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# TECHNICAL REPORT

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**95-26**

**The Äspö redox investigations in block  
scale**

**Project summary and implications for  
repository performance assessment**

Steven Banwart (ed.)

Dept. of Civil and Environmental Engineering,  
University of Bradford, UK

November 1995

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**SVENSK KÄRNBRÄNSLEHANTERING AB**

*SWEDISH NUCLEAR FUEL AND WASTE MANAGEMENT CO*

P.O.BOX 5864 S-102 40 STOCKHOLM SWEDEN

PHONE +46 8 665 28 00 TELEX 13108 SKB

FAX +46 8 661 57 19

# THE ÄSPÖ REDOX INVESTIGATIONS IN BLOCK SCALE

## PROJECT SUMMARY AND IMPLICATIONS FOR REPOSITORY PERFORMANCE ASSESSMENT

*Steven Banwart (ed.)*

**Dept. of Civil and Environmental Engineering,  
University of Bradford, UK**

November 1995

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# THE ÄSPÖ REDOX INVESTIGATIONS IN BLOCK SCALE

## Project Summary and Implications for Repository Performance Assessment

<sup>1</sup>Steven Banwart, Scientific Coordinator

<sup>2</sup>Erik Gustafsson

<sup>3</sup>Marcus Laaksoharju

<sup>4</sup>Karsten Pedersen

<sup>5</sup>Eva-Lena Tullborg

<sup>6</sup>Bill Wallin

<sup>7</sup>Peter Wikberg, Project Manager

<sup>8</sup>Margit Snellman

<sup>9</sup>Petteri Pitkänen

<sup>9</sup>Hilka Leino-Forsman

November 1995

<sup>1</sup>Dept. of Civil and Environmental Engineering, University of Bradford (UK); <sup>2</sup>GEOSIGMA AB, Uppsala; <sup>3</sup>GeoPoint AB, Sollentuna; <sup>4</sup>Dept. of Marine and General Microbiology, University of Gothenberg; <sup>5</sup>Terralogica AB, Gråbo; <sup>6</sup>Geokema AB, Lidingö; <sup>7</sup>SKB, Stockholm; <sup>8</sup>IVO, Vantaa (Finland); <sup>9</sup>VTT Espoo (Finland)

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## ABSTRACT

On March 13, 1991, tunnel construction at the Äspö Hard Rock Laboratory opened a vertical fracture zone at a depth of 70 meters. Three weeks later, a sharp dilution front was observed in the originally saline groundwater. This signaled the arrival of shallow surface water at the 70 m depth. There was a brief oxidizing disturbance at that time as indicated by the disappearance of dissolved iron from the inflowing groundwater. These results were expected based on earlier predictions of surface water and oxygen breakthrough times. After this initial period however, the fracture zone remained persistently anoxic.

Intensive anaerobic respiration resulted from the increased recharge. Rather than input of molecular oxygen, there was an inflow of reducing capacity in the form of young organic carbon. Microbial processes were extremely effective in using the carbon to scavenge oxygen and other oxidants from the shallow bedrock environment. Because the thin soils at this site were apparently so effective as a source of organic carbon, these processes may be even more pronounced at sites with more extensive soil cover.

## ABSTRACT (IN SWEDISH)

Den 13 mars 1991 bröt Äspö HRL tunneln genom en brantstående sprickzon på 70 meters djup under markytan. Tre veckor senare observerades en kraftig utspädning av det ursprungligen salta grundvattnet, till följd av att ytligt vatten då transporterats ned till 70 meters djup. En svag oxiderande störning indikerades samtidigt genom att allt löst järn i det inströmmande vattnet försvann. Resultaten överensstämde med de beräkningar som hade gjorts av genombrotts-tider för både ytligt vatten och för syre. Emellertid förblev vattnet efter denna kortvariga initiala störning anoxiskt under resten av experimentet (december 1993).

Den ökade vattenomsättningen i zonen förorsakade en intensiv bakteriell aerob förbränning av ungt organiskt material (med syre). Således ökade den reducerande kapaciteten genom tillskottet av ungt organiskt material. Mikrobiella processer visade sig mycket effektiva på att konsumera syre och andra oxidanter i den ytliga bergmassan. Eftersom även det relativt tunna jordtäcket i detta experiment visade sig vara en god källa för organiskt material kan man vänta sig att dessa processer får en ändå större betydelse på platser med tjockare jordtäckte.

