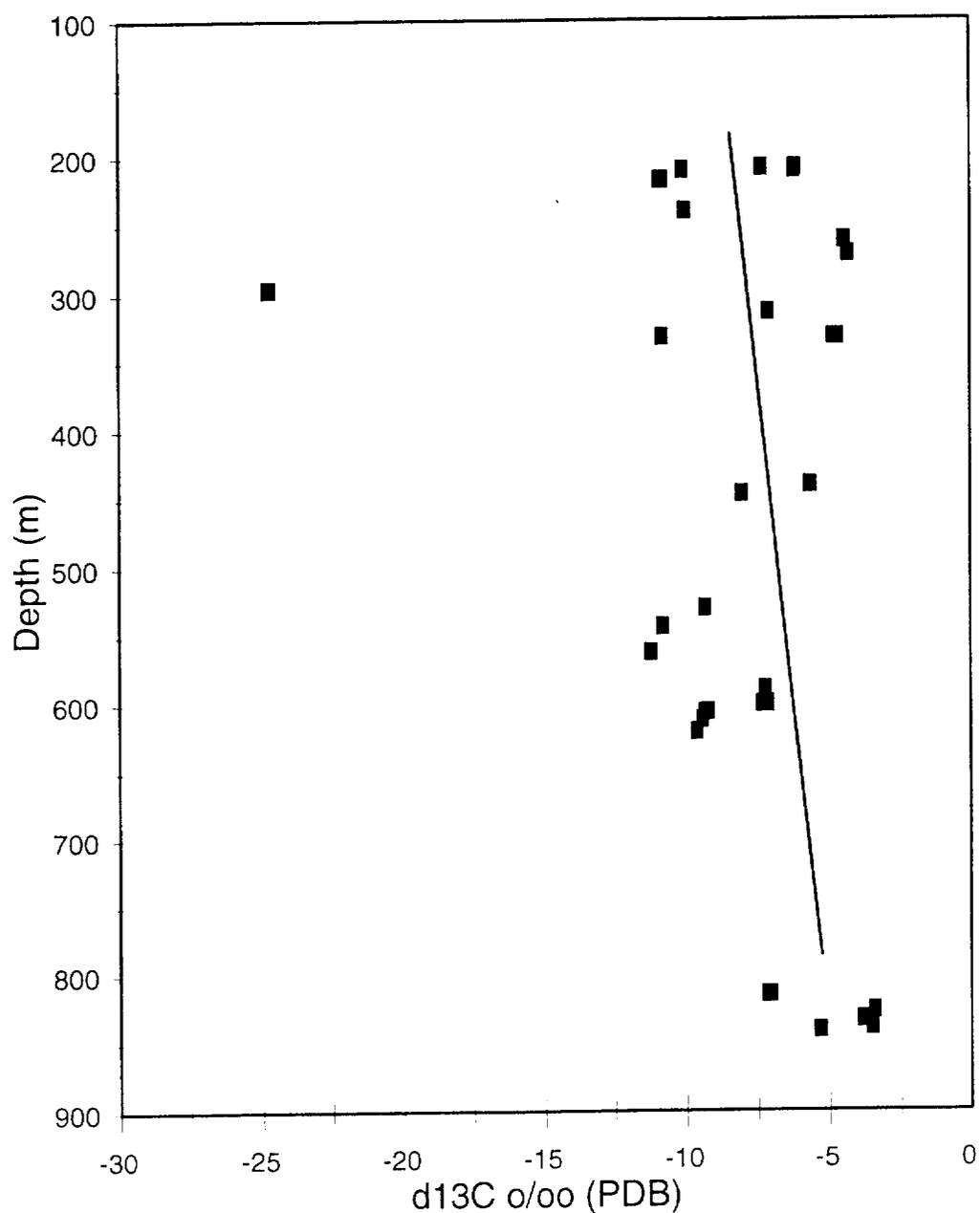


Figure 2. $\delta^{13}\text{C}$ values of calcite fracture fillings versus depth.

6. DISCUSSION

6.1. FRACTURE MINERALS

6.1.1. $\delta^{13}\text{C}$ isotopes

The $\delta^{13}\text{C}$ variation in the calcite fissure fillings display biogenic and typical atmospheric (-13 to -3 o/oo) values although one sample (-25 o/oo) and several in previous reports (Wallin, 1990; Tullborg and Wallin, 1992) show significantly lower values of -25 to -40 o/oo (fig 2).

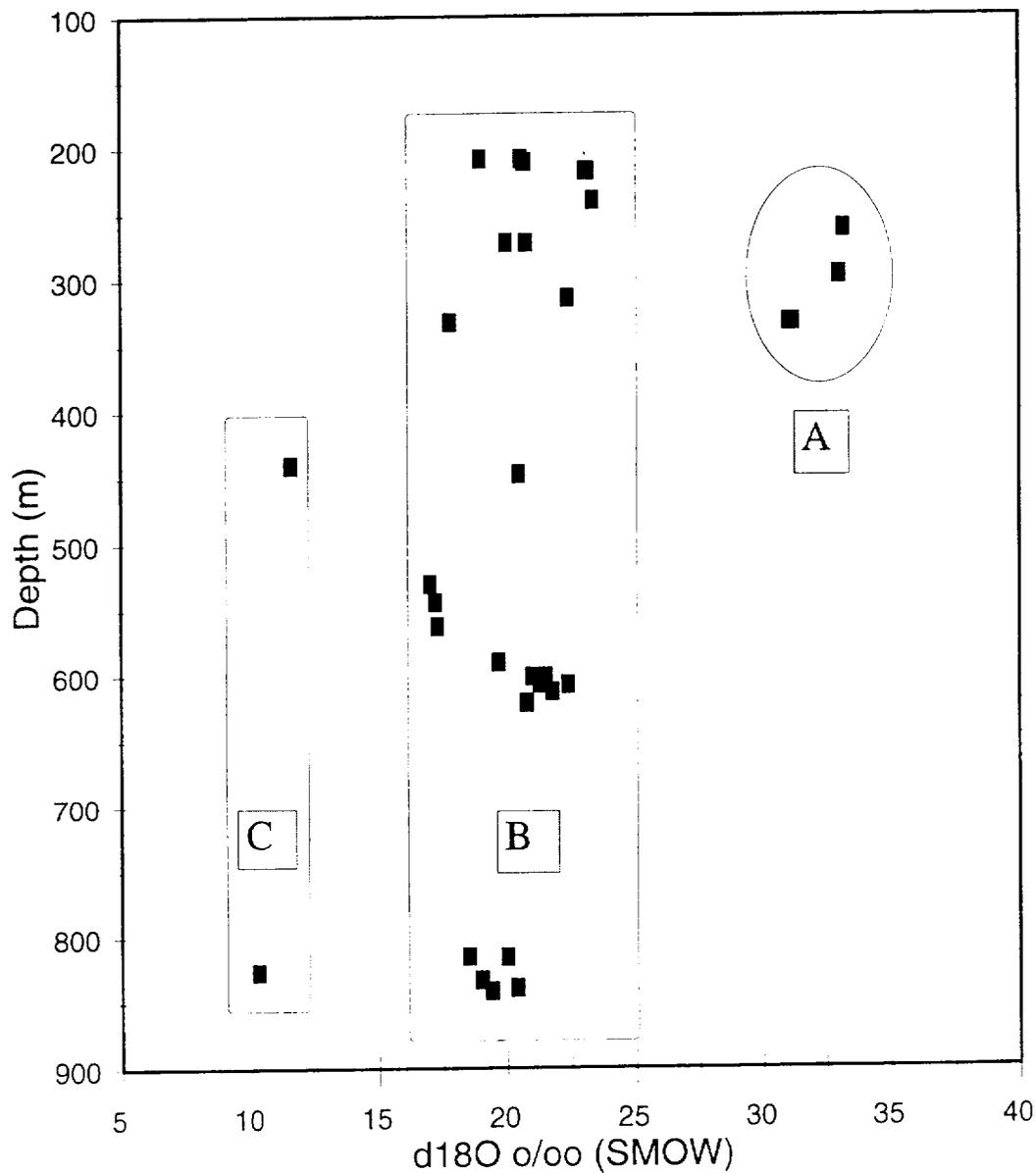


Figure 3. $\delta^{18}\text{O}$ values of calcite fracture fillings versus depth. 3 different groups appear A, B, and C. Group A show marine signatures and group B represent typical meteoric water precipitates. Group C may represent extremely depleted cold-water or high-latitude marine or meteoric waters.

