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REPORT**

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**Geochemical interpretation of
groundwaters from Finnsjön,
Sweden**

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GEOCHEMICAL INTERPRETATION OF GROUNDWATERS FROM
FINNSJÖN, SWEDEN

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the author(s) and do not necessarily coincide with those of the client.

Information on KBS technical reports from 1977-1978 (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) and 1986 (TR 86-31) is available through SKB.

Geochemical interpretation of groundwaters
from Finnsjön, Sweden

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ABSTRACT

Chemical and isotopic analyses of groundwaters taken from boreholes at the Finnsjön study site have been evaluated. The predominant rock type consists of granodiorite, and within the crystalline rock matrix, both the fracture network and its coating minerals have a large effect on the aqueous geochemistry of the site.

The tritium content of the samples has a positive correlation with total iron and organic carbon, and a negative correlation with Cl^- , Mn^{2+} and NH_4^+ . The very presence of this isotope in the waters is a strong indication that mixing of very young waters with older, deep waters has probably taken place during sampling.

The disagreement between the field and laboratory pH-values collected during 1979-1982 introduces a serious difficulty in the interpretation of that data.

Nevertheless, computer calculations with aqueous speciation models (WATEQ3 and EQ3NR) give a picture of the water-rock interactions. The mineral saturation indices of calcite, strontianite, rhodochrosite, and siderite show that the concentration levels of Ca^{2+} , Sr^{2+} , Mn^{2+} and Fe^{2+} are probably fixed by the aqueous carbonate system and its minerals. However, unreasonably high saturation indices of calcite (up to +1.7) confirm the uncertainties in the pH-values. Computer simulations with the EQ6 code show that $\text{CO}_2(\text{g})$ outgassing/ingassing might have contributed errors in the pH measurements during the sampling procedure. EQ6 simulations also show that mixing of waters from different aquifers might have induced transient over- or undersaturation of carbonate minerals.

Equilibrium between groundwaters and fluorite and barite appear to fix the concentrations of F^- and Ba^{2+} respectively.

Some of the sampled groundwaters reach relatively high salinities (chloride levels of 6 g l^{-1}). The origin of the saline components is still uncertain. There are some similarities between the ionic ratios of Finnsjön waters and Stripa groundwaters. Specially, the saline waters sampled at borehole Fi8 (which intercepts the Gåvastbo fault) have as high Ca/Mg and Br/Cl ratios as Stripa waters, and the lowest sulfate concentrations, indicating a greater degree of mineral-water interactions and lower redox potential than the rest of the samples.

1. INTRODUCTION

The Swedish utilities with nuclear power stations are characterizing, through SKB*, several sites as a preliminary step towards a complete safety assessment of a future repository of spent, un-reprocessed nuclear fuel (KBS-3, 1983; Karlsson, 1984; Bjurström and Papp, 1985). This report presents a geochemical interpretation of the deep granitic groundwaters of one of the sites: Finnsjön.

The most likely mechanism for release of radioactive elements from a deep bedrock repository to the biosphere is by transport in groundwater. Hence, geochemical studies are necessary to understand and estimate processes like radioactive element solubility, speciation, sorption on minerals, colloid formation, etc, all of which influence the amount of radioelements transported by groundwaters. An evaluation of the magnitude of these processes is also fundamental in judging and implementing numerical models of the rate of radioelement-groundwater transport through the hydrological system (i.e., the fracture network) in the crystalline bedrock that will surround the repository.

A comprehensive geochemical study of groundwaters in crystalline bedrock is also necessary to estimate the integrity towards corrosion and chemical changes of materials used in a nuclear repository (copper canister, bentonite buffer, concrete, etc).

Several geochemical studies of the deep groundwaters sampled in Swedish sites by SKB have already been reported (Jacks, 1978; Tullborg and Larson, 1983; Allard, 1982; Allard *et al.*, 1983; Smellie *et al.*, 1985; Ahlbom *et al.*, 1986), and the redox conditions at depth have also been studied (Wikberg *et al.*, 1983; Wikberg, 1985; Nordstrom and Puigdomènech, 1986). In the present study a special emphasis will be made on the description of rock-water interactions and aqueous speciation equilibria as calculated by sophisticated computerized models, because the complex chemical reactions taking place between metal ions and

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naturally occurring ligands in aquatic systems in contact with minerals, can only be evaluated with numerical computer calculations. Furthermore, this kind of speciation-solubility modelling has been somewhat neglected in previous reports (it must be noted however, that computer simulations have been reported for the evolution of typical groundwaters in contact with fuel matrix, canister material, bentonite buffer, and granitic bedrock (Grenthe *et al.* 1983; Fritz *et al.*, 1984; Fritz and Kam, 1985; Forsyth *et al.*, 1986)).

The Finnsjön study site is particularly interesting because some of the deep groundwaters sampled have high salinities (chloride concentrations up to 6 g/l). Hence, a geochemical description of this site will allow a better estimation of the geochemical consequences from changes in the hydrological or climatological conditions and the performance of a nuclear repository in crystalline bedrock.

1.1 The Finnsjön study site

The site is situated east of lake Finnsjön (about 140 km north of Stockholm). The topography, geology, hydrology and fracture zones have been previously reported (Almén *et al.*, 1979; Olkiewicz *et al.*, 1979; Carlsson *et al.*, 1980; Gustafsson and Klockars, 1981; Carlsson and Gidlund, 1983; Carlsson *et al.*, 1983; Magnusson and Duran 1984; Ahlbom *et al.*, 1986), and will only be shortly described here.

The topography is flat, between 40 and 20 m above sea level, with a general drainage direction towards the northeast. The Svecofennian rock consists mainly of leptite, ultramafic and mafic rocks, granodioritic gneiss and granite. All boreholes are drilled in the zone where the granodiorite predominates. The main fracture zones can be described as follows: (a) the Gåvastbo fault that has a NNW direction, is situated at the eastern part of the site and is penetrated by borehole Fi8, (b) the Brändan lineament that has a NNE direction, intersects the Gåvastbo fault NE of hole Fi5, and is penetrated by boreholes Fi5 and Fi10, and (c) a subhorizontal fracture zone (Brändan Zone 2) intercepted by boreholes Fi5, Fi6, Fi9, Fi10 and probably Fi7 (Ahlbom *et al.*, 1986).

The most common fracture mineral is calcite (Tullborg and Larson, 1982; Larson and Tullborg, 1984), but prehnite, laumontite, chlorite, pyrite, wairakite-analcime, epidote, dolomite, and unidentified clay minerals are also present.

2. COMPUTER PROGRAMS AND THERMODYNAMIC DATABASES

Computerized models are necessary tools for quantitative geochemical modeling of mineral-groundwater interactions. The computer codes of such models are used to perform the complex calculations involved in simultaneously establishing multicomponent speciation, activity coefficient corrections, and mineral saturation indices for groundwaters of given analytical composition.

A large number of computer programs have been reported in the literature (Nordstrom and Ball, 1984). However, because the quality of any model for natural waters depends both on its thermodynamic data base, and on its model for activity coefficient corrections, the two computer programs used in this report, WATEQ3 (Truesdell and Jones, 1974; Ball *et al.*, 1979, 1980, 1981; Nordstrom *et al.*, 1984), and EQ3NR (Wolery, 1979, 1983, program version: 3245c51, with thermodynamic database 3245c24) were selected for the quality and documentation of their thermodynamic data bases. The activity coefficient corrections are made in both computer models according to extended Debye-Hückel equations (Truesdell and Jones, 1974, for WATEQ3; Helgeson, 1969, for EQ3NR). Both programs were used to check for consistency in the calculations and to identify any differences in the thermodynamic databases. The results from either program are nearly identical, and for purposes of plotting, the results of EQ3NR calculations were used unless otherwise indicated in the text. A listing and a comparison of both thermodynamic databases is given elsewhere (Nordstrom and Puigdomènech, 1986, 1987).

The mineral saturation indices that result from the computer calculations and that are reported in section 6, are defined as $\log (IAP/K_{sp})$ where IAP is the ion activity product, and K_{sp} is the solubility product constant (see Drever, 1982, or Nordstrom and Munoz, 1985). Saturation indices greater than zero indicate that the mineral under consideration might precipitate from the

groundwater, while saturation indices lower than zero manifest that the mineral, if in contact with the groundwater, would have a tendency to dissolve. However, the calculations give no indication about the rate at which such processes might occur.

Simulations of groundwater mixing and CO₂(g) ingassing were performed with the EQ6 reaction path modelling program (Wolery, 1979).

3. GROUNDWATER SAMPLING AND ANALYSIS

Analytical data for groundwaters sampled in deep boreholes (up to 700 m) was taken from two previous reports (Laurent, 1982; Ahlbom *et al.*, 1986). Data for shallow boreholes (up to 130 m) has been reported by Gustafsson and Klockars (1981 and 1984) and Ahlbom *et al.* (1986). The sampling procedure and equipment used in the deep boreholes is described both in Laurent's report and by Wikberg (1985) and Almén *et al.* (1986).

The sampling procedure can be summarized as follows: several sampling zones, 2.7 m long, were sealed off with rubber packers at different levels of each borehole. Groundwater was pumped up and water samples were collected and sent for analysis to several laboratories, while pH was also measured in the field. For the most recent set of data (Ahlbom *et al.*, 1986) many analyses were performed in the mobile chemical laboratory (Wikberg, 1985; Almén *et al.*, 1986).

Some deficiencies in the sampling procedures must be pointed out for the data collected in the period Aug-1979 to Feb-1982 (boreholes Fi1 to Fi8, reported by Laurent, 1982). Firstly, none of the water samples were filtered. This will affect the values of most trace metals (e.g. iron, aluminium, etc), and total organic carbon. There is also a considerable discrepancy between field and laboratory values of pH, which will be discussed below. Finally, the sealing of the sampling zones, and the pumping rates were probably inadequate (Smellie *et al.*, 1985). This resulted in contamination of the pumped waters with either residual drilling fluids, or recently recharged surface waters forced to deeper levels through fracture systems, or both. It must then be understood that most of the groundwaters considered in this report are a mixture of waters from different sources.

3.1 Tritium contents and groundwater chemical composition

In order to examine the effect of the contamination mentioned above, it is convenient to establish which of the chemical components of the analyzed samples might have their source in old groundwaters that have interacted with the bedrock for long periods of time, and which components have their origin in the contaminating waters. Tritium is a particularly useful radioactive isotope because of its relatively short half life (≈ 12.5 years). A measurable tritium content (> 3 TU) in a water sample indicates that either it is very young water (less than about 40 years old) or that young water has mixed with older water from a different source.

No apparent correlation is found between tritium content and depth of sampling in Finnsjön (Fig. 1a). However, as can be seen in Fig. 1b, most of the saline samples have tritium contents under the detection limit (i.e., ≤ 3 TU), and none of the waters with more than 1000 mg/l chloride have a tritium contents higher than 7 TU. This indicates that the source of chloride (and in fact, also of other major saline components: sodium, calcium, etc.) is not associated with the tritium rich contaminating water, which as mentioned above, was either residual drilling fluid, or surface waters forced to deeper levels through fracture systems, or both.