## SUMMARY

During construction and operation of a deep repository for high level waste, the groundwater environment will be open to oxidizing surface conditions and surface water inflow. This project studied the possibility of oxygen intrusion into vertical fracture zones. This may occur during repository construction due to increased surface water inflow. Oxygen in the repository environment is a concern regarding canister corrosion. Oxygen in fracture zones can enhance the mobility of redox-sensitive radionuclides; Tc, Np, Pu, U. These elements are highly soluble and thus mobile under oxidizing conditions, while in the absence of oxygen they form sparingly soluble solid phases.

Construction of the access tunnel to the Hard Rock Laboratory intersected a vertical fracture zone at a depth of 70 meters. Changes in groundwater chemistry were then monitored for a period of three years. Mass balances for conservative and reactive natural tracers provided a basis for a site model of the fracture zone.

Groundwater dilution was the dominant process affecting the geochemistry of the site. There was associated Na-Ca ion-exchange. There is evidence for extensive lateral flow between recharge areas and the discharge point in the access tunnel. There was a significant transport of young organic carbon from the surface to the discharge borehole during recharge. Proposed microbial processes during lateral flow include anaerobic respiration coupled to reduction of iron hydroxide, methanogenesis, precipitation of calcite and secondary ferrous minerals. There is strong evidence to rule out sulfate reduction. Sulfate increased dramatically, possibly by desorption from fracture minerals. In this case, release of sulfate occurred due to adsorption competition with the large amounts of bicarbonate that accumulated in the groundwater during anaerobic respiration.

Fracture performance is affected by the extensive groundwater dilution and by the microbial processes that occur. Dilution affects aqueous speciation, radionuclide solubility and sorption, and the stability and mobility of colloids. Aerobic respiration provides an effective sink for oxygen, thus decreasing exposure of the repository to corrosive oxic waters. Maintaining anoxia favors low solubility for Technetium, Neptunium, Plutonium and Uranium. Reductive dissolution of iron hydroxide will release sorbed radionuclides, while formation of biogenic Fe(II) minerals can provide an effective reducing migration barrier to radionuclides and to future intrusion of oxygen from the surface.

## ACKNOWLEDGEMENTS

The authors wish to acknowledge a number of collaborators within SKB. Katinka Klingberg and Karl-Göran Nederfeldt did much of the hydrochemical monitoring and water chemistry analyses at the field laboratory at Äspö and frequently provided invaluable problem-solving skills with the field work. This included helping design and implement specialized sampling or analytical procedures for groundwater gases, frequent sampling at surface boreholes during sub-zero weather, collecting solid precipitates accumulated in packed-off borehole sections. Sverker Nilsson, manager of the SKB Biosphere Project, provided a great deal of help through sampling and chemical analyses by his team of soil and sediment specialists at Studsvik Eco och Safety AB (Nyköping); Björn Sundblad, Ove Landström, Ingrid Aggeryd, Lena Mathiasson.

Ann-Chatrin Nilsson at the Royal Institute of Technology (Stockholm) provided quality assurance and data base management, and helped with hydrochemical sampling and analysis at Äspö. Christina Skårman of GeoPoint AB (Sollentuna) carried out statistical modeling of site hydrochemistry and also helped with development and implementation of sampling techniques for colloids and solid precipitates from groundwater. Claude Degueldre of the Paul Scherrer Institute (Würlingen, Switzerland) provided guidance on sampling of colloids and precipitates and the analysis of the resulting data, as well as providing particle composition analyses.

Critically important results on microbiological activity and processes at the site resulted from the efforts of Karsten Pedersen's research group at the University of Göteborg; Johanna Arlinger, Nadi Jahromi, Susanne Ekendahl, Lotta Hallbeck. Rune Nordquist, GEOSIGMA AB (Uppsala) contributed to development of the conceptual model for groundwater recharge.

## 1. INTRODUCTION

The SKB concept for disposal of high level waste includes isolation of spent fuel in copper canisters buried several hundred meters in granite bedrock. Repository safety depends on the design of engineered barriers; canisters, buffer and backfill material. Safety assessment must, however, consider possible failure of these barriers. Exposure of the biosphere to long-lived radionuclides then depends on hydrology and radionuclide adsorption and solubility. Of special concern are the long-lived isotopes of Neptunium, Plutonium, Technetium, Iodine, and Cesium. For anoxic conditions, Np, Pu, Tc and U form sparingly soluble solids. Under oxic conditions they are highly soluble and thus mobile.