Therefore, it seems most likely that the most of the calcites were precipitated from either meteoric or a mixture of meteoric and marine waters, which agrees with the $\delta^{18}\text{O}$ isotope evidence from the same carbonates. Some of the lower values reaching -12 and -13 o/oo, occur in some fractures together with fluorite and may possibly be hydrothermal signatures as well. The slight increase in signature with depth (figure 2) may be attributed to a larger organic carbon input in the shallow waters. This is due to degradation of organic matter with CO_2 production which most likely is connected to the sulphate reduction which is taking place at Äspö (Wallin, 1992).

The extremely low $\delta^{13}\text{C}$ values which are observed in some carbonates are most likely attributed to a pure organic carbon source, with no influx of atmospheric signatures, presumably degradation of organic matter (Wallin, 1993; Banwart et al., 1993) or oxidation of deep seated (Arnorsen and Gunnlaugsson, 1985) and/or bacterially produced methane (Cheney and Jensen, 1965; Hathaway and Degens, 1965; Shultz and Calder, 1976). In either case there seem to be two major sources for the carbon observed in the calcite fissure fillings; one which is organic and one which is atmospheric.

6.1.2. $\delta^{18}\text{O}$ isotopes in calcites

The large spread in the $\delta^{18}\text{O}$ values (+10 to +35 o/oo) for the calcite fracture fillings indicate that these precipitated from isotopically distinct waters. Most of the $\delta^{18}\text{O}$ values resemble a typical meteoric signature, clustering around +17 to +23 o/oo. In fig. 3, these intermediate values are designated group B, whereas the higher values which are more characteristics of a marine signature are designated group A. Two samples have even lower values of about 10 to 11 o/oo and these are shown as group C. These lower signatures may be explained as precipitates from high latitude or cold climate waters. Similar lower values have previously been observed at Äspö (Tullborg and Wallin, 1992) and Laxemar (Wallin, 1990).

The group B isotopic signatures resemble values which are expected for calcites in equilibrium with the waters similar in $\delta^{18}\text{O}$ to those ground waters now observed at Äspö. To illustrate this, the calculated $\delta^{18}\text{O}$ values of calcite precipitates that would be in equilibrium with present-day Äspö ground waters are plotted versus depth in fig. 4. It is clearly seen that the expected calcites that would be precipitated from present-day waters fall within the range of the group B calcites. Moreover, no calcite precipitates would be expected to form with the group A and C isotopic compositions from present-day ground-water $\delta^{18}\text{O}$ values. Hence, we may conclude that these carbonate precipitates with higher values around +33 and +35 o/oo in the calcite must therefore have been formed earlier from other water types, including marine and extremely $\delta^{18}\text{O}$ depleted waters such as glacial melt waters. Typical marine calcite precipitates usually fall in a narrow range of +30 to +31 o/oo. The group A calcite values at Äspö are slightly higher but are still representative of a marine water signature. Obviously, there is evidence of both marine and meteoric

$\delta^{18}\text{O}$ signatures as reported previously (Wallin, 1990; Tullborg and Wallin, 1992). Despite the low $\delta^{18}\text{O}$ values observed, a two end-member mixing of the calcites would hence be expected considering the that these two water types must have entered the basement at Äspö during the post-glacial time.

Another explanation for the narrow range in the $\delta^{18}\text{O}$ of the ground water at Äspö is that the saline water now observed are marine waters depleted in $\delta^{18}\text{O}$ due to mixing of glacial melt waters or cold climate precipitation. This phenomenon is well known from high latitudes and may very well be one explanation for the isotopically light waters (see section ISOTOPIC EVOLUTION OF THE PALEOBALTIC below).

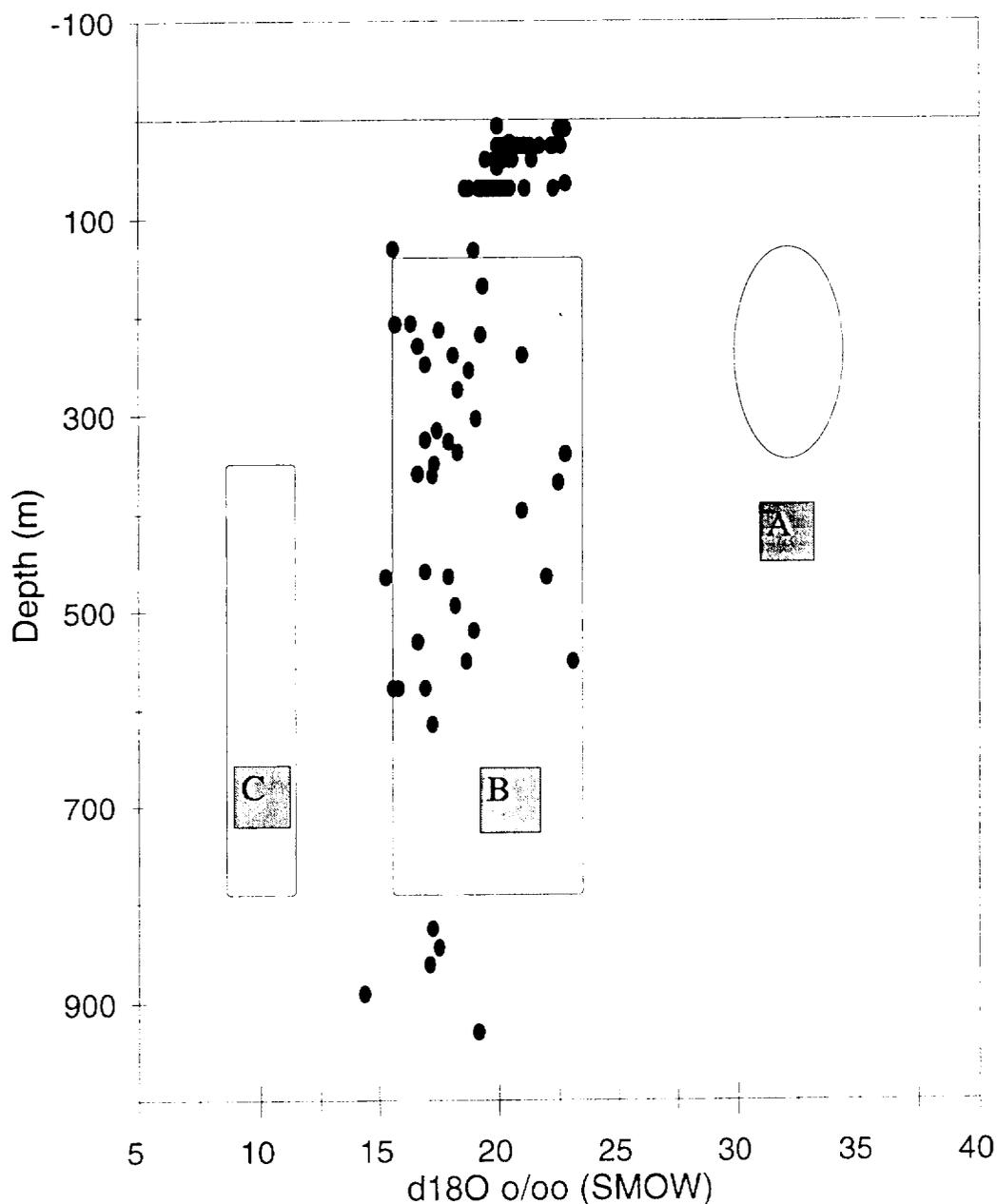


Figure 4. $\delta^{18}\text{O}$ -values of possible precipitates from the present ground water. All values assemble in the group B from figure 3.

In figure 5, $\delta^{13}\text{C}$ is plotted versus $\delta^{18}\text{O}$. Except for two samples, the groups that are well distinguished on the basis of $\delta^{18}\text{O}$ (fig. 3) are not separated on the basis of $\delta^{13}\text{C}$. This is not surprising in view of the different sources and processes represented by these two isotopic systems. The two samples with high $\delta^{18}\text{O}$ -values of +31 and +34 o/oo and low $\delta^{13}\text{C}$ values may have originated from an organic rich marine water, although more data is needed to further assess these possibilities.