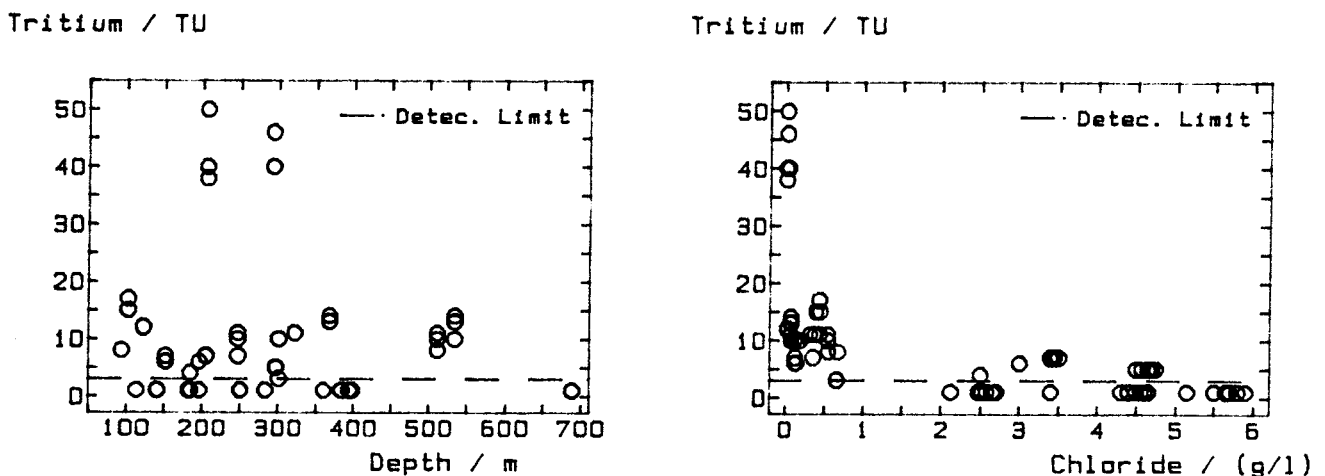
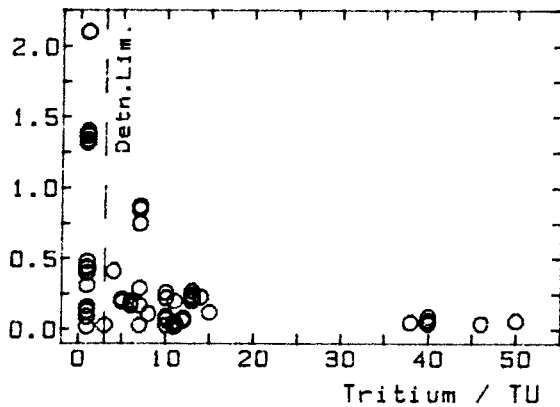


Figure 1. Tritium contents (in tritium units, $1 \text{ TU} = 1 \text{ } ^3\text{H}/10^{18}$ hydrogen atoms) in the samples from deep boreholes, as a function both of depth, and Cl^- concentration.

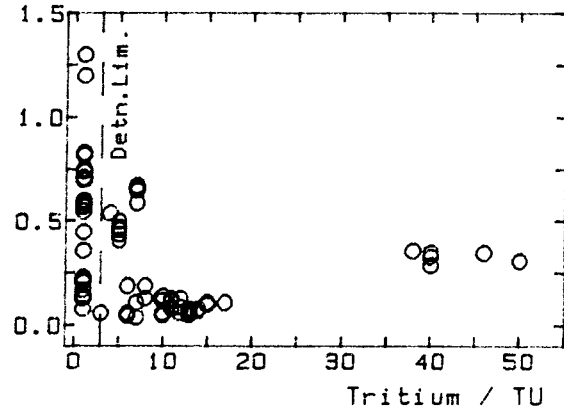
Thus, the saline waters at depth appear to be fairly isolated from surface fresh waters. This is confirmed by NH_4^+ and Mn^{2+} which are both indicators of low redox potential, and have high correlation with waters with low tritium contents (c.f. Figs. 2a-b).

This is not the case, however, for the analytical data on total iron and total organic carbon (TOC), which as seen in Figs. 2c-d, have a clear positive correlation with the tritium contents, and therefore, their high values are due to the contaminating components. Low iron concentrations and low TOC are probably associated with high salinity for these groundwaters.

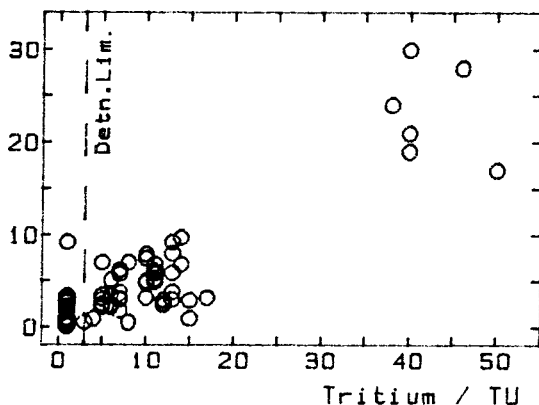
Ammonium / (mg/l)



Manganese / (mg/l)



Total Iron / (mg/l)



TOC / (mg/l)

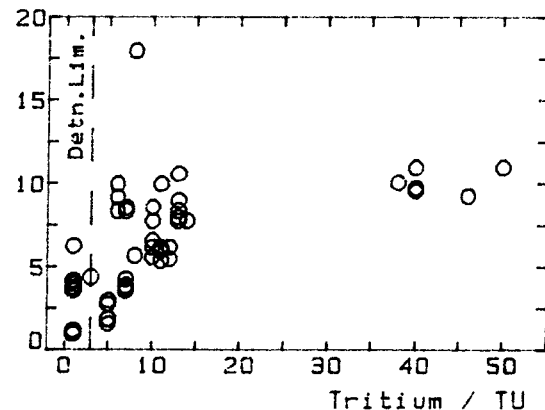


Figure 2. Tritium contents in the samples from deep boreholes, as a function of some chemical components (NH_4^+ , Mn, Fe-total and TOC (total organic carbon)).

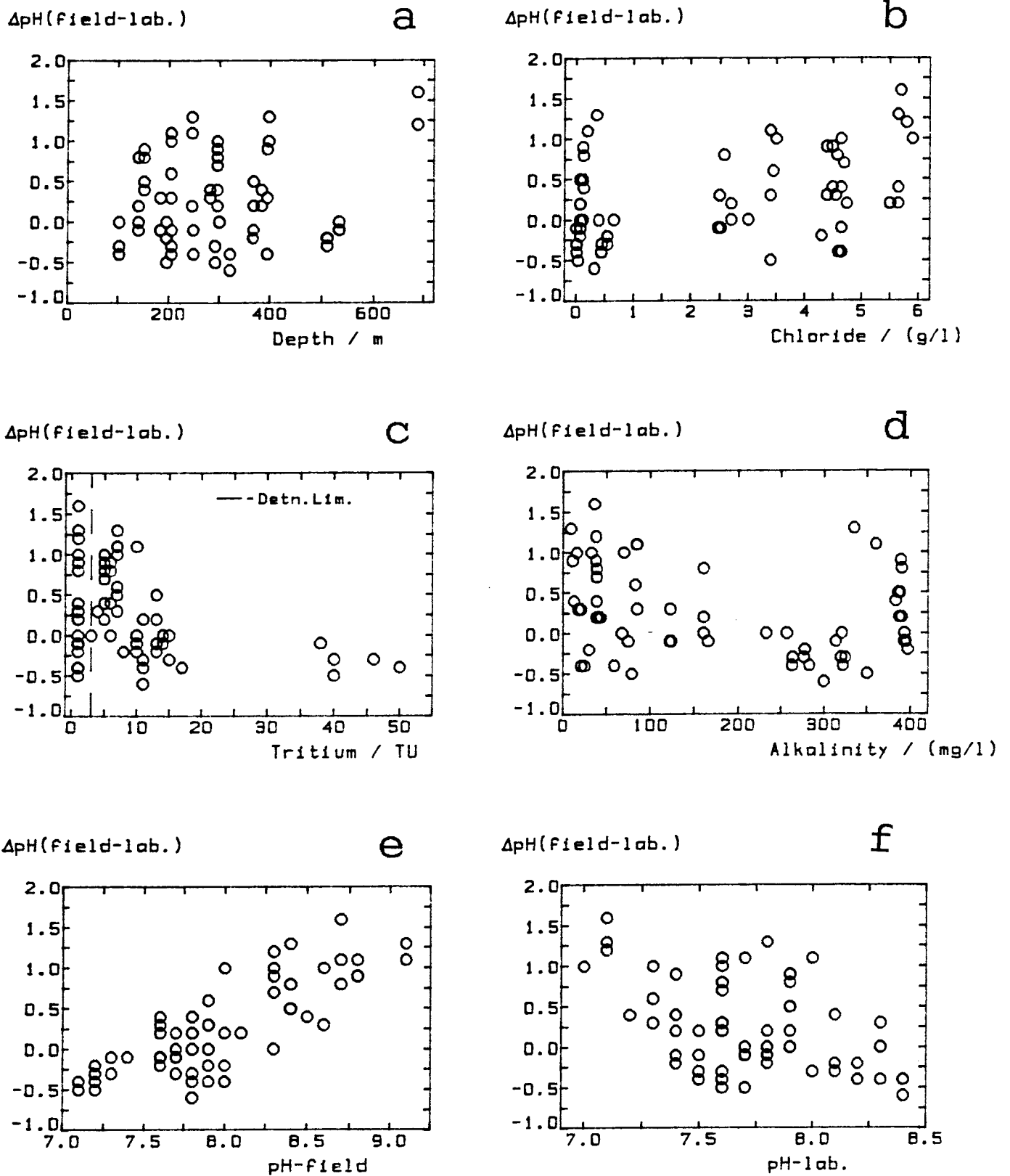


Figure 3. The difference between field and laboratory pH data plotted versus: a) depth, b) chloride, c) tritium contents, d) alkalinity, and e) pH_{field} and f) pH_{lab} values.

3.2 pH measurements

There is some disagreement between laboratory and field pH values for the earlier samples collected during the 1979-1982 period (Laurent, 1982). This is illustrated in Fig. 3, where it is seen that there is no clear correlation between the pH difference and such variables as sampling depth or chloride contents (c.f. Figs. 3a-b). Nevertheless, Figs. 3e-f show some relationship between ΔpH and the measured pH-values, specially with the field data (c.f. Fig. 3e). Even if we take an accuracy of ± 0.5 pH units as acceptable for the reported measurements, we have to consider reasons for a pH decrease in some of the data with $\text{pH}_{\text{field}} > 7.8$ to $\text{pH}_{\text{lab}} < 7.8$. A possibility indicated by Laurent (1982) is drift in the field measuring equipment. However, the data in Fig. 3c shows that all values with $\Delta\text{pH} > 0.5$ have < 15 tritium units, and therefore, the pH discrepancy has probably some relationship to the sampling procedure as well. The buffer capacity of most natural waters is a function of total carbonate and pH (Stumm and Morgan, 1981, p.175). As Fig. 3d shows, there is no correlation between ΔpH and the alkalinity of the groundwater samples, and the pH differences can not be ascribed to inherent difficulties in pH-measurements of waters with low buffer capacities.

An other possible contribution to the ΔpH -values found might be carbon dioxide outgassing/ingassing. This possibility is discussed later in sect. 6.1 ("Carbonate minerals", p. 19).

Because pH is a fundamental variable in aqueous chemistry, the lack of reliable pH data for most of the water samples has disastrous effects on the possibility of successful geochemical modelling of the site. The results of the computer calculations on mineral-solution equilibria in sect. 6, specially for carbonate minerals, are greatly affected by this uncertainty. Therefore, the discussion on the ΔpH -values will continue later in that section.

4. SALINE CONSTITUENTS

4.1 Chloride distribution

As Fig. 1b indicates, high chloride concentrations are associated with samples of low tritium contents. Furthermore, ^{14}C -ages up to 11000 years have been estimated for these waters

(Laurent, 1982). Figure 4 shows the dependence of chloride concentration on depth. Two kinds of boreholes are discerned, depending on their salt contents. The boreholes that penetrate the fracture zones Gåvastbo and Zone 2 (Ahlbom et al., 1986) show high salinities below the depth at which the fracture zones are penetrated (usually, ≈ 180 m, except for Fi7, where the probable intersection depth is the level at which high salinities have been reported by Ahlbom et al. (1986) i.e., ≈ 320 m). The Brändan Zone 2 fracture zone appears to have low hydraulic head, it discharges groundwater, and prevents mixing of the deep saline groundwaters with the shallow waters of recent meteoric origin (Ahlbom et al., 1986). The discharge along the Gåvastbo fracture zone (Gustafsson and Klockars, 1984) probably sets an eastern limit to the extent of the saline waters.