Performance assessment issues related to groundwater redox chemistry are:

1. The persistence of molecular oxygen, which can corrode copper metal, in the deep environment at the time of repository closure.
2. Production of hydrogen sulfide, which can corrode copper metal, in the deep environment after repository closure.
3. Dissolved oxygen in vertical fracture zones due to surface water inflow during construction and operation of the repository.

The Äspö Redox Experiment in Block Scale addresses molecular oxygen entering fracture zones during construction of a deep repository.

On March 13, 1991 construction of the access tunnel to the Äspö Hard Rock Laboratory (HRL) intersected a vertical fracture zone at a depth of 70 meters. The fracture zone hydrochemistry was then monitored through time. Groundwater sampling and analysis before intersection by tunnel construction, and examination of drillcores taken from the fracture zone early in the experiment, provide a reference state against which to compare subsequent evolution of groundwater conditions. The shallow groundwater is dilute while the native groundwater is extremely saline. Dilution of chloride ion is therefore a good indicator of surface water intrusion.

### 1.1 OBJECTIVES

The objectives of this experiment are:

1. to determine the extent of surface water intrusion induced by opening the fracture zone at a depth of 70 meters,
2. to observe if molecular oxygen transport from the surface or from the tunnel can create oxic conditions in the fracture zone,



3. to identify and quantify dominating transport and reaction processes; i.e. develop a site model for the fracture zone.

## 1.2 PREDICTION OF OXYGEN FRONT BREAKTHROUGH

We predicted the breakthrough times for surface water and dissolved oxygen to the 70 meter depth, expected upon intersection of the fracture zone (Banwart and Gustafsson, 1991; SKB Progress Report 25-91-06). The objective of these predictions was to list possible influences on oxygen transport and consumption, and to understand the relative importance of hydraulic and chemical parameters; porosity, wetted surface area, reducing capacity. Table 1 lists the results of these scoping calculations.

**Table 1. Prediction of Surface Water and Oxygen Front Breakthrough Times (Banwart and Gustafsson, 1991; SKB Progress Report 25-91-06).**

number of connected fractures	effective transmissivity ( $\text{m}^2 \text{s}^{-1}$ )	flow porosity	surface water arrival	oxygen front arrival
1	$1.0 \times 10^{-7}$	$1.0 \times 10^{-3}$	20.8 d	-
1	$1.0 \times 10^{-7}$	$1.0 \times 10^{-3}$	18.8 d	6 months
1	$1.2 \times 10^{-6}$	$2.0 \times 10^{-4}$	6.3 h	36 h
3	$4.0 \times 10^{-7}$	$2.5 \times 10^{-4}$	7.0 h	4.5 d
10	$4.0 \times 10^{-8}$	$2.5 \times 10^{-4}$	3.5 d	5 years
10	$4.0 \times 10^{-8}$	$2.5 \times 10^{-4}$	3.5 d	*10 months

We calculated surface water breakthrough times using analytical solutions for flow in homogeneous porous media. Multiplying surface water inflow ( $\text{L h}^{-1}$ ) by concentration of  $\text{O}_2(\text{aq})$  ( $\text{mole L}^{-1}$ ), at  $\text{O}_2(\text{aq})$  saturation, estimated the oxygen input rate ( $\text{mole L}^{-1} \text{h}^{-1}$ ). Retardation of oxygen was estimated by dividing the reducing capacity ( $\text{mole eq. L}^{-1}$ ) of the fracture zone by the oxygen input rate ( $\text{mole eq. L}^{-1} \text{h}^{-1}$ ). The reducing capacity is the amount of dissolved reductants;  $\text{Fe(II)}(\text{aq})$ ,  $\text{Mn(II)}(\text{aq})$  and organic carbon., as well as iron(II) sites on the inner pore surfaces of the granite block confining the fracture flow path. The volume of granite available for reaction with oxygen was estimated using the average diffusion depth for a non-reactive tracer during the time for oxygen breakthrough. This estimate is conservative because we know that oxygen reacts rapidly with reducing minerals such as biotite (White and Yee, 1985). If these reactions occur within the granite pores, and are coupled to slow diffusion through the rock matrix, then enhanced mass transfer of oxygen from the flow path will occur.