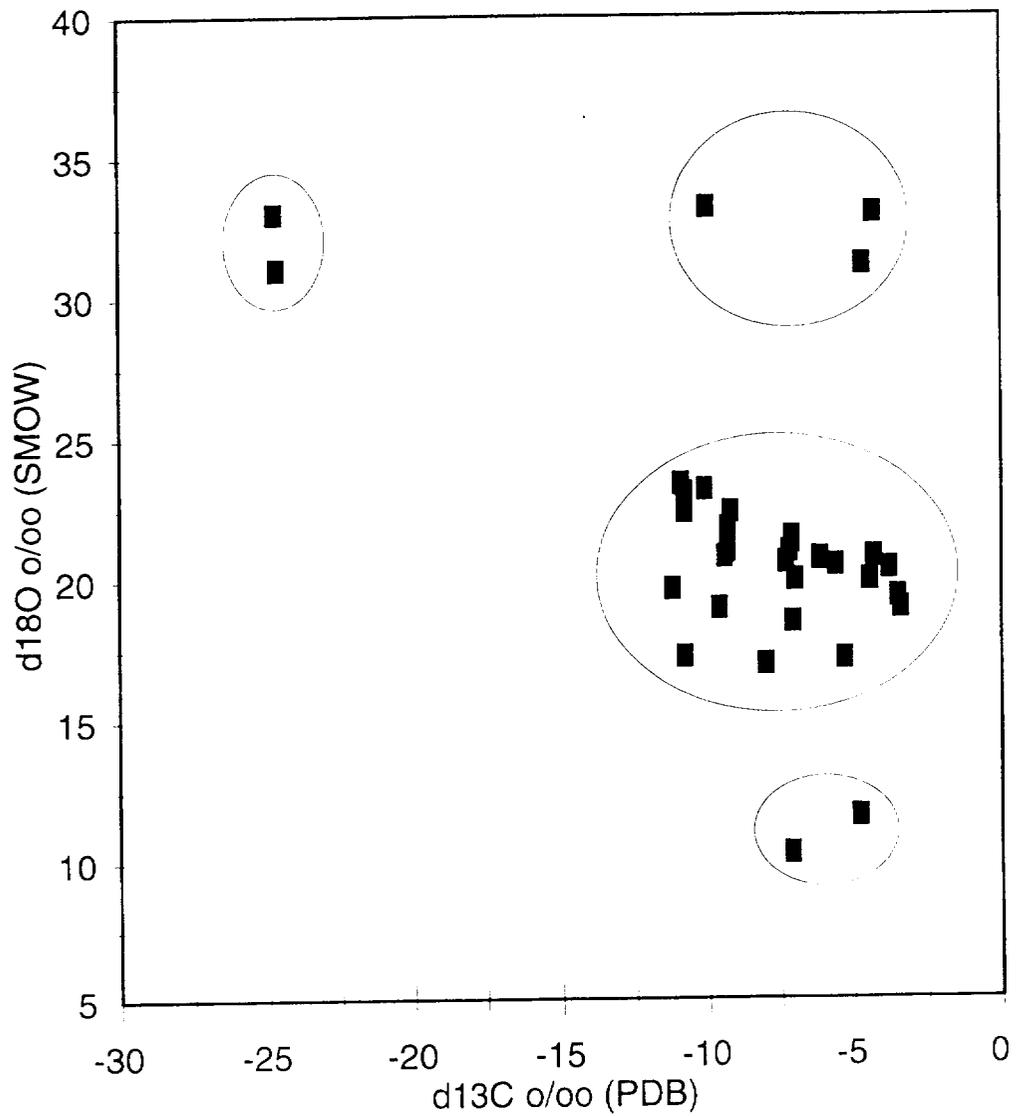


Figure 5. $\delta^{18}\text{O}$ -values plotted versus $\delta^{13}\text{C}$ -values in calcite fracture fillings.

6.1.3. $\delta^{87}\text{Sr}$ isotopes

$\delta^{87}\text{Sr}$ values in the calcite precipitates ranges between -3.6 and +9.9 o/oo. Sr isotopes do not fractionate in nature so the $\delta^{87}\text{Sr}$ values of the calcites directly reflect those of the waters from when they precipitated. In addition, it is

interesting to note that at Äspö the concentration of Ca in the ground water correlate very well with the Sr concentration (fig. 6).

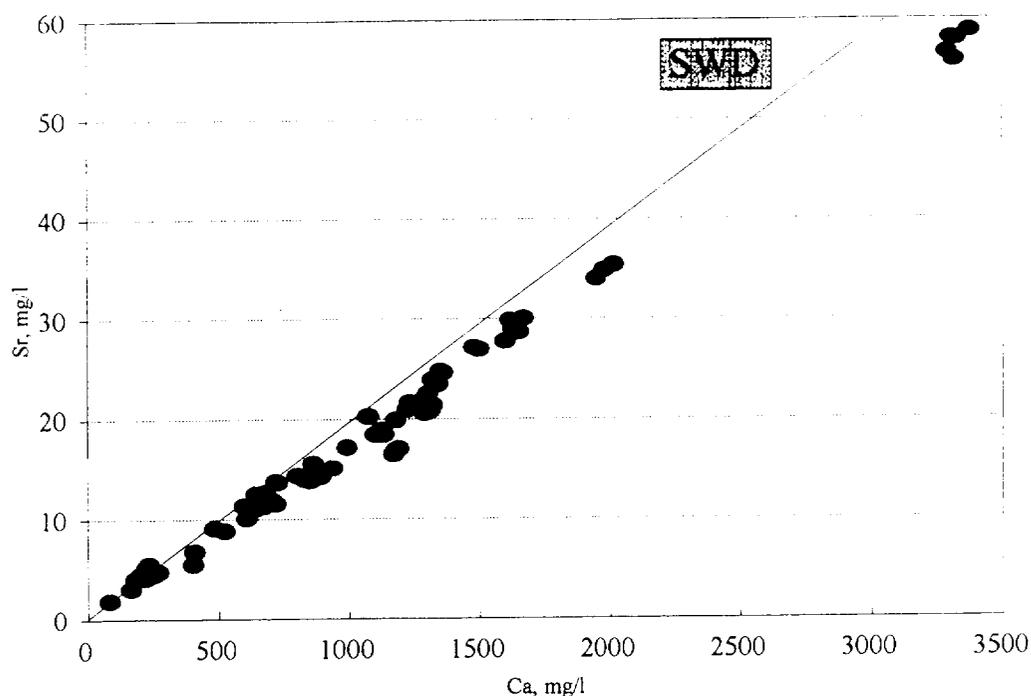


Figure 6. Sr versus Ca concentrations in the ground water.

Two groups of calcites are distinguished in fig. 7 where $\delta^{87}\text{Sr}$ values in the carbonates and the ground water are plotted versus depth. Five samples of calcites from 800 to 850 m have $\delta^{87}\text{Sr}$ values +0.6 and -3.6 o/oo. Calcites at shallower depths have a much larger range in $\delta^{87}\text{Sr}$ between -1.2 and +9.9 o/oo but most are greater than +3.3 o/oo. Only the two calcite samples with the largest $\delta^{87}\text{Sr}$ values of +9.8 and +9.9 o/oo could have precipitated from water isotopically similar to present-day ground water with $\delta^{87}\text{Sr}$ values between +9.9 and +13.9. Either the calcite fracture fillings were precipitated from an older and isotopically distinct ground water system or the source waters acquired less radiogenic Sr (low $\delta^{87}\text{Sr}$) prior to precipitating the calcites. The range of $\delta^{87}\text{Sr}$ of the calcites is three times larger than the range in $\delta^{87}\text{Sr}$ of the ground-water and unlike the ground water values, the calcite $\delta^{87}\text{Sr}$ displays no systematic change with depth. These features suggest two possible scenarios. The first is that the calcites represent a long history of ground-water evolution with isotopically different ground waters at Äspö at different times in the past. The oxygen isotopic compositions of these multiple ground waters would have been similar to those of the modern ground water. The second scenario would call for localized water-rock interaction and acquisition of variable amounts of low $\delta^{87}\text{Sr}$ strontium prior to or during the precipitation of the calcites. The oxygen isotopic compositions of the water would be largely buffered from any significant change in this scenario.