4.2 Ionic ratios

Ionic ratios may be used to classify and differentiate water types and their sources (White et al., 1963). In Figure 5 the calcium to magnesium ionic ratio (by weight) is compared with the ratios for seawater and Stripa groundwaters. The waters pumped

Chloride / (g/l)

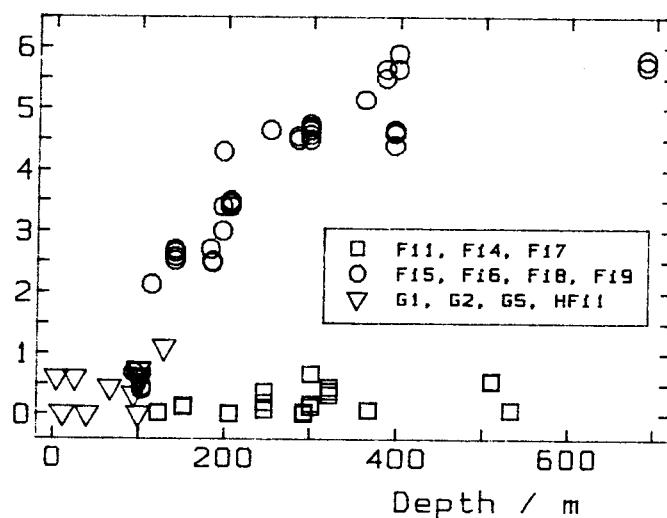
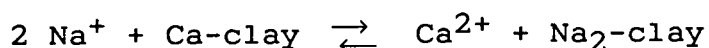


Figure 4. Chloride concentrations plotted against depth.

from borehole Fi8 clearly diverge from the rest of the Finnsjön groundwaters, and have ratios similar to those found in Stripa. Therefore, either the Fi8-waters (that are contained in the fractures of the Gåvastbo fault) have another origin, or they have another degree of evolution produced by either biological or rock-water interactions. Figure 6 shows the Ca/Mg vs Br/Cl ionic ratios (by weight) for the SKB study sites investigated. As seen, the Br/Cl ratios range from values close to seawater up to values approaching those found in Stripa. Based on the evidence provided by anion analysis of fluid-inclusions and microfracture fluids leached from Stripa drillcores, Nordstrom et al. (1985) has proposed that the source of salinity at the Stripa site is associated with fluid inclusion leakage rather than entrapped seawater. Figure 6 suggests that the same source of salinity may be affecting the composition of most of the groundwaters at Finnsjön.

An ion exchange mechanism on clay minerals might be a sink for sodium and a source of calcium (Jacks, 1973 and 1978; Mizukami et al., 1977). In Figure 7, the ion activity product corresponding to the reaction:



is plotted against chloride concentrations. The values found are similar to the ratios in other granitic groundwaters of Sweden (Jacks, 1973) and differ slightly from the values reported for waters in the Seikan tunnel ($\log \{ \text{Ca}^{2+} \} / \{ \text{Na}^+ \}^2 = 0.23$, Mizukami et al., 1977).

4.3 Chloride correlations

Chloride is a convenient normalizing factor to define possible sources of other saline constituents. This is due to the fact that it is one of the most conservative anions in natural waters, as Cl^- is seldom involved in chemical processes like redox reactions and mineral dissolution or precipitation. Chloride also gives a clearer picture than depth, because as it has already been pointed out, it is associated with groundwaters that have a smaller amount of contaminating young components (c.f. Fig. 1), and therefore it is (at least in part) related to the age of the waters.

The alkaline and alkaline earth concentrations of the ground-

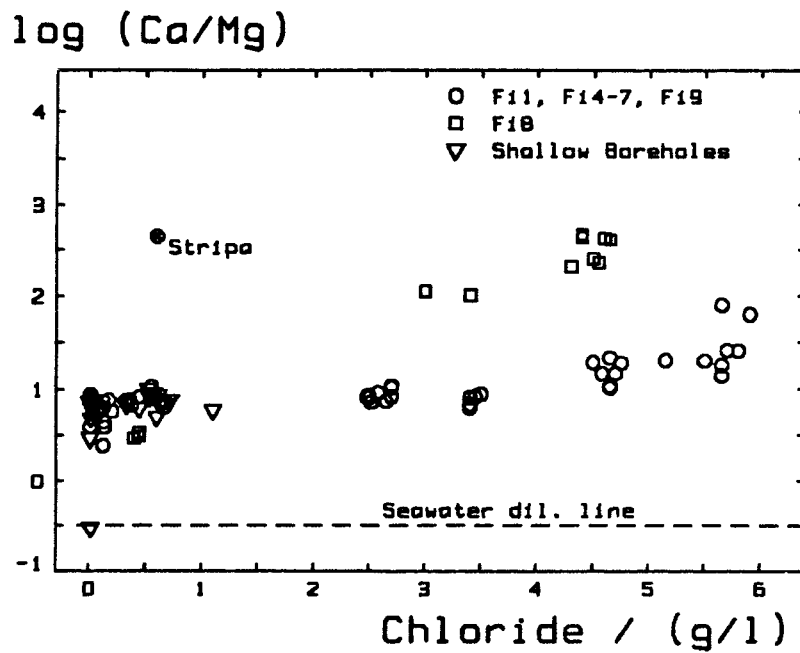


Figure 5. Plot of Ca/Mg ionic ratios (by weight) against chloride concentrations.

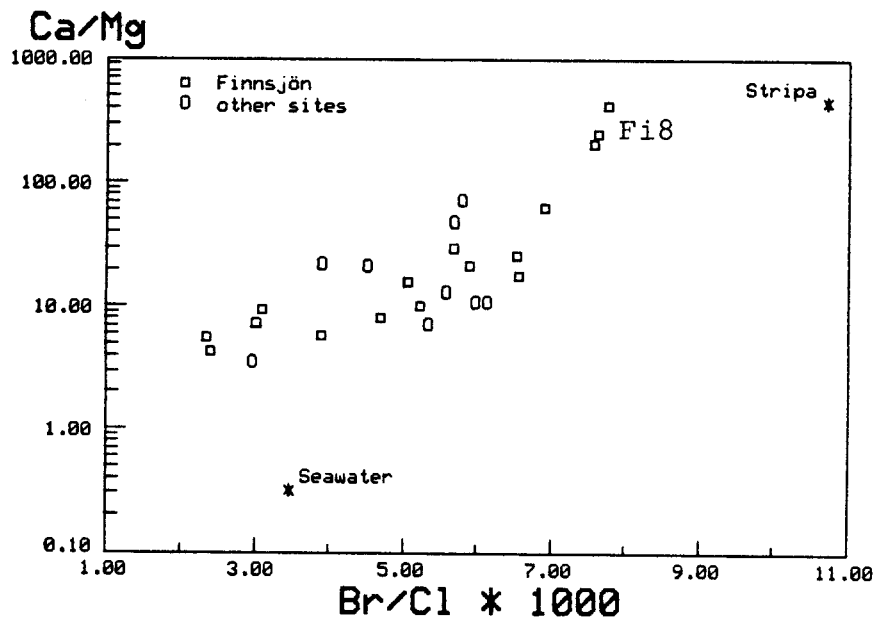
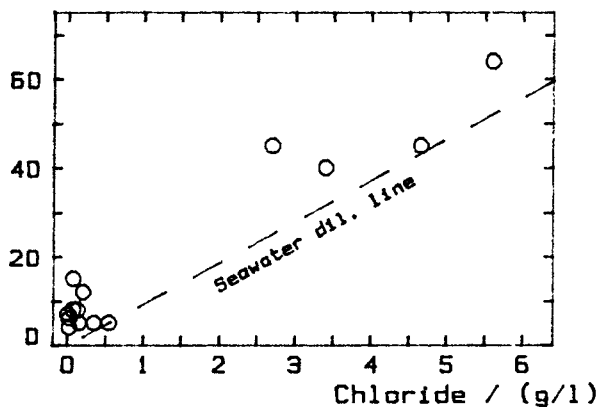


Figure 6. Plot of Ca/Mg against Br/Cl ionic ratios (by weight) for several SKB study sites.

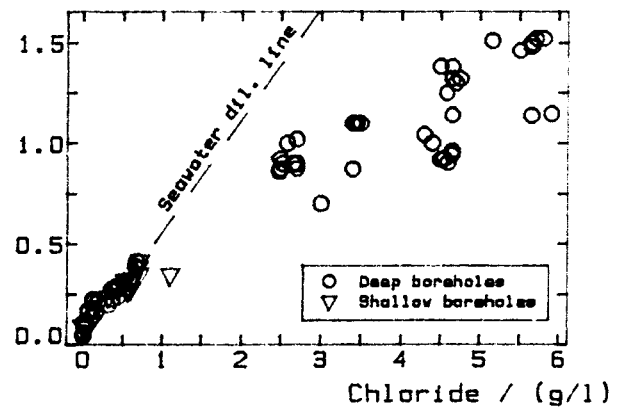
Strontium has a dependence upon chloride concentrations similar to that of sodium or calcium, while barium concentrations do not correlate with chloride. The concentration levels of these elements is probably regulated by mineral solubility equilibria (c.f. section 6).

Figure 10 shows the concentrations of F^- , Br^- , HCO_3^- and phosphate as function of chloride. The maximum levels of fluoride and bicarbonate, are controlled by calcium concentrations through fluorite and calcite solubility equilibria. Sulfate reducing bacteria decrease the water contents of this anion and produce sulfur and sulfide. The samples of Fi8 show the lowest SO_4^{2-}/Cl^- ratios, reflecting either a greater age, or increased bacterial activity, or both.

Lithium / ($\mu g/l$)



Sodium / (g/l)



Potassium / (mg/l)

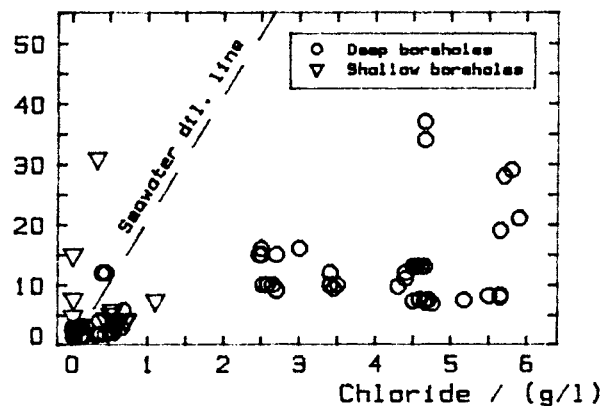


Figure 8. Alkaline metal cation contents as a function of chloride concentration.

4.4 Possible sources of salinity

The salt contents of the groundwaters in the Finnsjön study site may have its origin in either (a) relict seawater, or (b) fluid inclusions, or (c) residual igneous/metamorphic fluids, or finally, (d) mineral alteration, or a combination of any of the four (Ahlbom *et al.*, 1986).