\*Diffusion Coefficient,  $D = 10^{-14} \text{ m}^2 \text{ s}^{-1}$ ; compared to  $D = 10^{-13} \text{ m}^2 \text{ s}^{-1}$  used otherwise

A sharp dilution front arrived in the access tunnel 21 days after intersection of the fracture zone. An oxidizing disturbance subsequently occurred between days 25 - 50, as evidenced by the disappearance of dissolved iron in the inflow to the access tunnel. At that time, the results were in accordance with what was expected. After this time, however, the fracture zone rapidly returned to reducing conditions with intensive anaerobic respiration of organic carbon. The initial and boundary conditions used in the predictions were incorrect. Contrary to our model formulation, the input of organic carbon from the soils and sediments overlying the fracture zone was much larger than the input of dissolved oxygen.

1. Dissolved oxygen should have been treated as an initial condition which was flushed from the system when the fracture zone was opened by tunnel construction. Further input of dissolved oxygen was not significant.
2. There was, however, a constant flux of organic carbon from the soils and sediments at the upper boundary of the fracture zone. This continuous input added reducing capacity. Microbial respiration provided an efficient catalytic pathway for organic carbon to scavenge oxidants in the system, thereby maintaining anoxia.

### 1.3 OBSERVED RESULT AND SIGNIFICANCE OF RAPID SURFACE WATER INFLOW

Three years after the initial disturbance by tunnel construction, the fracture zone remains persistently anoxic. Molecular oxygen is apparently consumed in the most shallow reaches of the fracture zone, and in a relatively thin reactive "skin" around the access tunnel. The influx of organic carbon increases rates of anaerobic respiration within the fracture zone. These results show that organic carbon can play an important role in maintaining anoxia in the upper groundwater environment under the highly disturbed hydraulic conditions created by tunnel construction. This implies that even thin soil covers, as at this site, are important controls on groundwater redox status during the construction and operation phase of a deep repository.

## 2. SITE DESCRIPTION

The Äspö Hard Rock Laboratory (HRL) is located on the Baltic coast near the city of Oskarshamn in S. E. Sweden. The access tunnel to the HRL starts at the coastline and proceeds approximately 4 km out under the sea floor and terminates under the island of Äspö. The experimental site is on the small island of Hälö lying between the coastline and Äspö. Figure 1 shows the location of the HRL and the fracture zone studied in this project.