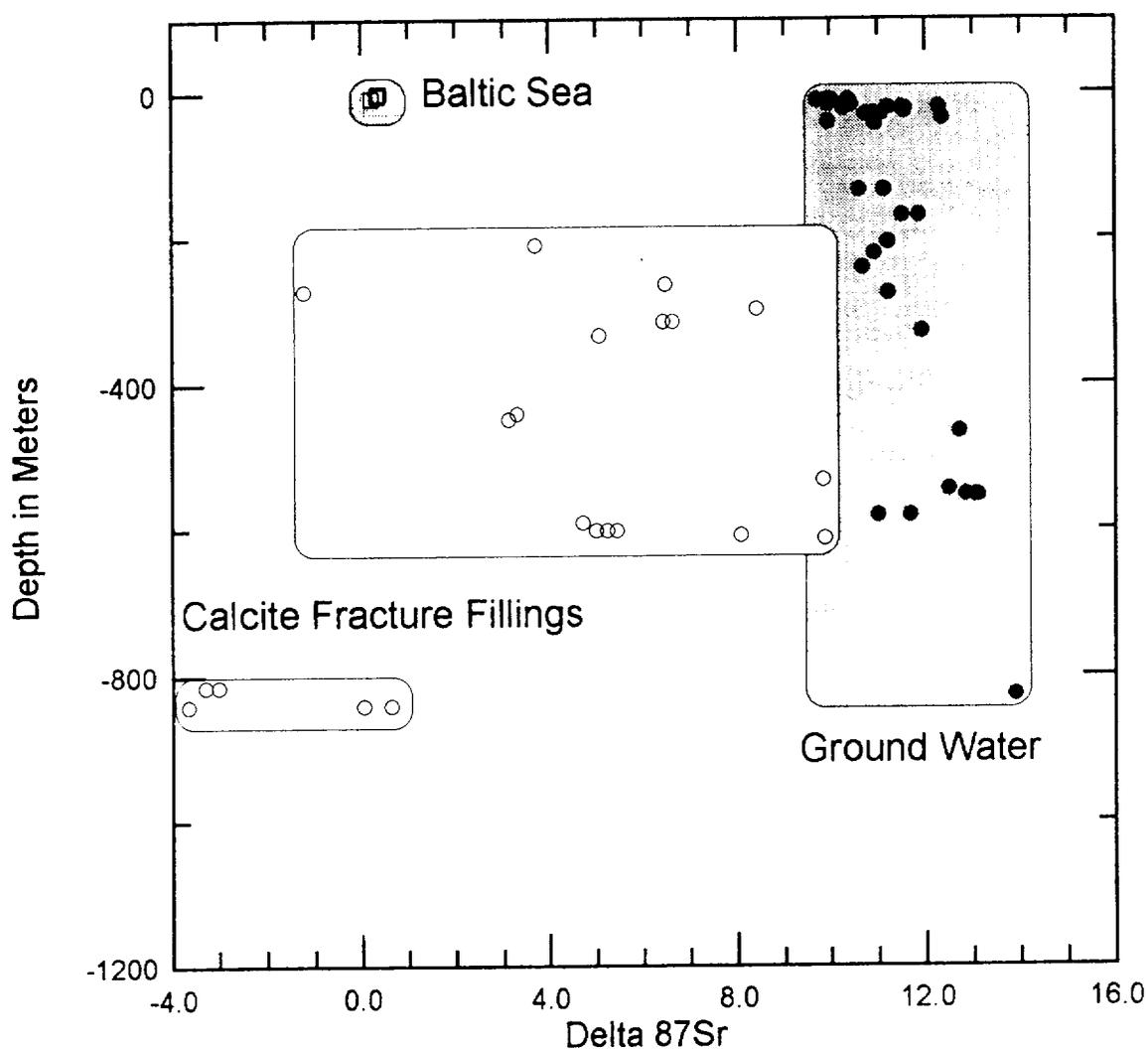


Figure 7. $\delta^{87}\text{Sr}$ values in calcite fracture fillings (open circles) and ground water (filled circles) plotted versus depth.

Strontium in the modern ground water is not in equilibrium with strontium in the rock mass. Rb and Sr analyses of 20 whole-rock samples suggest that the present day mean $\delta^{87}\text{Sr}$ value of the rock mass would be about 2.5 o/oo, a value substantially lower than the ground water values. Feldspars and biotite were separated from a coarse-grained, strongly foliated granodiorite at the site of Äspö Village near KAS02 with the following results: plagioclase, 1926 ppm Sr with a $\delta^{87}\text{Sr}$ of -6.4 o/oo; microcline, 678 ppm Sr with a $\delta^{87}\text{Sr}$ of +9.4 o/oo; and biotite with 45.2 ppm Sr with a $\delta^{87}\text{Sr}$ of +986 o/oo. The exceedingly large $\delta^{87}\text{Sr}$ for the biotite is the result of a large Rb/Sr and its Precambrian age. Ground water could acquire $\delta^{87}\text{Sr}$ larger than the bulk-rock values if it reacted preferentially with biotite. However, this possibility is not supported by the low potassium contents of the ground water nor by studies of

other saline ground waters in crystalline rock which indicate that plagioclase dominates the water-rock interaction, thus producing $\delta^{87}\text{Sr}$ values even lower than the bulk-rock values (e.g. McNutt, 1987).

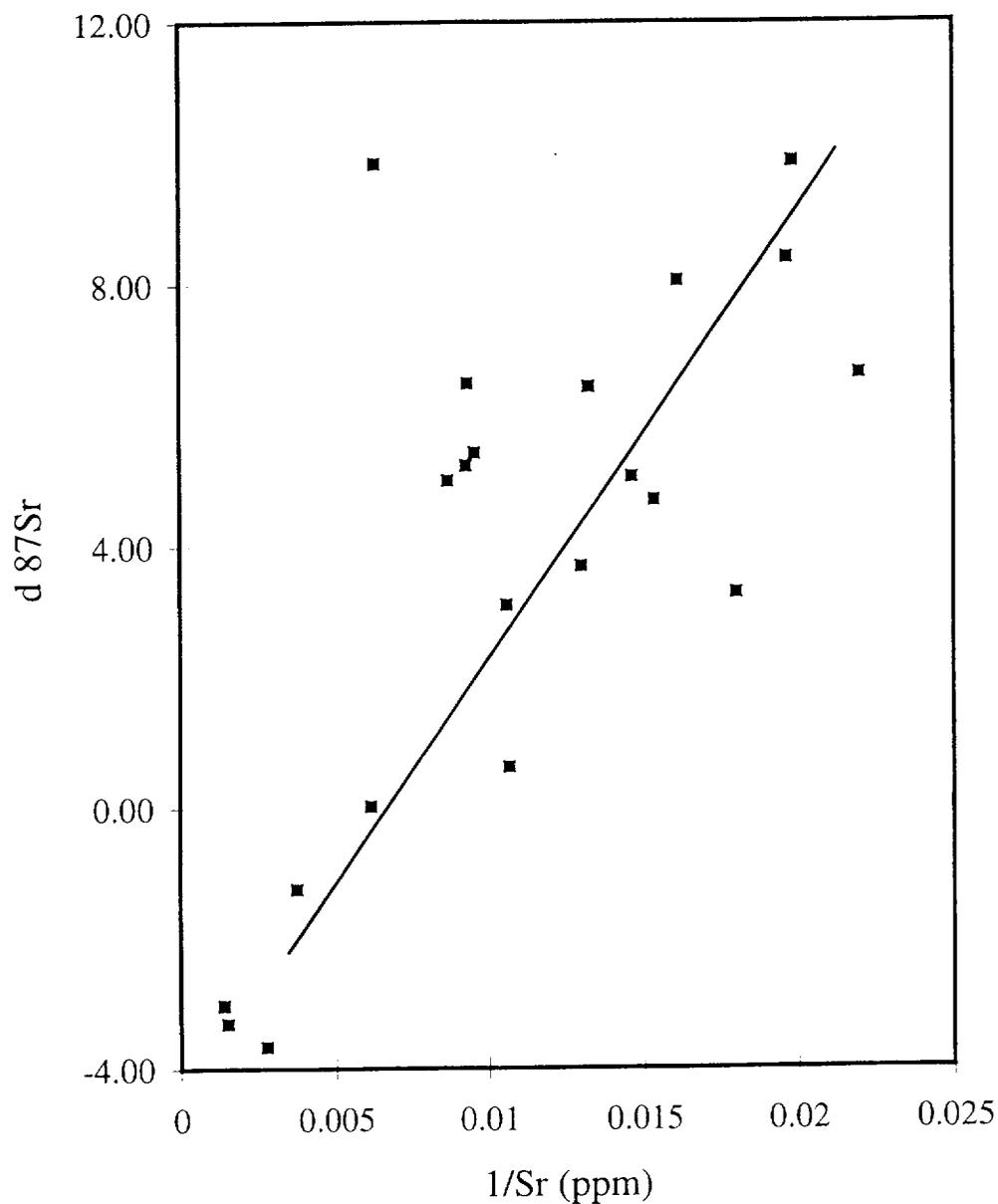


Figure 8. $\delta^{87}\text{Sr}$ values in the calcites fracture fillings plotted versus $1/\text{Sr}$. The crude correlation may indicate progressive water-rock interaction prior to precipitation of the calcite.