The Ca/Mg and Br/Cl ionic ratios (c.f. Figs. 5-6) have intermediate values between seawater and the groundwaters sampled at the Stripa mine (Nordstrom *et al.*, 1985), where the Br/Cl and I/Cl ratios of the groundwaters were found to coincide with the ionic ratios of the fluid inclusions in the Stripa granite. The

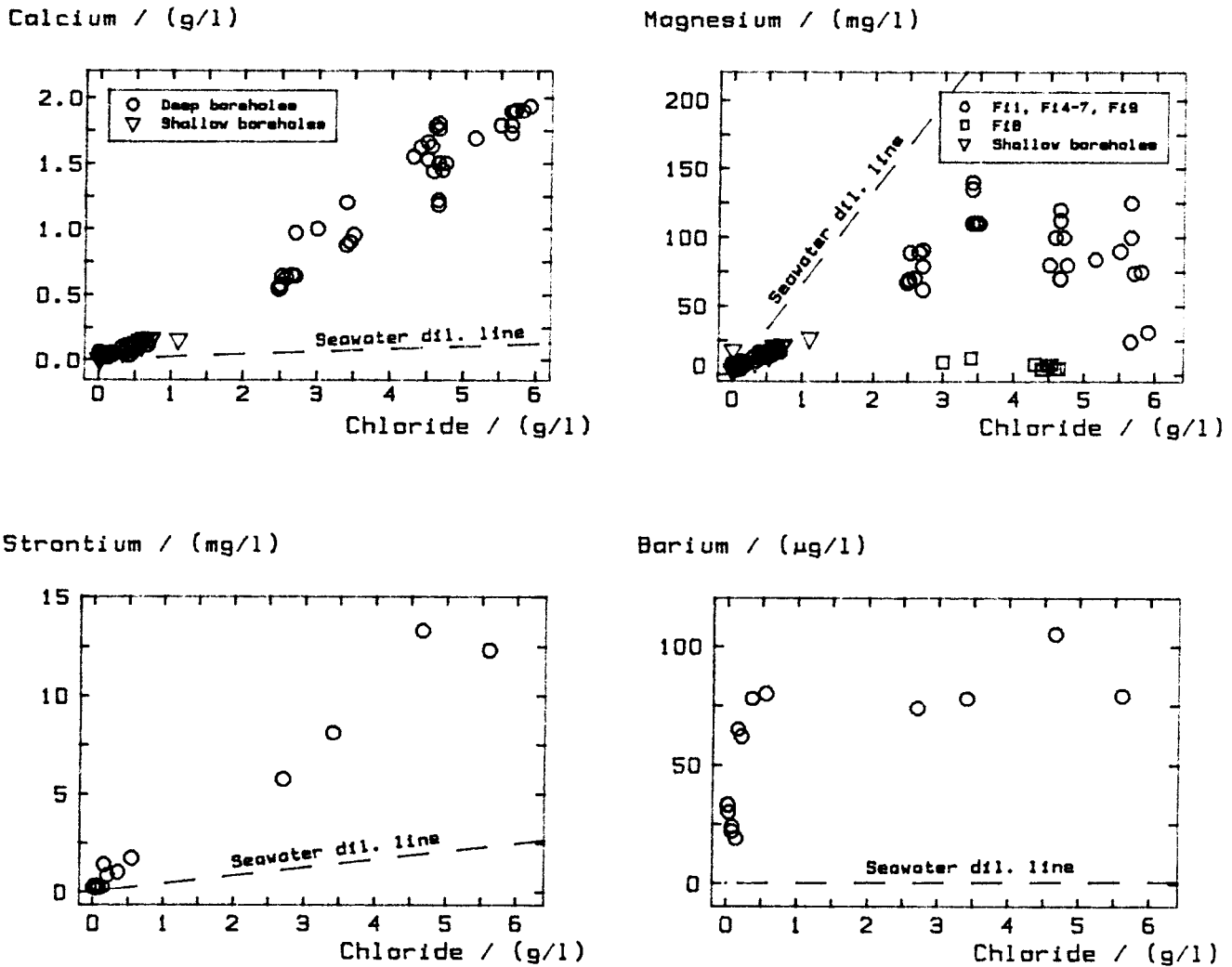


Figure 9. Alkaline earth contents as a function of chloride concentration.

similarity between the Finnsjön and Stripa ionic ratios is higher for the samples taken from borehole Fi8, which runs through the Gåvastbo fault. Iodide has only been analyzed for borehole Fi9 (Ahlbom *et al.*, 1986), and the I/Cl gravimetric ratios ($(13 \pm 2) \cdot 10^{-6}$) are again intermediate between seawater and groundwaters from Stripa. The values of the ionic ratios seem to indicate that fluid inclusion and microfracture fluid leaching may have contributed to the groundwater salinity.

On the other hand, the chloride correlations shown in Figs. 8-9 have close resemblance to the correlations found in the Seikan tunnel in Japan (Seki *et al.*, 1986), where seawater has interacted

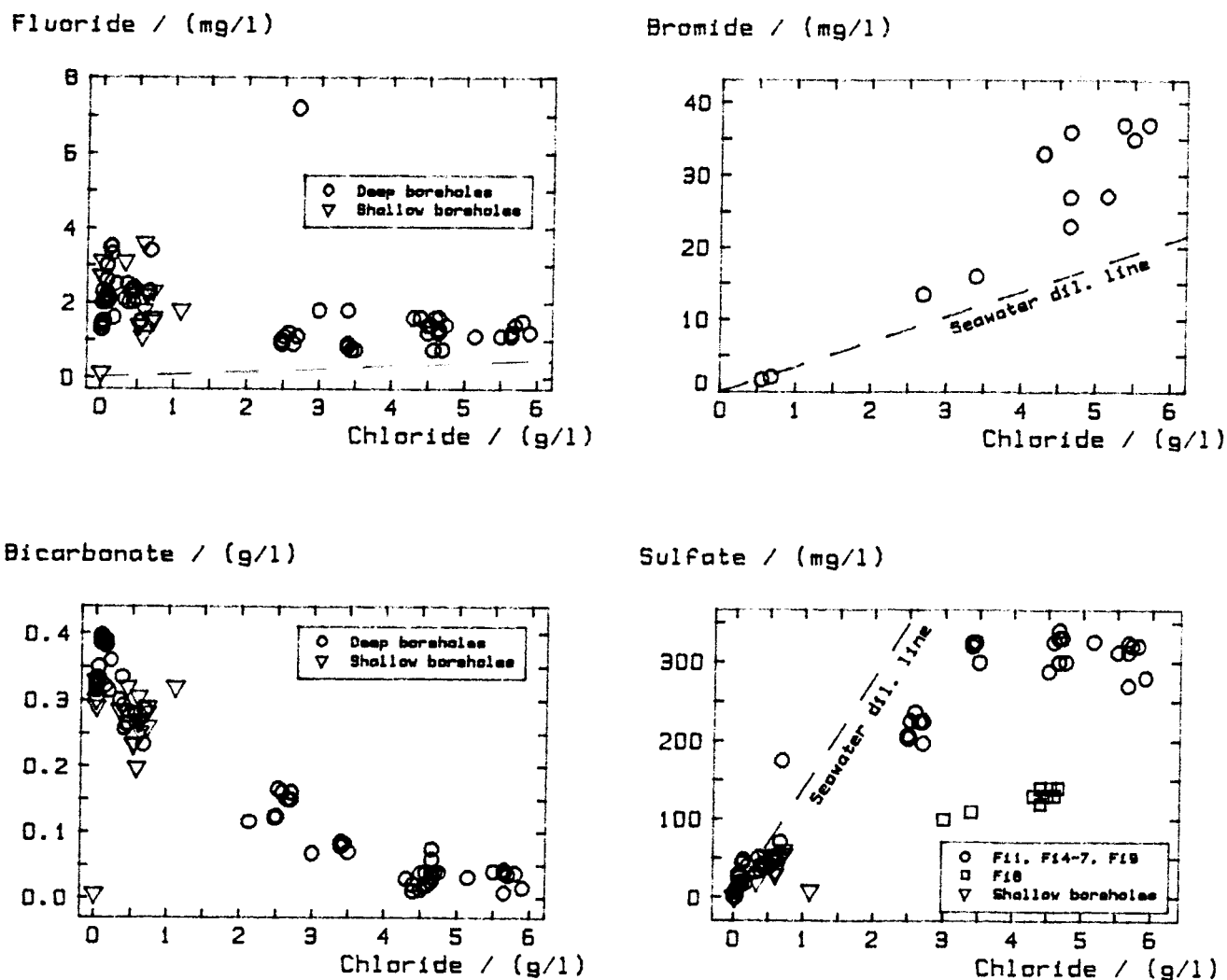


Figure 10. Fluoride, bromide, bicarbonate and phosphate contents as a function of chloride concentration.

with volcanogenic andesitic tuffs, and the chemical composition has been affected by cation exchange on clays. The modified seawater has increased its calcium content, and decreased sodium, potassium and magnesium concentrations, except at low salinities, where an increase of sodium (with respect to the seawater dilution line) was found (compare with Fig. 8). Similar trends are also found in granitic groundwaters, as in the Stripa mine (Nordstrom et al., 1985), the Carnmenellis granite (Edmunds et al., 1984), the Canadian shield (Frape et al., 1984), and Värmdö (Jacks, 1973).

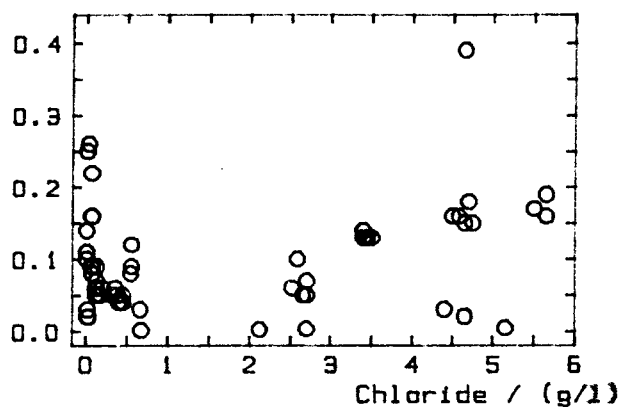
It appears that groundwaters in crystalline rocks, and some other geochemical environments, are characterized by high calcium contents, and low potassium and magnesium concentrations. These common chemical compositions are the result of changes imposed by rock-water interactions at low temperature during long periods of time on waters which originally had different compositions. As the chemistry of the groundwaters might be independent of its original composition, the source of chloride remains open to debate, and invites future isotopic studies.

5. NON-SALINE CONSTITUENTS

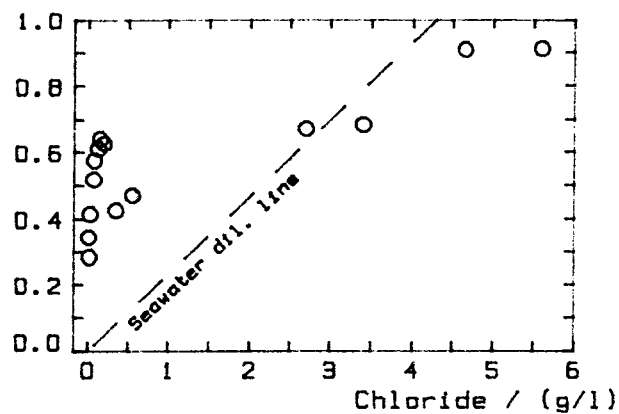
Boron and phosphate concentrations are plotted in Figure 11 versus chloride contents. Phosphorous levels show no special trend with chloride and might be regulated by solubility equilibria of phosphates of divalent metals (Ca^{2+} , Mn^{2+} , etc). There is no trend either for boron with chloride, indicating that the concentrations of boric acid might be regulated by adsorption processes.

The concentrations of iron and manganese are also plotted in Figure 11 as a function of chloride concentrations. High values for total iron at low chloride concentrations (and high tritium values, c.f. Fig. 2) are due to contamination of the sampling zone by fresh waters rich in $\text{O}_2(\text{g})$ and $\text{CO}_2(\text{g})$, which induced the production of Fe(III), mainly from weathering of fissure filling sulfide and silicate minerals (White and Yee, 1985). Any Fe(III) resulting from the oxidation reactions is immediately precipitated, at the pH values of the groundwaters, as suspended amorphous hydroxide particles or as a coating on mineral grains etc (Whittemore and Langmuir, 1975; Singh and Subramanian, 1984).