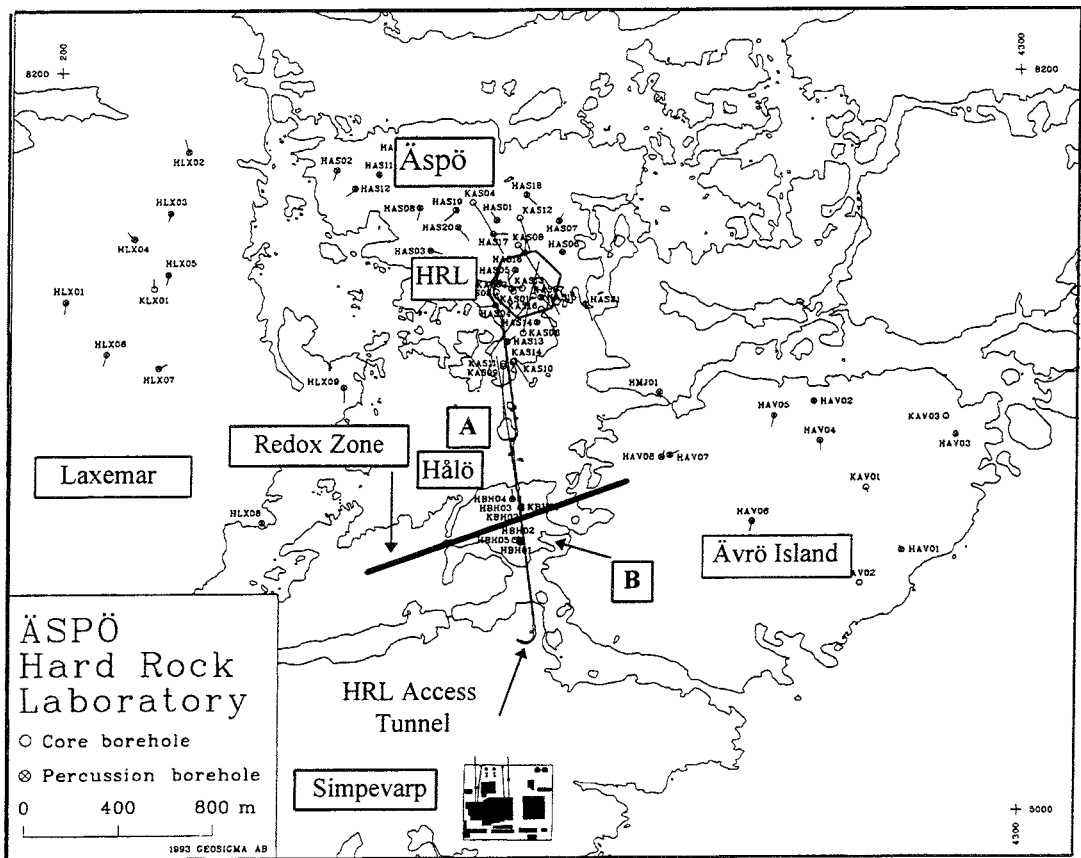


Figure 1. Locator map showing the Äspö Hard Rock Laboratory (HRL) and the fracture ("Redox") zone on Hälö island studied in this project. The access tunnel to the HRL is shown as a heavy black line starting at Simpevarp on the Baltic coast and passing under the floor of the archipelago to the island of Äspö.

The island of Hålö comprises a slightly undulating topography of well exposed rock 5 - 10 m above sea level. The geology is characterized by a red to gray porphyritic granite-granodiorite known locally as "Småland" granite, belonging to the vast Transscandinavian Granite-Porphry Belt (Gaal and Gorbetshev,1987) with U-Pb intrusion ages between 1760 - 1840 Ma (Johansson,1988), i.e., late- to post-orogenic in relation to the Svecofennian origin (1800-1850 Ma). The major fractures and fracture zones control recharge, discharge and ground water flow through the island(s) (Smellie and Laaksoharju,1992).

Figure 2 is a representation of the cross-section of the fracture zone studied. It transects the island of Hålö and appears from the surface as a small depression in the exposed granite. The depression is 2-5 m wide, 2-3 meters deep, and extends (220 m) laterally across the northern tip of the island. The access tunnel to the Hard Rock Laboratory slopes downwards toward Äspö, intersecting the fracture zone at a depth of 70 meters.

The topography along the fracture zone defines a catchment area, on Hålö itself, of 10,000 m<sup>2</sup>. Considering average annual precipitation (550-675 mm) and evapotranspiration (500 mm) leaves 50-175 mm each year for runoff and groundwater recharge. This corresponds to a maximum recharge of 1.0 - 3.3 L min<sup>-1</sup> from Hålö alone. Prior to intersection of the fracture zone by tunnel construction, the water table above the tunnel was approximately 0.5 m below the ground surface and approximately 1.5 m above the surrounding level of the Baltic Sea. There was only a slight drawdown in the water table during the experiment, i.e., the fracture zone remained hydraulically saturated.

Within the depression, directly above the tunnel, there is a 0.2 m deep layer of organic-rich soil. This soil overlies a zone of re-worked sand and gravel extending to 0.5 meters, below which a layer of glacial clay extends to at least 1 meter depth. A percussion borehole drilled from the surface showed a granite base at a depth of 5 meters. A moraine layers exists between the glacial clay and the granite, as indicated by loose moraine fragments during attempts to drill a borehole into the fracture zone at a depth of only 3 meters.

The plane of fracture is approximately vertical and is clearly visible from the interior of the access tunnel as a band of water-bearing fractured rock with a nominal width of 1 meter. The tunnel intersects the vertical plane of the fracture perpendicularly at a distance 513 meters from the tunnel mouth.