The possibilities that the calcites record localized water-rock interaction is suggested by the crude correlation between $\delta^{87}\text{Sr}$ values and reciprocal Sr concentrations (fig. 8). A linear relationship in this type of plot is often considered to be consistent with mixing of two end members. The scatter

displayed by the data in fig. 8 could indicate a system with two major end members but also with additional complexities.

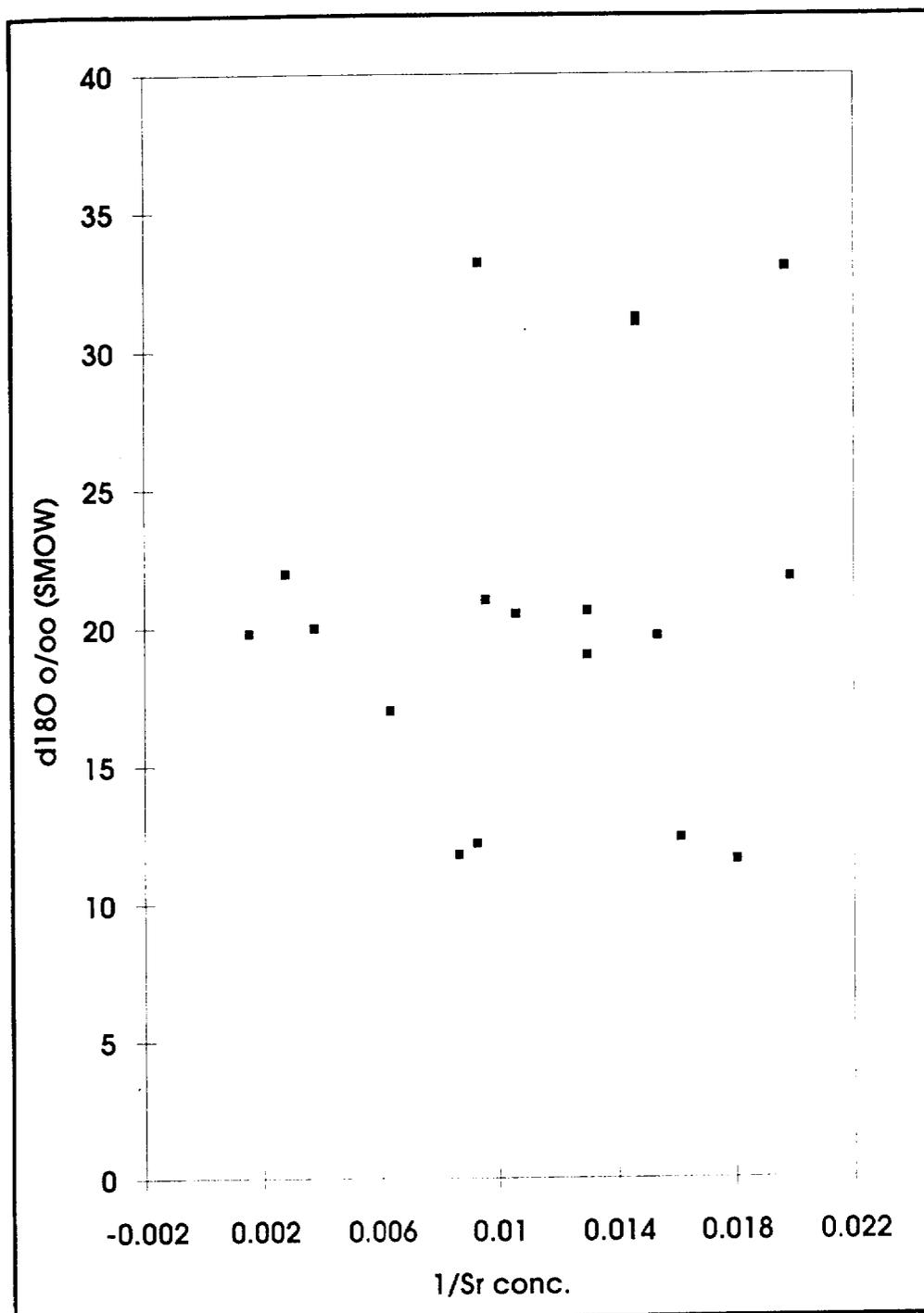


Figure 9. $\delta^{18}\text{O}$ -values in the calcites fracture fillings plotted versus $1/\text{Sr}$.

This array can be approximated by two end members with $\delta^{87}\text{Sr}$ values between -3 and -4 ‰ and Sr contents of 600 ppm. The other end member would have a $\delta^{87}\text{Sr}$ value of +8 ‰ or larger and 50 ppm Sr. This apparent mixing array could represent ground water similar to that which presently exists in the rock mass preferentially reacting with plagioclase feldspar (small $\delta^{87}\text{Sr}$ and large Sr contents) in fractures during precipitation of calcite.

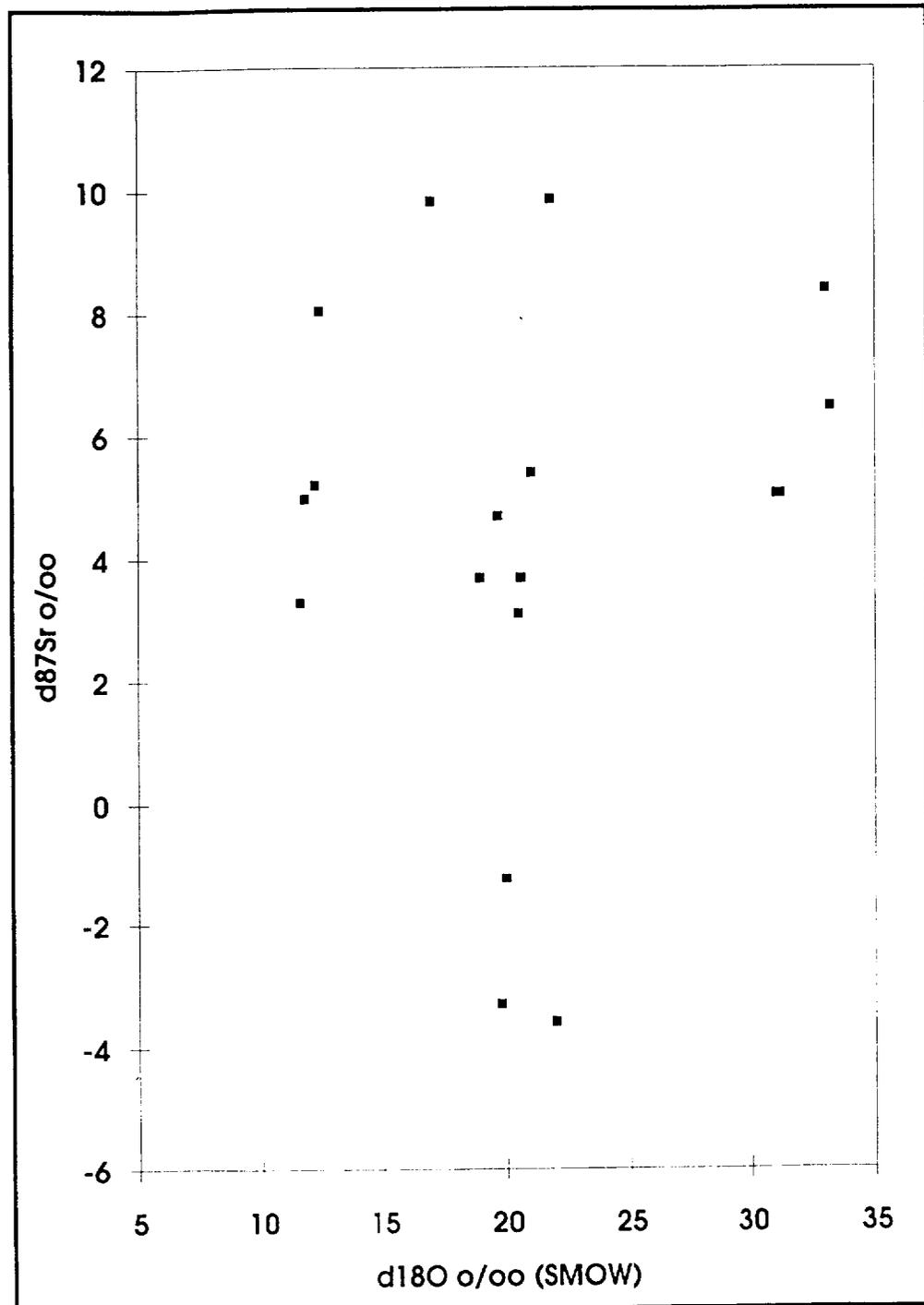


Figure 10. $\delta^{87}\text{Sr}$ plotted versus $\delta^{18}\text{O}$ -values in the calcite fracture fillings.