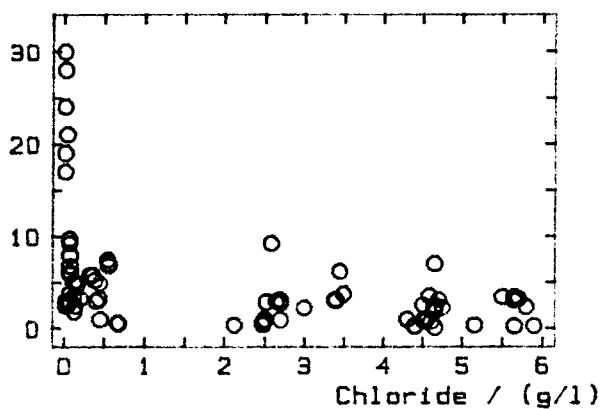
Phosphate / (mg/l)



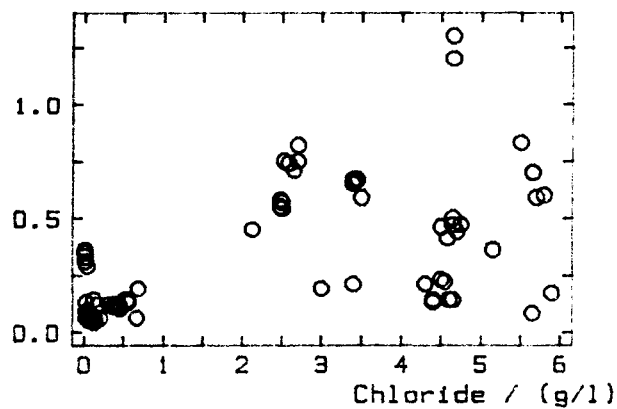
Boron / (mg/l)



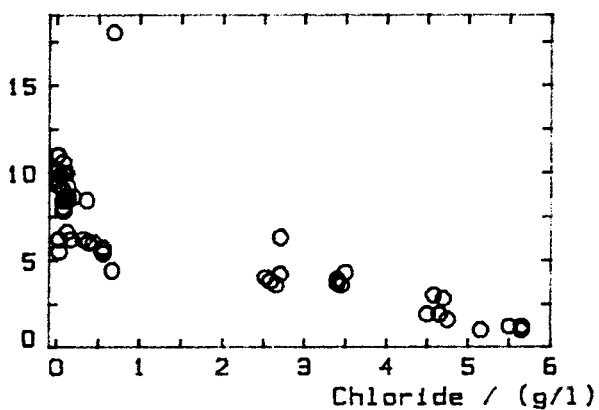
Total Iron / (mg/l)



Manganese / (mg/l)



TOC / (mg/l)



Nitrogen Species / (mg/l)

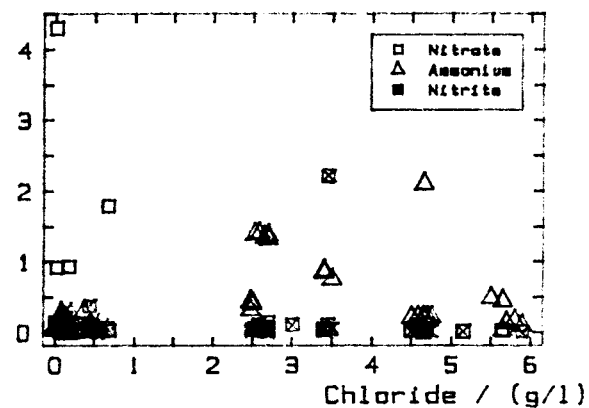


Figure 11. Groundwater concentrations of phosphate, boron, total iron, manganese, total organic carbon (TOC) and nitrogen species (NO_3^- , NO_2^- and NH_4^+) versus $[\text{Cl}^-]$.

The particles that were pumped up, were subsequently dissolved during the acid sample preservation and gave unrealistic results (up to 30 mg/l) of total "dissolved" Fe.

Manganese is soluble only as Mn(II) species, and in its higher oxidation state, Mn(IV), it forms very insoluble oxides (Stumm and Morgan, 1981, p. 433). Although erroneously high values for the analyzed Mn-concentrations might be an artifact from the fact that most of the samples were not filtered, the highest values are found (c.f. Fig. 11) in samples with high chloride and low tritium contents (c.f. Fig. 2). These are the waters where low redox potentials are expected to prevail, and therefore, waters in which the solubility of manganese minerals would be expected to be higher. From an inspection of the Fe and Mn correlations with chloride (c.f. Fig. 11), the conclusion is reached that either there are no suspended particles containing manganese hydroxides, or the particles that contain iron hydroxides are deficient in Mn.

Several experimental studies have shown the importance of humic compounds on the distribution of trace metals in natural aqueous environments (Davies-Colley *et al.*, 1984; Davis and Leckie, 1978; Laxen, 1985). In Finnsjön organic matter has a negative correlation with chloride and tritium (c.f. Figs. 2 & 11), and high values have their source in contaminating superficial waters.

Nitrogen compounds have a special importance to SKB's nuclear waste management program because copper is planned to be used as canister material, and because of the impact that nitrate has on copper corrosion (Mattsson, 1980; Francis, 1985) and the importance of ammonia on the thermodynamic stability of copper (Rickard, 1970a and 1970b). The chemistry of nitrogen compounds in natural environments can produce several oxidation states, including $\text{NH}_3/\text{NH}_4^+$, R-NH_2 , $\text{N}_2(\text{g})$, $\text{N}_2\text{O}(\text{g})$, NO_2^- and NO_3^- . Transformations between the different nitrogen compounds is catalyzed by different bacteria species (Reddy and Patrick, 1984). Nitrate in groundwaters usually originates from either industrial waste or fertilizers, and in Finnsjön the higher $[\text{NO}_3^-]$ -values are found at low chloride concentrations (Fig. 11), where the samples have a larger contamination of superficial waters, and the redox potentials are expected to be higher.

Ammonium is found in silicate minerals replacing potassium (Stevenson, 1962), and might be produced by reduction (decay of $R-NH_2$ to NH_3) of organic nitrogen (Stanford et al., 1975). In Finnsjön, the higher values for ammonium concentration are found in samples of low tritium (Fig. 2) and high chloride (Fig. 11). Ammonium also correlates positively with manganese (Fig. 12). This is due to the fact that both Mn(II) and ammonium are only thermodynamically stable in reducing conditions (Emerson et al., 1979).

6. SOLUTION-MINERAL EQUILIBRIA

6.1 Carbonate minerals

Calcite is the most common fracture filling mineral in the Finnsjön site, and complete studies have been reported of their chemical and isotopic composition (Tullborg and Larson, 1982; Larson and Tullborg, 1984). Carbonate minerals are important because of their pH-buffering capacity, and fracture sealing potential. The saturation indices of calcite and other carbonate minerals are shown in Figs. 13 and 14. The values of $\log(IAP/K_{sp})$ higher than ≈ 1.0 are unreasonable, and must be due to either erroneous pH-values or analytical errors. A variation of $pH = \pm 0.5$ corresponds to a variation in the saturation index of ± 0.4 (just

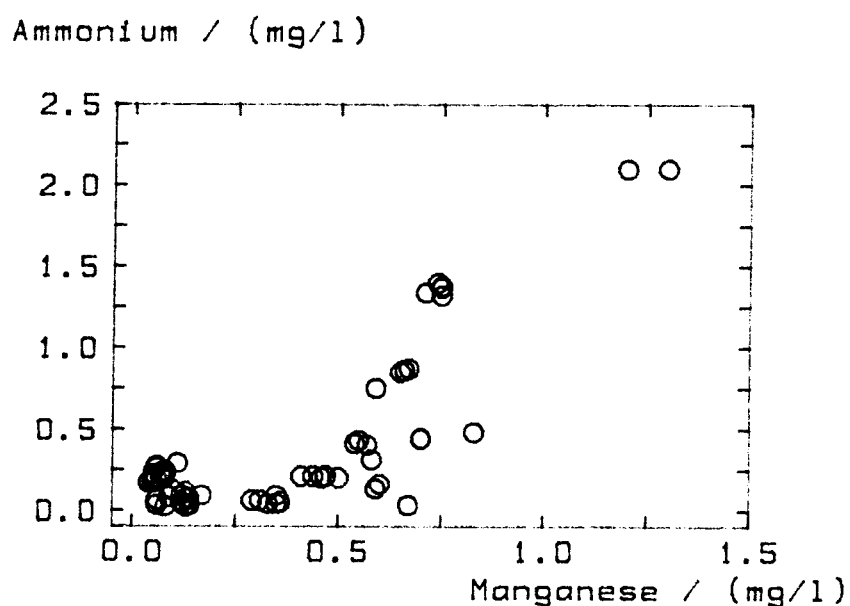
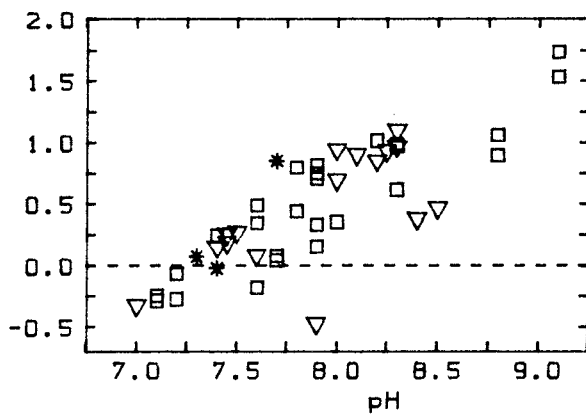


Figure 12. Groundwater levels of ammonium plotted against manganese(II) concentrations.

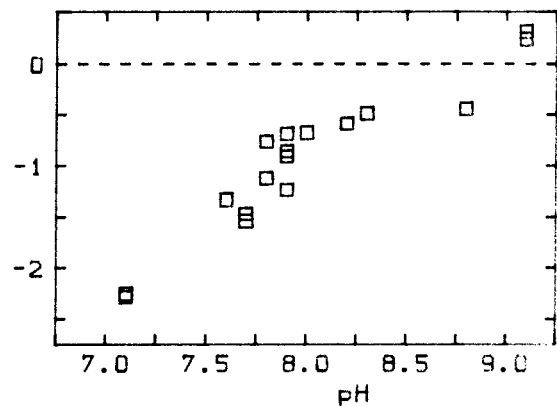
for comparison, we can mention here that an error in the temperature of 8°C gives only a variation in $\log(IAP/K_{sp})$ of ± 0.09). Analytical errors would give random and smaller variations in the saturation index of calcite.

The systematic undersaturation for strontianite (c.f. Fig 14) indicates that the solubility control for strontium could be a solid solution of Sr^{2+} in calcite (Stumm and Morgan, 1981, p. 291). The same might be true for the other carbonates, although the scatter in the analytical data (c.f. Figs. 13 and 14) does not allow any definite conclusion.