# INVESTIGATIONS OF SUB-SURFACE REDOX PROCESSES AT THE ÄSPÖ HARD ROCK LABORATORY, SWEDEN

S. Banwart, E. Gustafsson, M. Laaksoharju, A-C. Nilsson, K. Pedersen, E-L. Tullborg, B. Wallin and P. Wilberg

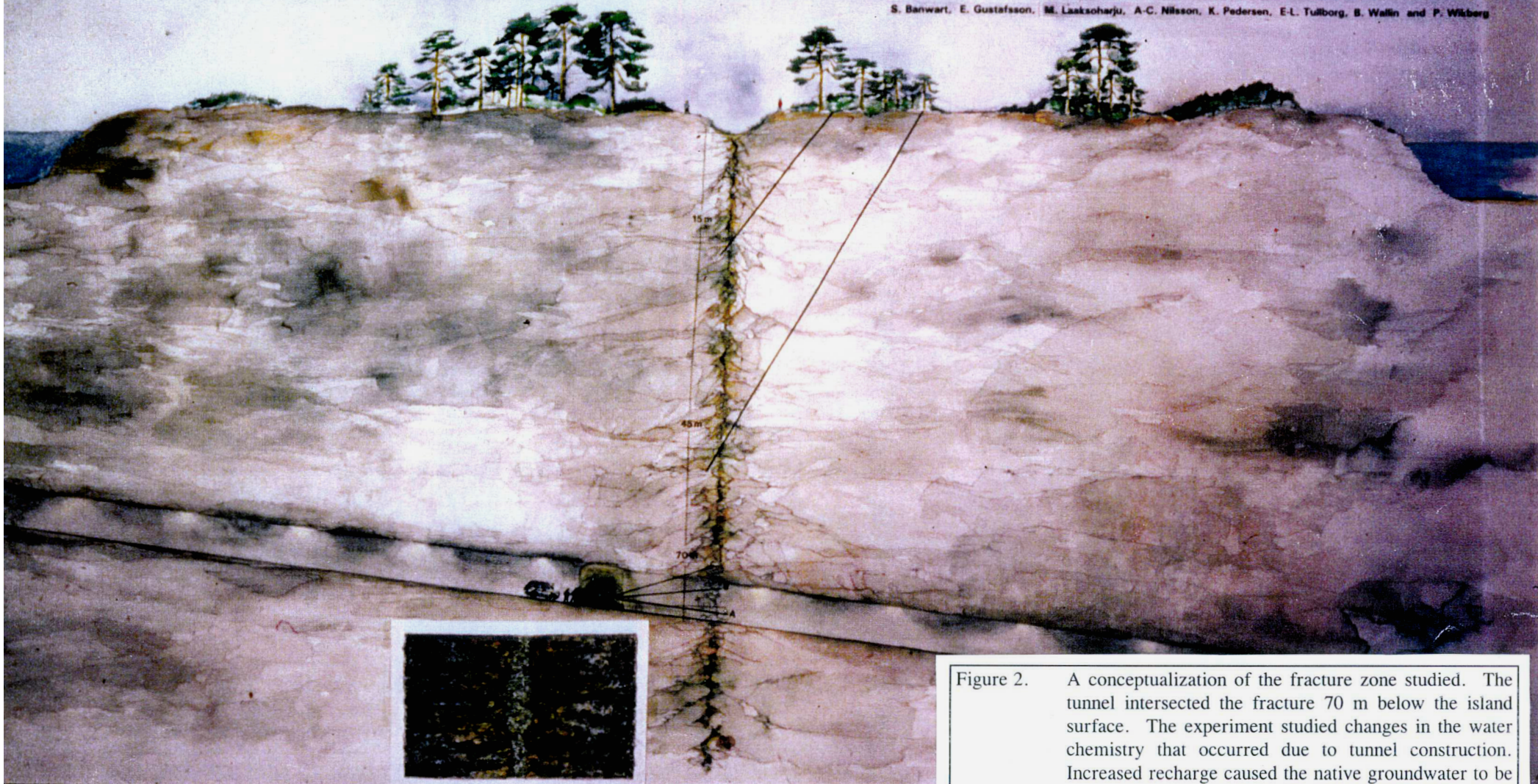


Figure 2. A conceptualization of the fracture zone studied. The tunnel intersected the fracture 70 m below the island surface. The experiment studied changes in the water chemistry that occurred due to tunnel construction. Increased recharge caused the native groundwater to be diluted. Anaerobic microbial processes were stimulated by transport of soil carbon from the surface, which also helped maintain the anoxia in the bedrock.

Table 2 lists characteristic compositions of the dominant hydrochemical reservoirs. Based on the groundwater classification for Äspö (in The Proceedings of the 2nd Äspö International Geochemistry Workshop, Äspö International Cooperation Report in preparation, M. Laaksoharju and B. Wallin, Eds.) and the location of this fracture zone within the Baltic Archipelago, we identified three dominant water types at this site; dilute shallow recharge water ( $[\text{Cl}^-]=10 \text{ mg L}^{-1}$ ), brackish native groundwater ( $[\text{Cl}^-]=5000 \text{ mg L}^{-1}$ ), and Baltic Sea water ( $[\text{Cl}^-]=2000\text{-}4000 \text{ mg L}^{-1}$ ). Figure 3 shows how the composition of local groundwaters are classed according to composition.