As noted above, $\delta^{18}\text{O}$ would be largely buffered from this water-rock interaction and in fact no correlation exists between $1/\text{Sr}$ and $\delta^{18}\text{O}$ (fig. 9) or between $\delta^{87}\text{Sr}$ and $\delta^{18}\text{O}$ (fig. 10).

6.1.4. Laser analyses

The wide spread in the $\delta^{18}\text{O}$ and $\delta^{87}\text{Sr}$ values of the carbonates reflect isotopically distinct waters from which the calcites precipitated. Although an age framework for these vein fillings has not yet been established, the calcites record a dynamic paleohydrology. During the analyses of the calcite fissure fillings it was observed that even from the same carbonate vein filling the $\delta^{18}\text{O}$ and $\delta^{87}\text{Sr}$ values could vary by as much as up to 3 ‰. This is not an analytical problem but rather reflects isotopic differences in the calcite at a very fine scale which is difficult to sample by conventional techniques. Where possible, however, detailed sampling of the crystals showed that the isotopic signatures were uniform within individual growth zones.

A detailed study with the laser was initiated in order to carefully examine the detailed isotopic record contained within the very fine calcite growth zones. The results from the laser microscope is shown in fig.11 and 12. Three different generations of calcite were distinguished. The size of the crystal was about 4 mm in diameter and it was cut in half and polished on one side (fig. 11, 12). The three different generations were etched by the laser beam and the analysed CO_2 showed variations in the $\delta^{13}\text{C}$ as well as the $\delta^{18}\text{O}$ (table 4). Two of the generations showed similar isotopic signatures whereas the third laser run shows over 2 ‰ difference for both carbon and oxygen.

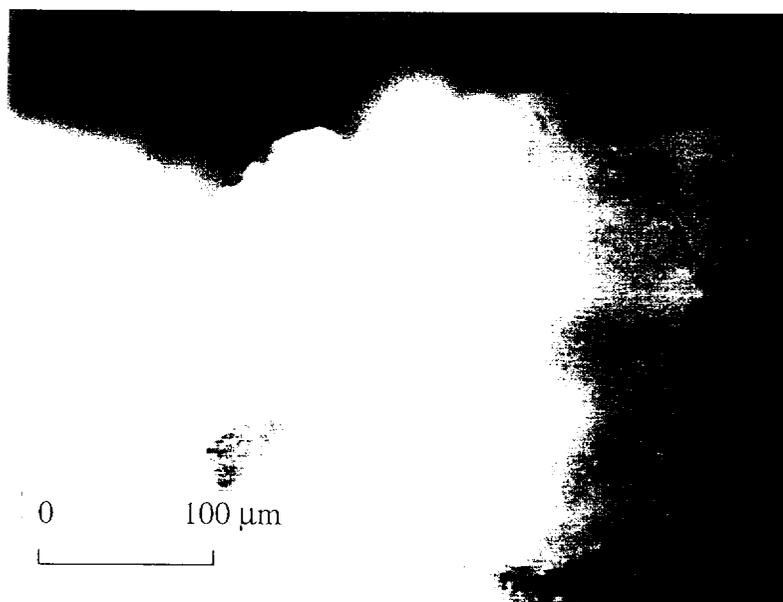


Figure 11. Picture showing the calcite crystal before the laser etching.

The results of this prototype laser investigation designed to characterize the different calcite generations in the fissure fillings was very successful. A detailed study of the calcite at Äspö is therefore planned for the second fiscal year. Different calcite generations will be separated and $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and $\delta^{87}\text{Sr}$ analyses will be conducted from exactly the same samples where possible.

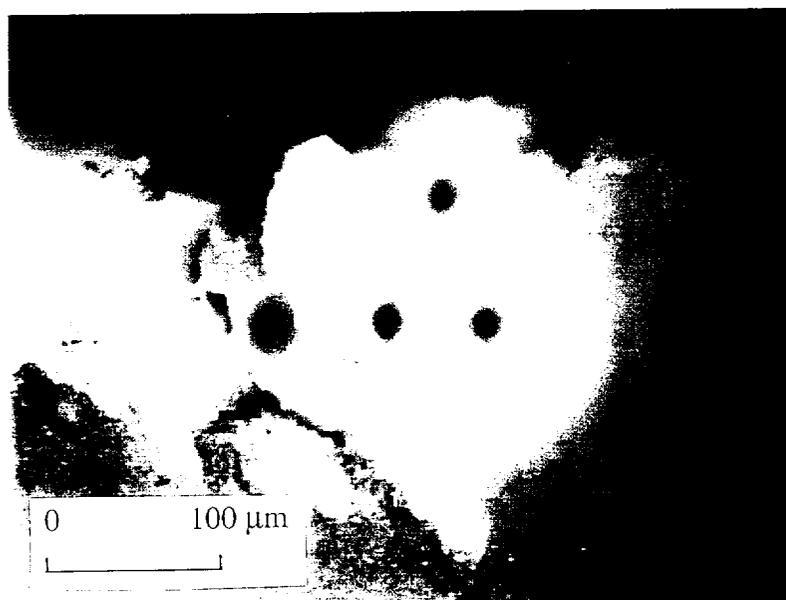


Figure 11. Picture showing the thin laser etching of the calcite crystal.

6.2. GROUND WATER

6.2.1. δD and $\delta^{18}\text{O}$ -isotopes

A large number of δD - and $\delta^{18}\text{O}$ -isotopes have been analysed in the shallow and deep ground water at Äspö during the past several years. Almost all of the samples plot on the lower side of the meteoric water line (fig. 13). This depletion in the δD relative to $\delta^{18}\text{O}$ could reflect evaporative enrichments of the heavy isotopes prior to recharge in the rock mass or possibly small degrees of water-rock interaction. It may also reflect a relative depletion in δD in comparison to $\delta^{18}\text{O}$ due to climatic effects.

The large range of highly correlated δD and $\delta^{18}\text{O}$ values could in part be explained by mixing of present-day Baltic Sea water ($\delta\text{D} = -50$ o/oo and $\delta^{18}\text{O} = 6.5$ o/oo) and $\delta^{18}\text{O}$ -depleted water which could be related to the latest ice age.

This is more or less supported by the fact that a depletion in $\delta^{18}\text{O}$ is accompanied by an increase in chlorinity. However, the $\delta^{87}\text{Sr}$ values pose a problem with regard to mixing of modern Baltic Sea water as shown by fig. 10). This is discussed further in Section 6.3.