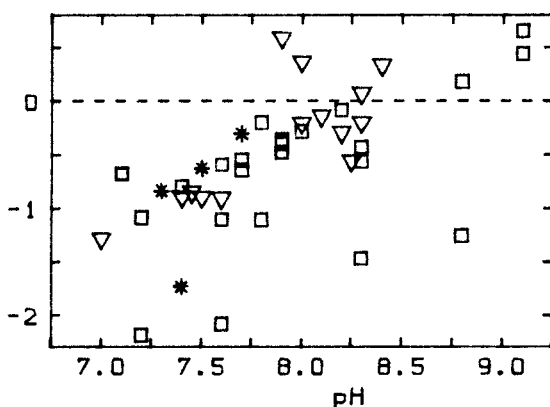
Calcite:
 $\log(IAP/K_{sp})$



Strontianite:
 $\log(IAP/K_{sp})$



Rhodochrosite:
 $\log(IAP/K_{sp})$



Siderite:
 $\log(IAP/K_{sp})$

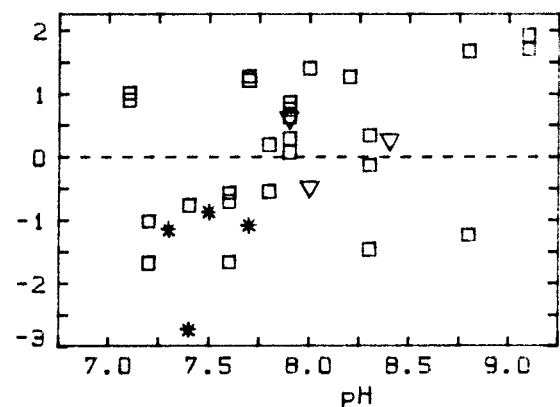


Figure 13. Saturation indices of carbonate minerals plotted as a function of field pH. Data for both deep boreholes (squares: Laurent, 1982; stars: Ahlbom et al., 1986); and shallow boreholes (triangles).

The discrepancy between field and laboratory pH, which is shown in Figure 3, introduces a serious uncertainty on the saturation indices of carbonate minerals. The fact that high pH differences correspond to samples with low tritium values (c.f. Fig. 3c) indicates that the most affected samples are old groundwaters with little or no contamination of superficial waters.

One of the possible reasons for the Δ pH-values, is $\text{CO}_2(\text{g})$ outgassing/ingassing due to measurement delays, both in the field and in the laboratory. The effect of 10% $\text{CO}_2(\text{g})$ outgassing in

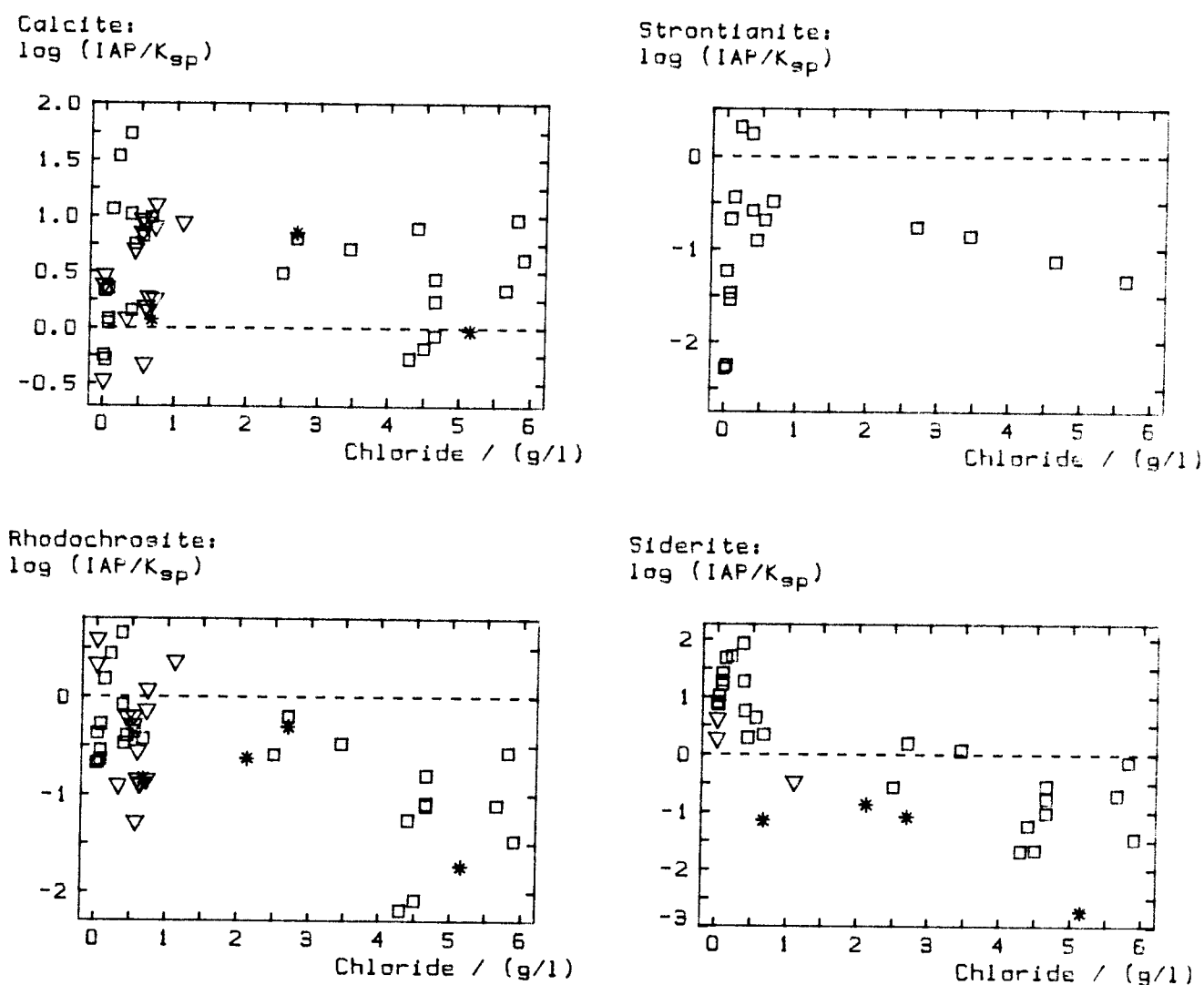


Figure 14. Saturation indices of carbonate minerals plotted as a function of chloride concentrations. Data for both deep boreholes (squares: Laurent, 1982; stars: Ahlbom et al., 1986); and shallow boreholes (triangles).

water samples with alkalinities of 310 or 210 mg/l, would be an increase in either 0.35 or 1.0 pH units respectively (Pearson et al., 1978).

The pH differences shown in Figure 3 would thus indicate a greater CO₂(g) ingassing of the samples in the laboratory as compared with the ones in the field (or alternatively, a greater outgassing of the field samples as compared with the lab. samples).

The ingassing hypotheses is supported by the fact that calculated $\log p_{\text{CO}_2}$ has the lowest values (c.f. Fig. 15) in waters with high pH (and high ΔpH , c.f. Fig. 3e). Furthermore, lower values than the atmospheric level ($\log p_{\text{CO}_2} = -3.48$) are not expected after an outgassing process.

On the other hand, calcite saturation indices seem to support the outgassing possibility, which can be visualized by simulating the reverse reaction, i.e., an addition of CO₂(g) to an actual sample. Figure 16 shows the effect (calculated with the EQ6 computer program (Wolery, 1979)) of CO₂(g) increase on sample Fi4 800123 (247 m depth) which has $\text{pH}_{\text{field}}=9.1$, $\Delta\text{pH}=1.3$ and a saturation index of 1.74 (one of the largest values).

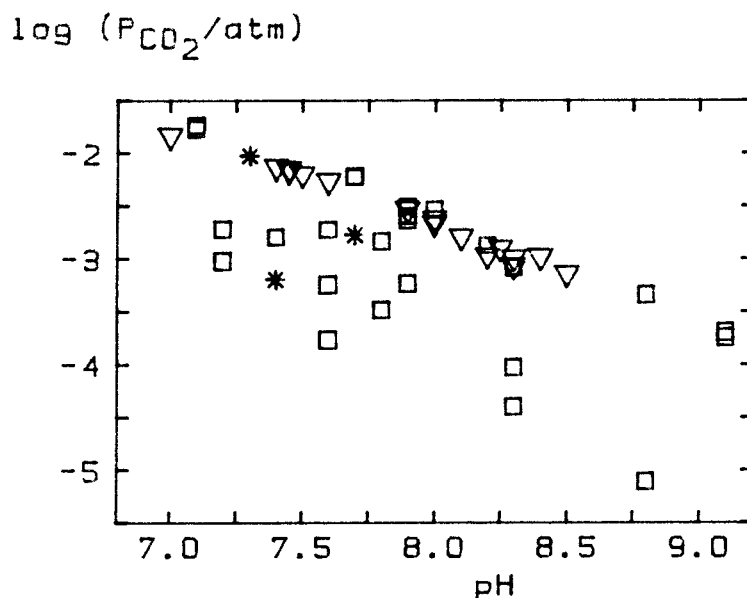


Figure 15. Calculated values of CO₂(g) partial pressure plotted against field pH. Data for both deep boreholes (squares: Laurent, 1982; stars: Ahlbom et al., 1986), and shallow boreholes (triangles).

After an addition of $7 \cdot 10^{-3}$ mol/l (i.e., a $\approx 12\%$ increase in total inorganic carbon) the pH has decreased to ≈ 7.8 (the value measured in the laboratory), and the partial pressure of $\text{CO}_2(\text{g})$ has reached values well above atmospheric levels. Calcite saturation is reached after an addition of $1.3 \cdot 10^{-3}$. The results of the simulation shown in Fig. 16, indicate that carbon dioxide

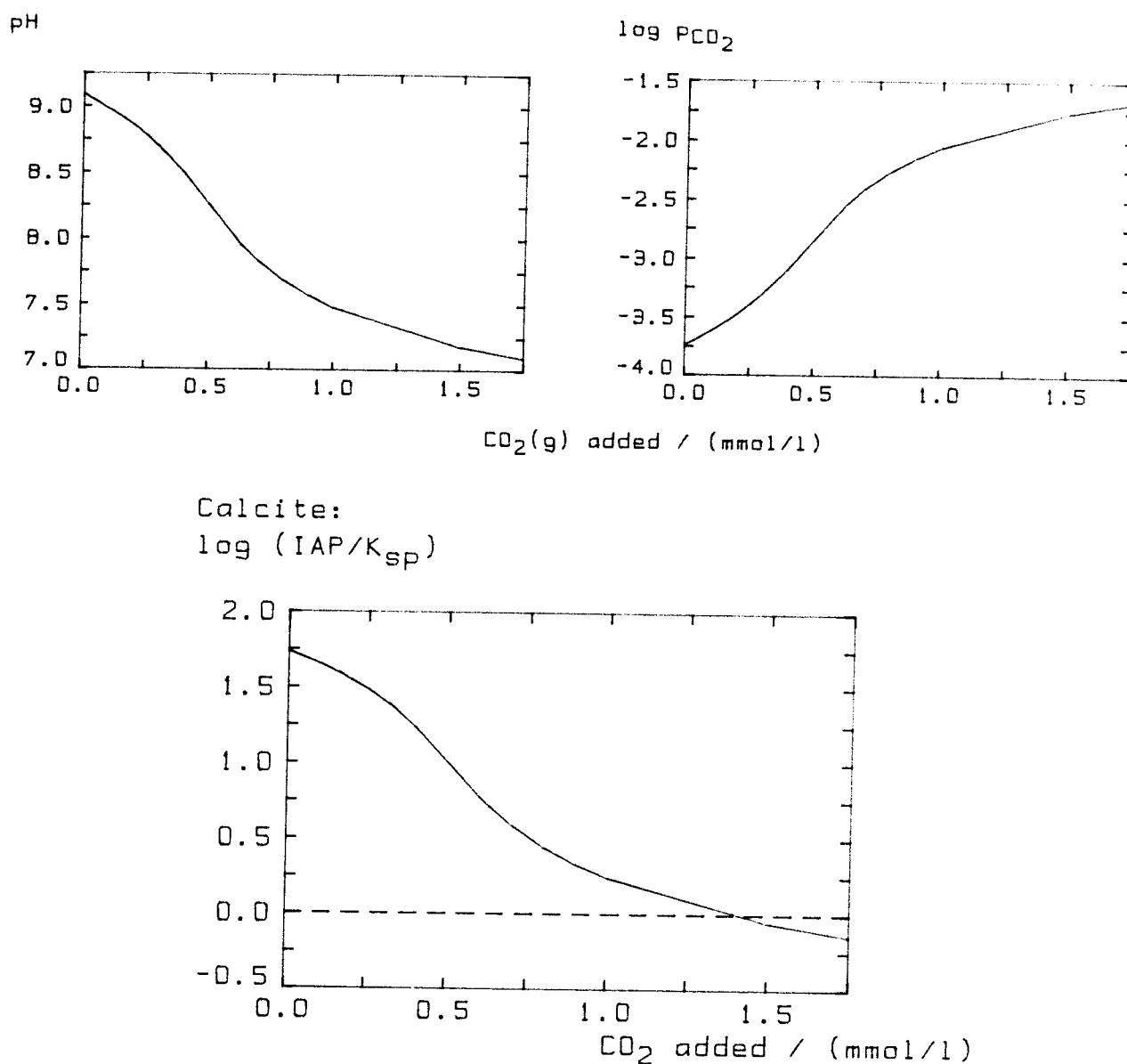


Figure 16. Results of an EQ6 simulation showing the effect of $\text{CO}_2(\text{g})$ addition on sample Fi4 800123 (247 m).

outgassing might have contributed to the abnormal calcite saturation indices and to the Δ pH-values observed.