**Table 2. Chemical Composition of Shallow and Native Groundwater and Baltic Seawater**

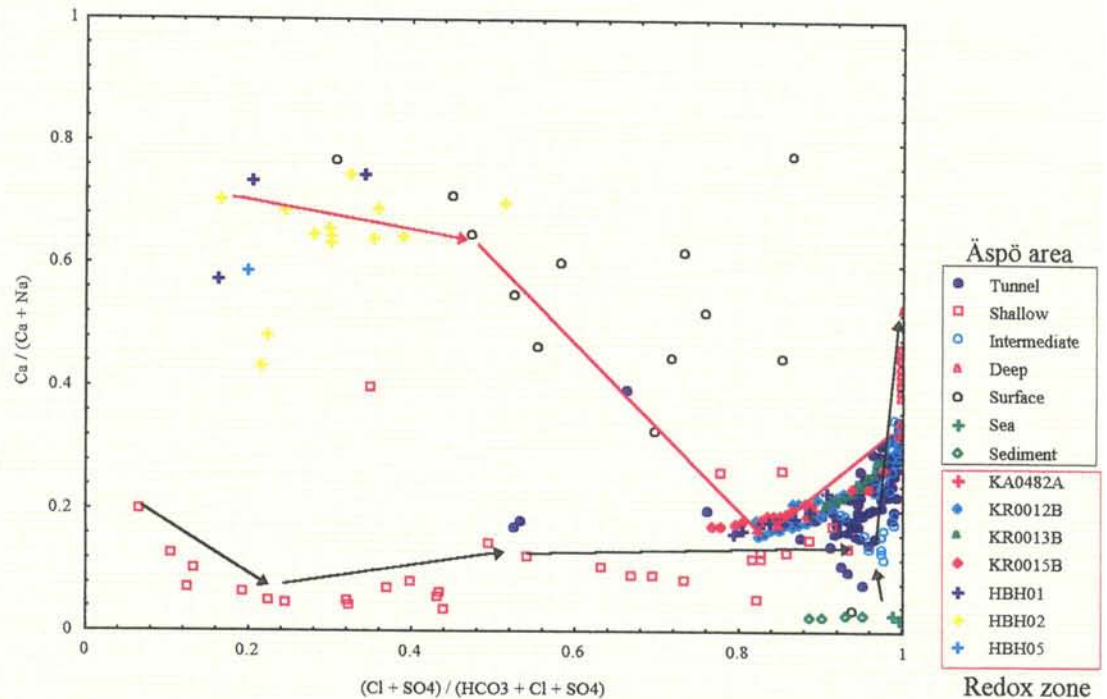
Variable	Shallow Groundwater	Native Groundwater	Baltic Seawater
$[\text{Cl}^-]$ , mg L <sup>-1</sup>	6.0	4890	3760
$[\text{Na}^+]$ , mg L <sup>-1</sup>	10.3	1480	1960
$[\text{Ca}^{2+}]$ , mg L <sup>-1</sup>	43	1250	94
$[\text{Mg}^{2+}]$ , mg L <sup>-1</sup>	3.3	132	234
$[\text{HCO}_3^-]$ , mg L <sup>-1</sup>	114	42	90
$[\text{SO}_4^{2-}]$ , mg L <sup>-1</sup>	19.5	60	504
$[\text{Si}]_{\text{total}}$ , mg L <sup>-1</sup>	6.8	5.6	0.2
$[\text{Fe}]_{\text{total}}$ , mg L <sup>-1</sup>	0.95	0.6	0.2
$[\text{Mn}]_{\text{total}}$ , mg L <sup>-1</sup>	0.43	0.94	0.05
TOC, mg L <sup>-1</sup>	20.0	*0.5	14
pH	6.6	7.5	8.2
$\delta^{18}\text{O}$ , ‰ SMOW	-10.2	-11.3	-5.9
3H, TU	60	8.4	42

**Shallow Groundwater:** sampled Sept. 12, 1991 (day 182) 24 meters along surface borehole HBH02 (15m depth from surface).

**Deep Groundwater:** sampled March 12, 1991 (day -4) from borehole KA0483 drilled into fracture zone at 70 meter depth prior to intersection by tunnel construction.

**Baltic Seawater:** sampled august 28, 1992 (day 534) from 2 m depth off the north shore of Hålö

\* TOC (total dissolved organic carbon): was not analyzed in the sample taken from KA0483, but was estimated from data for similar groundwater types on Äspö.