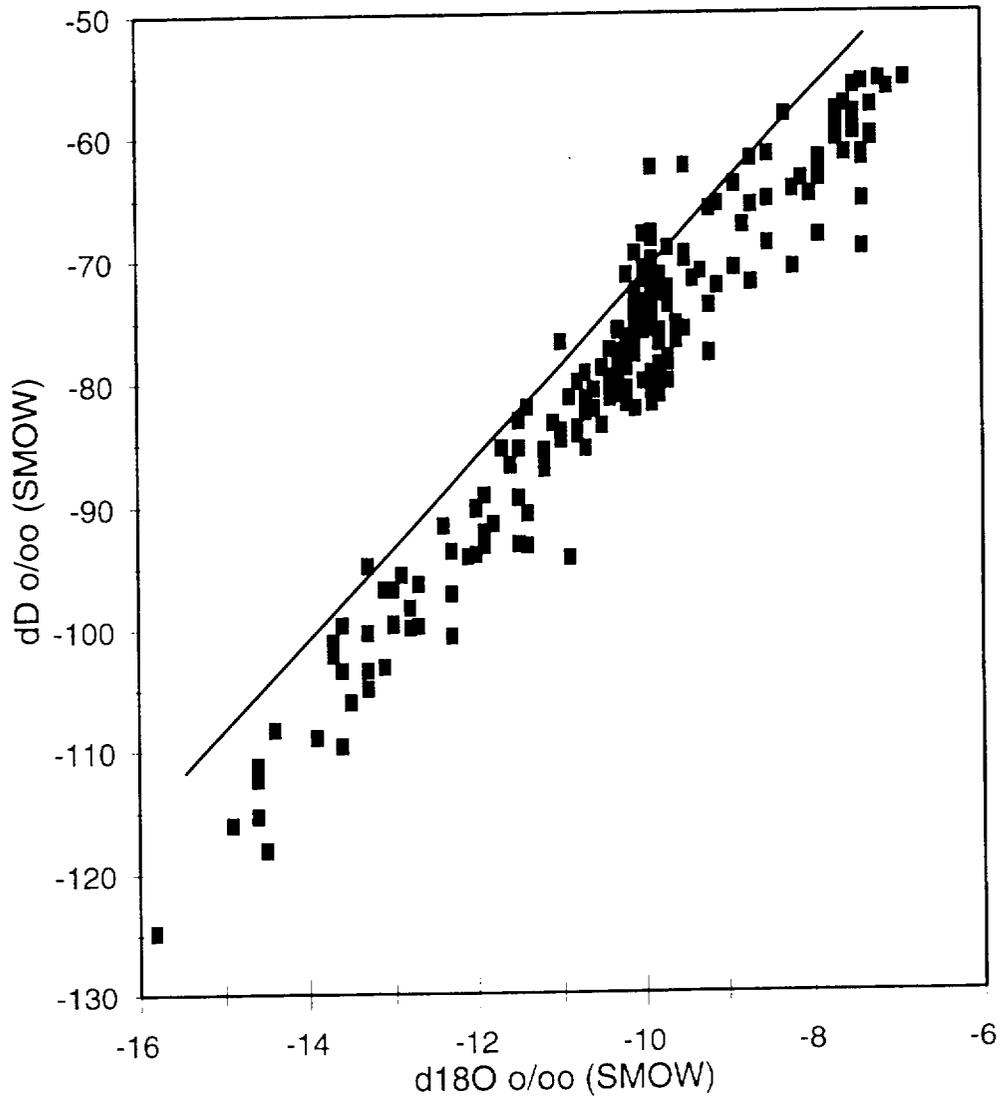


Figure 13. δD plotted versus $\delta^{18}\text{O}$ in the ground water at Äspö.

6.2.2. $\delta^{34}\text{S}$ isotopes in dissolved sulphates

The new $\delta^{34}\text{S}$ data, coupled with the previously determined data, support the concept of multiple sources of sulphur in the dissolved sulphate. Shallow and intermediate ground waters have been analysed during the first year of this study and most of the $\delta^{34}\text{S}$ results show marine signatures together with contributions of reduced sulphur. In the plot of $\delta^{34}\text{S}$ versus depth (fig. 14),

there is large difference in the $\delta^{34}\text{S}$ values between the shallow water (+17 to +21 ‰) and deep ground water (+8 to +10 ‰). The larger values are typical of marine signatures and some of the values coincide with the Baltic water signatures of +19 ‰.

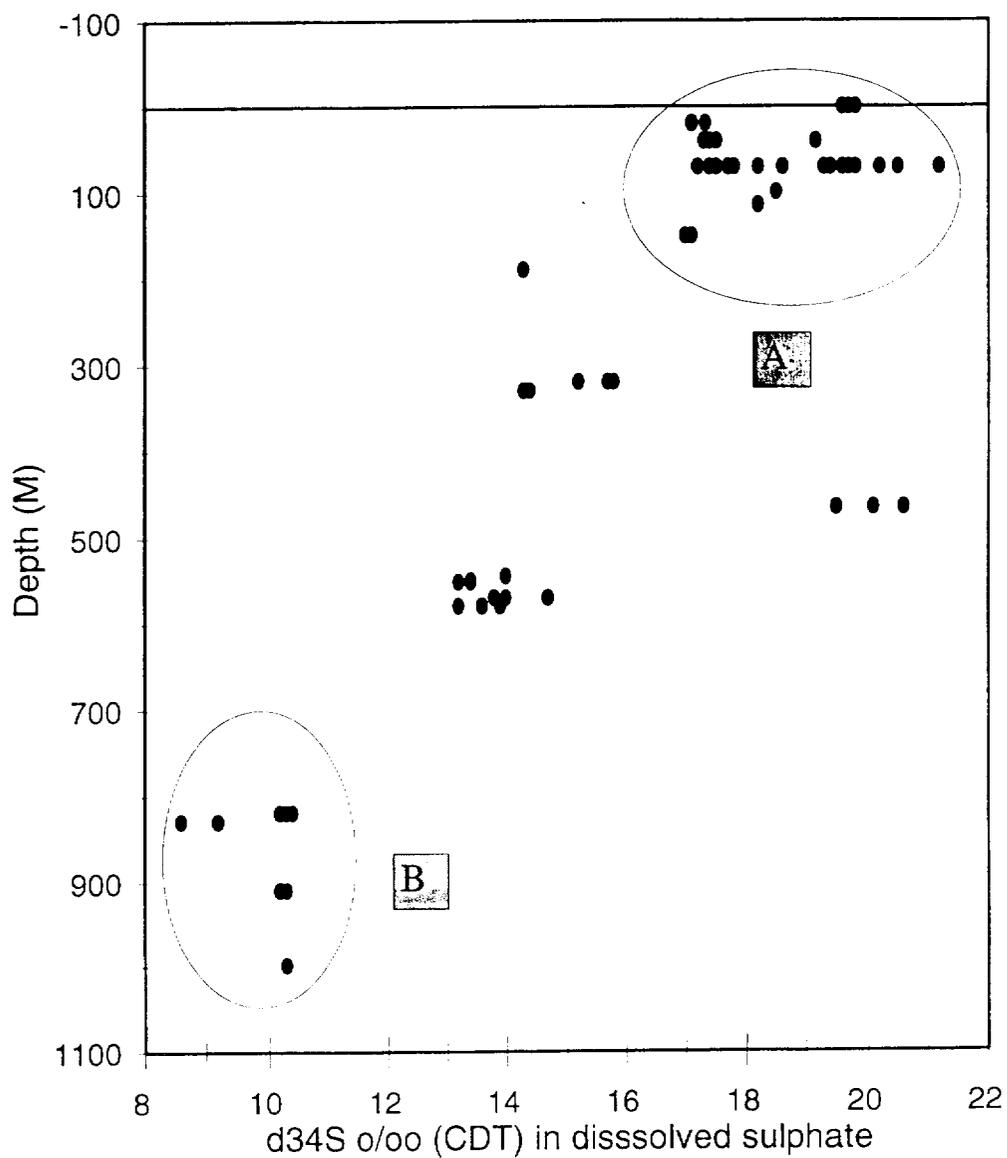


Figure 14. $\delta^{34}\text{S}$ of the dissolved sulphate versus depth. Group A in the shallow waters show typical marine signatures around +18 and +20 ‰. Intermediate waters display values around +13 and +15 ‰ and the deep water, group B, has values around +10 ‰.

We know from earlier studies (Banwart et al., 1992) that some of these waters may originate from minor proportions of Baltic water injections. Computer modelling of these shallow ground waters suggests that there may be isolated water lenses of "fossil marine waters" which are residing in the near surface fractures. The variation in $\delta^{34}\text{S}$ isotopes in the shallow ground water is most likely caused by a mixing of meteoric water enriched in sulphate and minor proportions of waters with a marine signature.

Accept for three samples ($\delta^{34}\text{S}$ of +19 and +20 o/oo), the intermediate waters have $\delta^{34}\text{S}$ values between +13 to +16 o/oo (fig. 14). This apparent systematic decrease to the lower $\delta^{34}\text{S}$ values of these intermediate waters may be a result of contribution of reduced sulphur from fracture filling sulphides and from the basement rocks. This could results from large scale injections of oxygenated waters which oxidised sulphides present. Such water influx could easily have occurred during the isostatic movements attendant with ice recession of the last glacial period. The $\delta^{18}\text{O}$ -isotope variation in these intermediate waters show signs of mixing between meteoric and marine waters, which is supports such this concept.