However, since the tendency for most field pH values is to be greater than the pH_{lab} values (c.f. Fig. 3e), $\text{CO}_2(\text{g})$ ingassing is likely to be the dominant process, and some calcite supersaturation must be considered real.

6.2 Mixing of carbonate waters

Mixing of groundwaters from different aquifers might generate non-linear under- or oversaturation of minerals (Runnells, 1969). Particular attention has been given to mixtures of waters containing dissolved carbonate species (Plummer 1975, Wigley and Plummer 1976). If the mixing of groundwaters takes place immediately before sampling, a transient over- or undersaturated condition is created for carbonate minerals like calcite, etc. Even the measured pH in the field might then differ from the laboratory values if enough time has elapsed and mineral precipitation (or particle dissolution) has occurred.

Laurent (1982, p. 3-4) makes some comments on "deviant sampling zones", and the possibility of drilling water dilution, specially for Fi4 at 247 m. We have made a simulation (again with the EQ6 program (Wolery, 1979)) of a mixing process between a non-

Table 1. Chemical composition (mg/l) of the two waters used as end-members in the EQ6 mixing simulation presented in Figure 17.

	Non saline water (\approx Fi4, >247 m)	Saline groundwater (\approx Fi5, 384 m)
pH	7.7	7.7
SO_4^{2-}	45.0	320.0
HCO_3^-	324.3*	16.25*
Cl^-	130.0	5600.0
Na^+	184.36	1536.5
Ca^{2+}	25.0	1800.0
Mg^{2+}	5.0	100.0

* values giving saturation with calcite.

saline water and a saline groundwater (c.f. Table 1). Both waters were assumed to be in equilibrium with calcite, and to have the same pH. The results of the EQ6 calculations are shown in Figure 17, which clearly demonstrates that calcite oversaturation may be obtained. In particular it should be noted that calcite saturation indices as high as 0.7 are obtained for a mixture containing only 10% of the saline groundwater. The simulation also illustrates the fact that pH, $\text{CO}_2(\text{g})$ partial pressure, and calcite

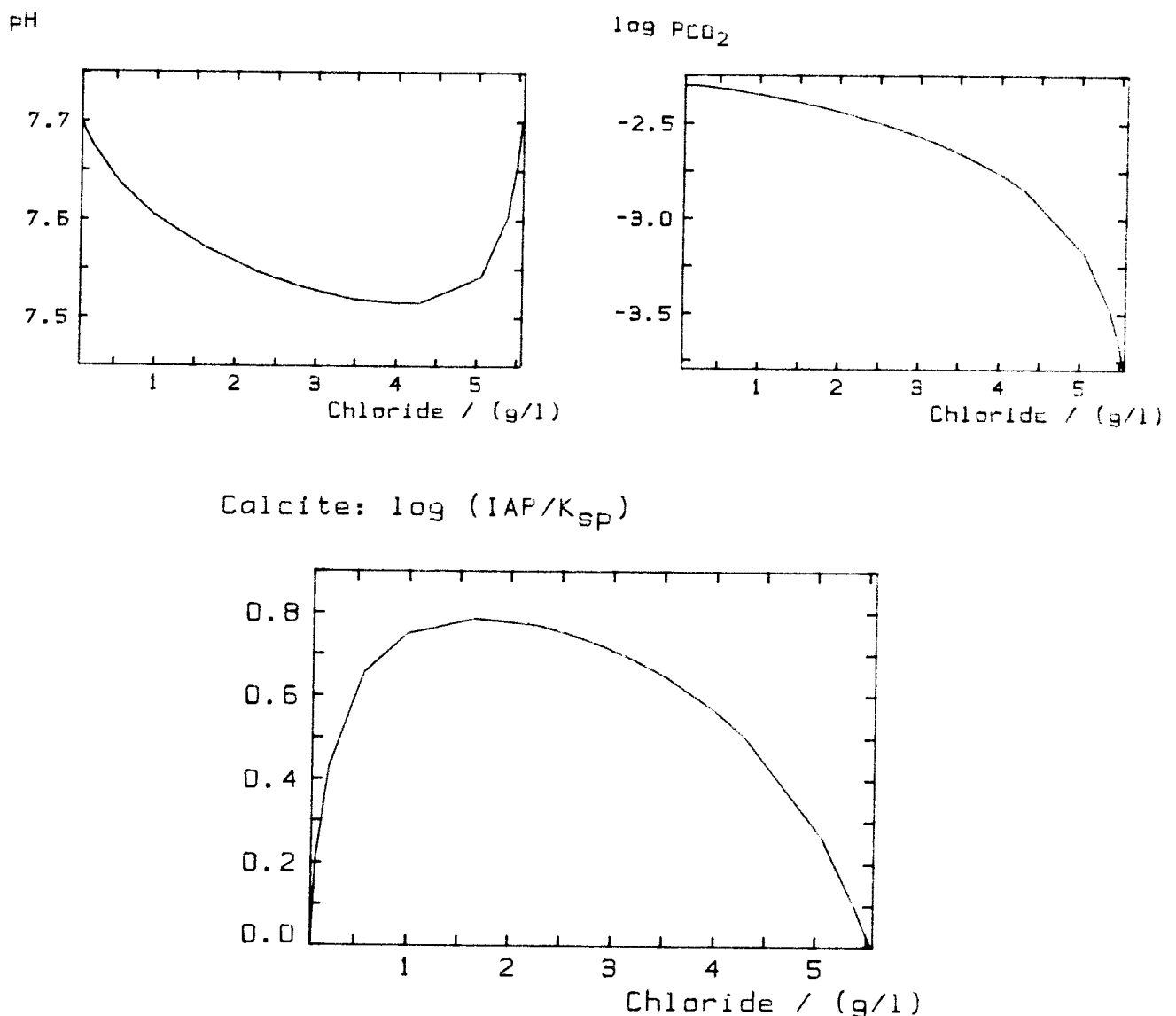


Figure 17. Results of an EQ6 simulation showing the effect of mixing the groundwaters given in Table 1.

saturation index are not linearly dependent on the global mixture composition.

The simulation presented in Figure 17 should not be taken as a thorough study of the possible effects of groundwater mixing in the Finnsjön site. Both super- and undersaturation conditions (as well as pH increase and decrease) might be achieved from mixtures of appropriate end-members (Wigley and Plummer, 1976).

6.3 Non-carbonate minerals

The activity of silica is shown in Figure 18. The data imply saturation with cristobalite. However, a steady state silica concentration could also be reached by opposed dissolution and precipitation reactions of aluminosilicate minerals (Lassaga, 1981, p. 11).

The relative stability of weathering mineral products is shown in Figure 19. Most of the waters fall into the kaolinite field, except for potassium where many groundwaters appear to be stable with the feldspar. It should be noted however, that there is some uncertainty in the values plotted in Figure 19: errors in pH-values will give corresponding deviations in the data plotted in the diagrams.

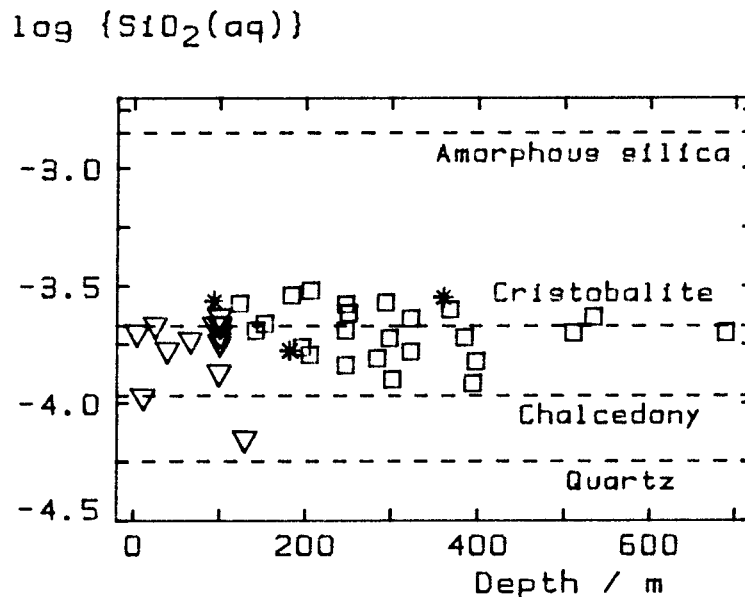


Figure 18. Activity of silica plotted as a function of depth. Data for both deep boreholes (squares: Laurent, 1982; stars: Ahlbom et al, 1986), and shallow boreholes (triangles).

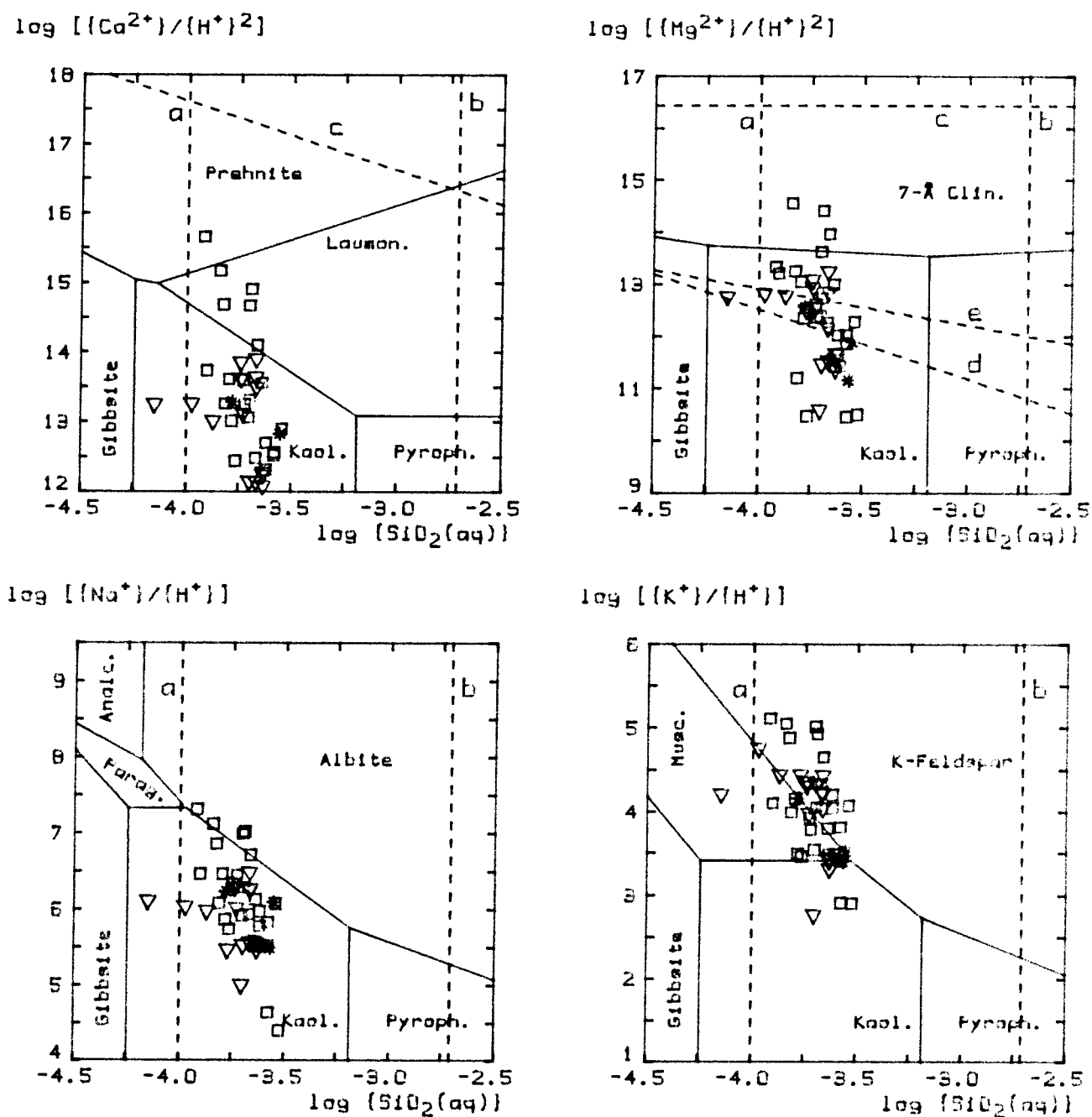
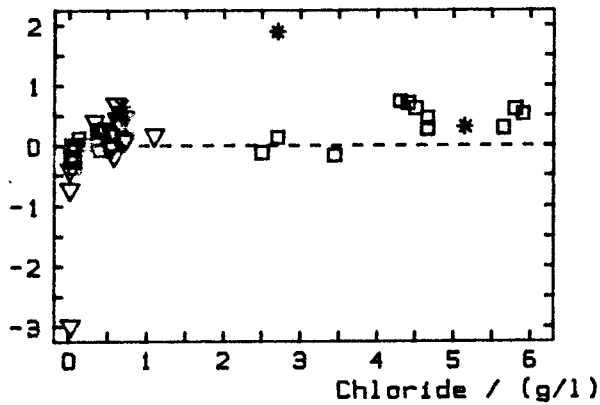
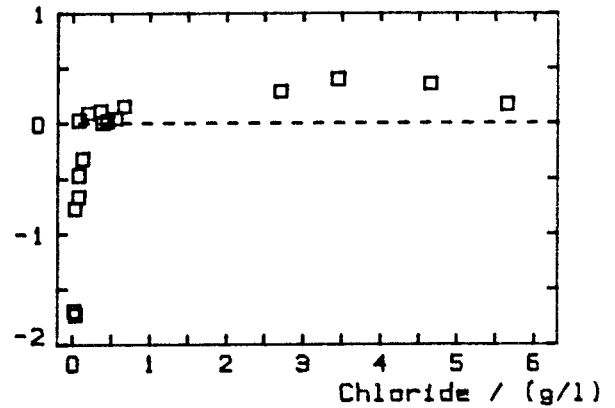


Figure 19. Phase relations in the systems $\text{HCl-H}_2\text{O-(Al}_2\text{O}_3\text{)-SiO}_2\text{-CaO/MgO/Na}_2\text{O/K}_2\text{O}$ at 25°C (adapted from Bowers *et al.*, 1984). Saturation limits: quartz (a), amorphous silica (b), wollastonite (c, in calcium diagram), brucite (c, in magnesium diagram), talc (d), and antigorite (e). For the magnesium diagram, metastable 7-Å chlinochlore is considered instead of its stable counterpart 14-Å chlinochlore. Data for both deep boreholes (squares: Laurent, 1982; stars: Ahlbom *et al.*, 1986), and shallow boreholes (triangles).

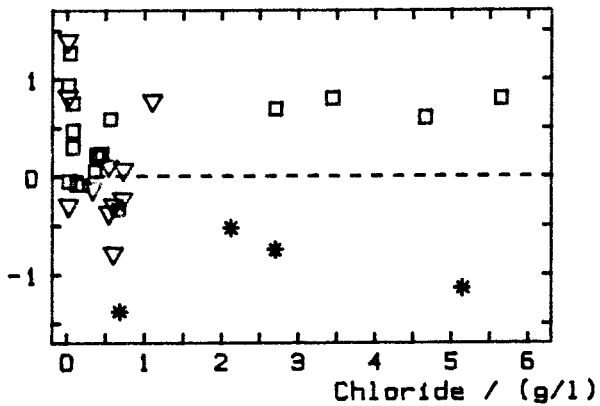
Fluorite:
 $\log (IAP/K_{sp})$



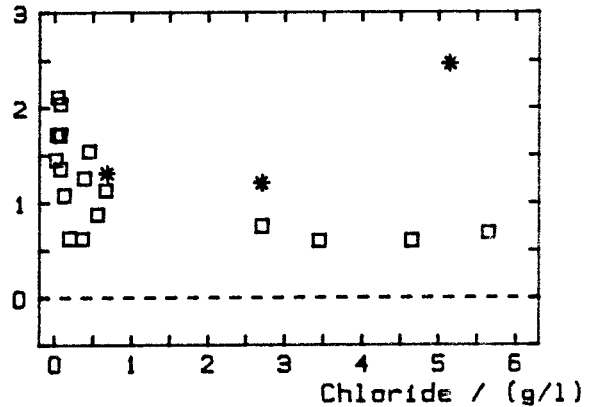
Barite:
 $\log (IAP/K_{sp})$



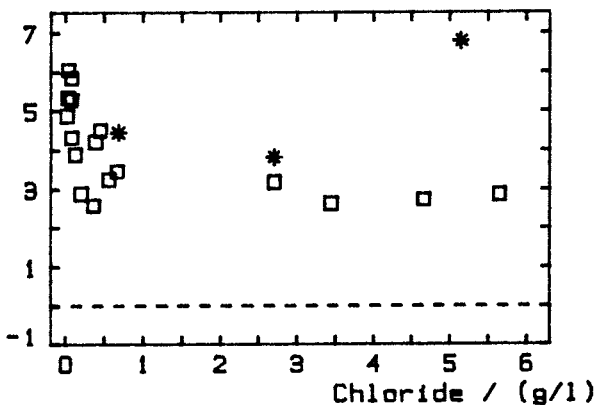
$MnHPO_4(cr)$:
 $\log (IAP/K_{sp})$



Gibbsite:
 $\log (IAP/K_{sp})$



Kaolinite:
 $\log (IAP/K_{sp})$



Laumontite:
 $\log (IAP/K_{sp})$

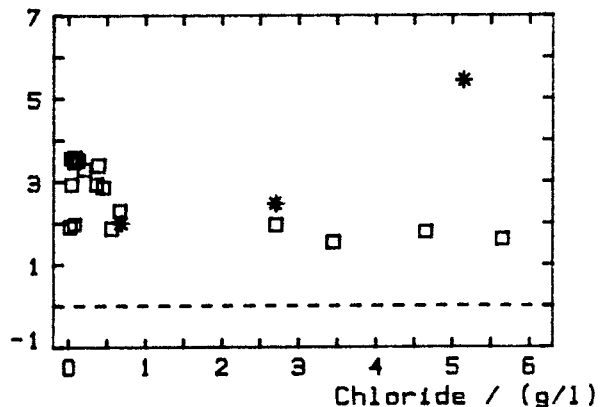


Figure 20. Saturation indices of fluorite, barite, $MnHPO_4(cr)$, and the aluminum-containing minerals gibbsite, kaolinite and laumontite. Data for both deep boreholes (squares: Laurent, 1982; stars: Ahlbom et al., 1986), and shallow boreholes (triangles).

The calculated saturation indices for barite ($\text{BaSO}_4(\text{cr})$), fluorite ($\text{CaF}_2(\text{cr})$), and $\text{MnHPO}_4(\text{cr})$ are shown in Figure 20, together with the saturation indices of gibbsite ($\text{Al}(\text{OH})_3(\text{cr})$), kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(\text{cr})$) and laumontite ($\text{Ca}(\text{Al}_2\text{Si}_4\text{O}_{12}) \cdot 4\text{H}_2\text{O}(\text{cr})$, zeolite group).

Except for one value, all the values for fluorite suggest that fluoride concentrations are limited by the equilibrium reaction with this mineral. Fluorite saturation is also found in Stripa groundwaters (Nordstrom et al., 1985) and other Swedish groundwaters (Jacks, 1978). The same is true for the barium concentrations, which are regulated by the solubility of the sulfate.

The phosphate concentrations reported by Ahlbom et al. (1986) are systematically lower than the values reported previously. This affects the saturation indices of the phosphate minerals, including the manganese phosphate shown in Figure 20. It is uncertain whether this is due to the difference in sampling methods and analytical procedures or due to geochemical differences of the groundwater aquifer sampled. This is a point that should be further investigated, because phosphate is one of the ligands of most importance for uranium transport in the groundwaters of the SKB study sites.

Aluminum concentrations appear to be slightly high, as shown by the oversaturations plotted in Figure 20. However, errors in pH and sampling procedures might influence the results of the calculations even in this case because of the strong pH-dependence of Al^{3+} hydrolysis.

7. CONCLUSIONS

Because of problems during groundwater sampling of most of the waters in Finnsjön, the geochemical interpretation of the site is limited.

However, the following points have been established:

- o - the Ca/Mg and Br/Cl ionic ratios of the saline samples show some similarities with Stripa groundwaters, specially for the Fi8 borehole, which at the same time shows the lowest SO_4^{2-} concentrations, indicating lower redox potentials. This borehole penetrates the Gåvastbo

fault, and the groundwaters sampled here might have gone through a different hydrological pathway than the waters sampled in the other boreholes.

- o - the disagreement between field and laboratory pH measurements collected during 1979-1982 introduces a serious difficulty for the geochemical interpretation of the data. Unnaturally high saturation indices for calcite (up to +1.7), confirm the uncertainties in the groundwater pH-values.
- o - simulations with the EQ3NR/EQ6 computer codes show that CO₂(g) degassing/ingassing during sampling may have caused errors in the measured pH values, and ingassing appears more likely
- o - the high tritium contents of the waters is a good indication that mixing of young waters or drilling fluids with old waters has probably taken place during sampling. Tritium concentrations have a positive correlation with total iron and organic carbon, and a negative correspondence with chloride, manganese and ammonium.
- o - simulations of groundwater mixing (calculated with the EQ3NR/EQ6 code package) show that mixing during sampling (due to high pumping rates and/or insufficient borehole packing) may have induced transient over- or undersaturation of carbonate minerals
- o - saturation indices (calculated with the EQ3NR and WATEQ3 computer models) for calcite, strontianite, rhodochrosite and siderite show that the concentrations of Ca²⁺, Sr²⁺, Mn²⁺ and Fe²⁺ might be limited by carbonate mineral-groundwater interactions
- o - EQ3NR and WATEQ3 computer calculations show that most of the groundwaters appear to be in equilibrium with fluorite and barite

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Roger Thunvik, Royal Institute of Technology,
Stockholm

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Kåre Tjus* and Peter Wikberg**
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