The isolated high $\delta^{34}\text{S}$ values at about 450 m depth in fig. 14 may therefore be conserved "marine signatures" of the dissolved sulphate of waters that have penetrated to this depth without reacting with sulphides. In this case, the ingress of these waters to depth may have been relatively recent suggesting the presence of local fast pathways downward into the rock mass.

The rapid drop in $\delta^{34}\text{S}$ values from 500 m depth to about 900 m is most likely due to a Raleigh distribution of reduced sulphur due to an extensive sulphate reduction (Wallin, 1992). The is a typical pattern in a closed system (Bågander, 1977; Bågander, 1980; Hallberg, 1984) where the deeper values around 10 ‰ is the initial sulphate value. All higher values from the deeper part and up to the 500 m level represents the residual sulphate. Previous work at Äspö reports very low $\delta^{13}\text{C}$ values of the calcite, exceeding -25 ‰ supporting a closed system for the reduction. The CO_2 produced due to the degradation of the organic matter give rise to low $\delta^{13}\text{C}$ signature calcites. This reaction leads to formation of sulphides with relatively low $\delta^{34}\text{S}$ isotopic signatures around -20 ‰ . These values are not uncommon at Äspö in the pyrites examined by Wallin (1992), which hence support a ongoing sulphate reduction in the ground water at Äspö.

6.2.3. $\delta^{87}\text{Sr}$ isotopes

Five samples of Baltic Sea water collected in the vicinity of Äspö have $\delta^{87}\text{Sr}$ values between +0.2 and +0.4 ‰ (fig. 10). These are consistent with other measurements of samples throughout the Baltic Sea (Löfvendahl et al., 1990; Andersson et al., 1992). In marked contrast, ground water has $\delta^{87}\text{Sr}$ values between +9.9 and +13.9 ‰ with a mean of about +11.5 ‰. Clearly, the saline ground waters at Äspö are not the result of intrusion of unmodified

modern Baltic Sea water. Yet the stable isotope data from the calcite fissure fillings (see above) suggest that a component of marine waters have been residing at Äspö.

6.3. ISOTOPIC EVOLUTION OF THE PALEOBALTIC

$\delta^{18}\text{O}$ decreases linearly with increasing chlorinity in ground water at Äspö (Tullborg and Wallin 1992). The negative $\delta^{18}\text{O}$ -signatures around -13 ‰ are typical values of the meteoric water of higher latitudes, whereas the less negative values around -7 ‰ are more representative of the modern Baltic Sea water values. The inverse relation between the $\delta^{18}\text{O}$ and chloride at Äspö ground water in comparison to the Baltic sea water may be explained in different ways. In the North Atlantic, $\delta^{18}\text{O}$ -values of the Arctic sea water show a decrease in $\delta^{18}\text{O}$ with a decrease in salinity (Faure, 1986). This decrease of the isotopic signature is attributed to high latitude and consequently colder climate, but also to the large input of meteoric and melt water. Since these low $\delta^{18}\text{O}$ readings are observed in the northern marine waters, such characteristics may give rise to the low $\delta^{18}\text{O}$ signatures in combination with typically marine readings of the chloride. One possible scenario to develop such waters in the ancient Baltic sea may be a mixing of marine waters and early melt water from the ice during the recession. This means that an isolated nonsaline stage of the Baltic sea, followed by a marine intrusion should easily attain low $\delta^{18}\text{O}$ signatures and moderately high chloride concentrations.

It is well known that during an infreezing stage of a large ice sheet from an isolated marine environment, the residual marine water will increase in salinity. Moreover, the $\delta^{18}\text{O}$ isotope fractionation factor for ice in equilibrium with water is only 1.002, which means that the $\delta^{18}\text{O}$ -value of the residual water is about -2 ‰ (depleted in $\delta^{18}\text{O}$) relative to the ice which is formed. Therefore, the formation of sea ice leaves the $\delta^{18}\text{O}$ value of the water essentially unchanged, but causes a significant increase in salinity, similar to the observed ground waters at Äspö. However, the observed water at Äspö is much more negative in $\delta^{18}\text{O}$ than would be expected from a normal sea water freezing. In order to explain such a phenomenon, the initial setting in $\delta^{18}\text{O}$ may have been depleted by a large input of high latitude ocean water or cold diluted water.

A solution to the contradiction between the strontium and stable isotope ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) signatures of some of the calcite precipitates is attained if it is assumed that the strontium in Baltic Sea water has undergone a significant decrease in $\delta^{87}\text{Sr}$ since the last glaciation. The intermediate ground water at Äspö is suggested to be as old as 6000 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 6000 years ago contained strontium with much larger ^{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 $\delta^{87}\text{Sr}$ of about +29 ‰ whereas runoff from the south has a value of about +1.2 ‰ (Löfvendahl et al., 1990). 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 $\delta^{87}\text{Sr}$ values like the modern runoff from the Precambrian terrane. Accordingly, we offer the hypothesis that increased influx of Precambrian strontium overwhelmed the runoff from the Phanerozoic terrane to the south to the extent that the $\delta^{87}\text{Sr}$ 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 $\delta^{87}\text{Sr}$ values of Löfvendahl 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) would have increased the $\delta^{87}\text{Sr}$ value of the Baltic to +13 ‰.

The discrepancy of the observed $\delta^{18}\text{O}$ -values as well as the $\delta^{87}\text{Sr}$ values may therefore solely be due to the accumulation of post glacial runoff waters which are extremely negative in $\delta^{18}\text{O}$ as well. In addition, the sulphate $\delta^{34}\text{S}$ values (about +14 to +15 ‰) which are observed at an intermediate depth at Äspö are significantly lower than 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, accordingly to the discussion of the high Sr readings in the 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. This hypothesis can be tested by obtaining and analysing $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ and $\delta^{87}\text{Sr}$ of carbonate or phosphate shell or bone material from bottom sediments of the Baltic that extend back to approximately 6000 years. Therefore, we propose to obtain such core material to characterise the strontium isotope evolution of the Baltic for at least the past 6000 years. The parallel study of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ systematics will certainly show the isotopic variation of the ancient Baltic stages.

7. CONCLUSIONS

The most significant result from the first year study of this project is conclusion that several waters have been involved in the formation of the calcite fissure fillings at Äspö. This indicates a complex paleohydrology which must be better understood if credible predictions of future hydrology are to be made. We can easily distinguish several end-members, however it is essential that same samples are used for both $\delta^{18}\text{O}$ and $\delta^{87}\text{Sr}$ for future measurements. A detailed study including $\delta^{18}\text{O}$ analyses of silicates, laser analyses of calcites ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$), $\delta^{87}\text{Sr}$ analyses of water and calcites, and

radiogenic isotope ^{206}Pb , ^{207}Pb , ^{232}Th , ^{230}Th and ^{240}U analyses of calcites and water are under way.

The following results and conclusions from the first year study contribute importantly to the hydrological picture at Äspö.

- * Evidence of fossil marine waters with depleted $\delta^{18}\text{O}$ signatures.
- * $\delta^{18}\text{O}$, $\delta^{34}\text{S}$ and $\delta^{87}\text{Sr}$ evidence of mixing of marine and meteoric waters at Äspö.
- * $\delta^{87}\text{Sr}$ signatures in the calcite suggest two source for the Sr--one marine and one continental runoff and/or contribution from the basement rock.
- * $\delta^{34}\text{S}$ values of the dissolved sulphate show a multiple source, including marine sulphur, reduced sulphur from the basement and biogenic reduced sulphur due to sulphate reduction.

Finally, we have demonstrated that a comprehensive isotopic approach to ground water studies utilizing **a combination of stable and radiogenic isotopes can yield critical and relevant data for developing an understanding of the origin and evolution of the ground water** at Äspö in particular and in the circum-Baltic region in general.

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Björn Gylling¹, Luis Moreno¹,

Ivars Neretnieks¹, Lars Birgersson²

1 Department of Chemical Engineering
and Technology, Royal Institute
of Technology, Stockholm, Sweden

2 Kemakta Konsult AB, Stockholm, Sweden

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