**Figure 3.** A modified Piper Plot showing the main groundwater types from the fracture zone and Äspö. Ca, Na, SO<sub>4</sub>, HCO<sub>3</sub> and Cl refer to molar concentration of each solute. The water sampled from different locations are broadly grouped into 1) fresh recharge water whose composition plots in the upper left hand quadrant, 2) deep saline groundwater which plots in the lower right hand quadrant, 3) Baltic Sea water which plots in the middle of the vertical axis along the right hand boundary. A possible evolution line for the Äspö groundwaters is shown with black arrows. The possible mixing line for the fracture zone is shown with red arrows.

The deep groundwaters of Äspö, samples taken from the 1200 meter deep borehole at Laxemar and the native groundwater sampled from the fracture zone at the start of the experiment fall closely together within the deep groundwater group. This indicates that the native groundwater in the fracture zone has a composition that is very similar to other groundwaters in the area.

Samples not grouped within these broad classes of water types are likely to be mixtures of them. This holds for samples taken from the fracture zone.

These waters fall between the recharge water and deep groundwater groups. The composition of groundwater in the fracture zone is dominated by dilution of the native groundwater by the rapidly inflowing recharge water.

Significant inflow of seawater to the fracture is not likely because the samples taken during the experiment plot farther away from the seawater group than the native groundwater sampled at the start of the experiment; i.e. there was evolution away from waters with seawater composition.

Figure 4 summarizes the fracture zone mineralogy and the Fe(II) content of host rock and fracture minerals based on characterization of drillcores taken from the three boreholes in the side tunnel (Tullborg, 1995, in SKB Progress Report 25-95-06). The unaltered host rock is a typical granite composed of 30% quartz, 30% plagioclase, 30% K-feldspar, and 10% biotite.

Upon approaching the altered section of the drillcores, there is increasing hydrothermal oxidation of the rock. Complete oxidation of magnetite to hematite and extensive alteration of biotite to chlorite characterize the altered layer. Micro-fractures, filled with what appears to be iron oxyhydroxide, appear when approaching the fracture surface. Chlorite, calcite and epidote are the most abundant fracture minerals. Clay minerals, iron oxyhydroxides, and some hematite occur.

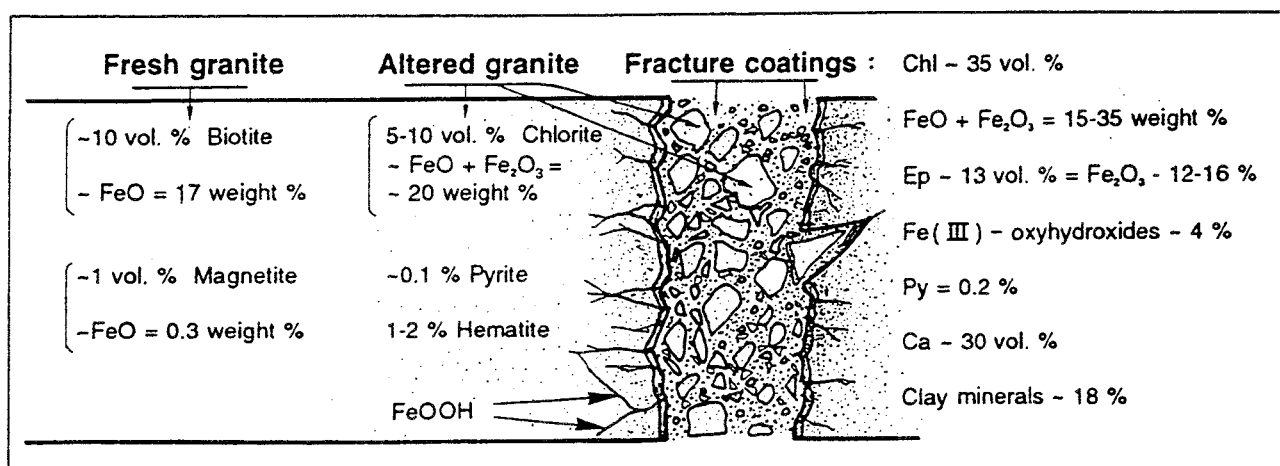


Figure 4. A representation of mineralogy in the host granite, in the altered layer at the fracture surface and in the fracture-filling material (Tullborg, 1995, in SKB Progress Report 25-95-06, Chapter 4).



### 3. EXPERIMENTAL METHODS

Experimental and analytical methods for all investigations are described in detail in the final report for this project (Banwart et al., 1995, in SKB Progress Report 25-95-06).

#### 3.1 SEQUENCE OF PROJECT ACTIVITIES

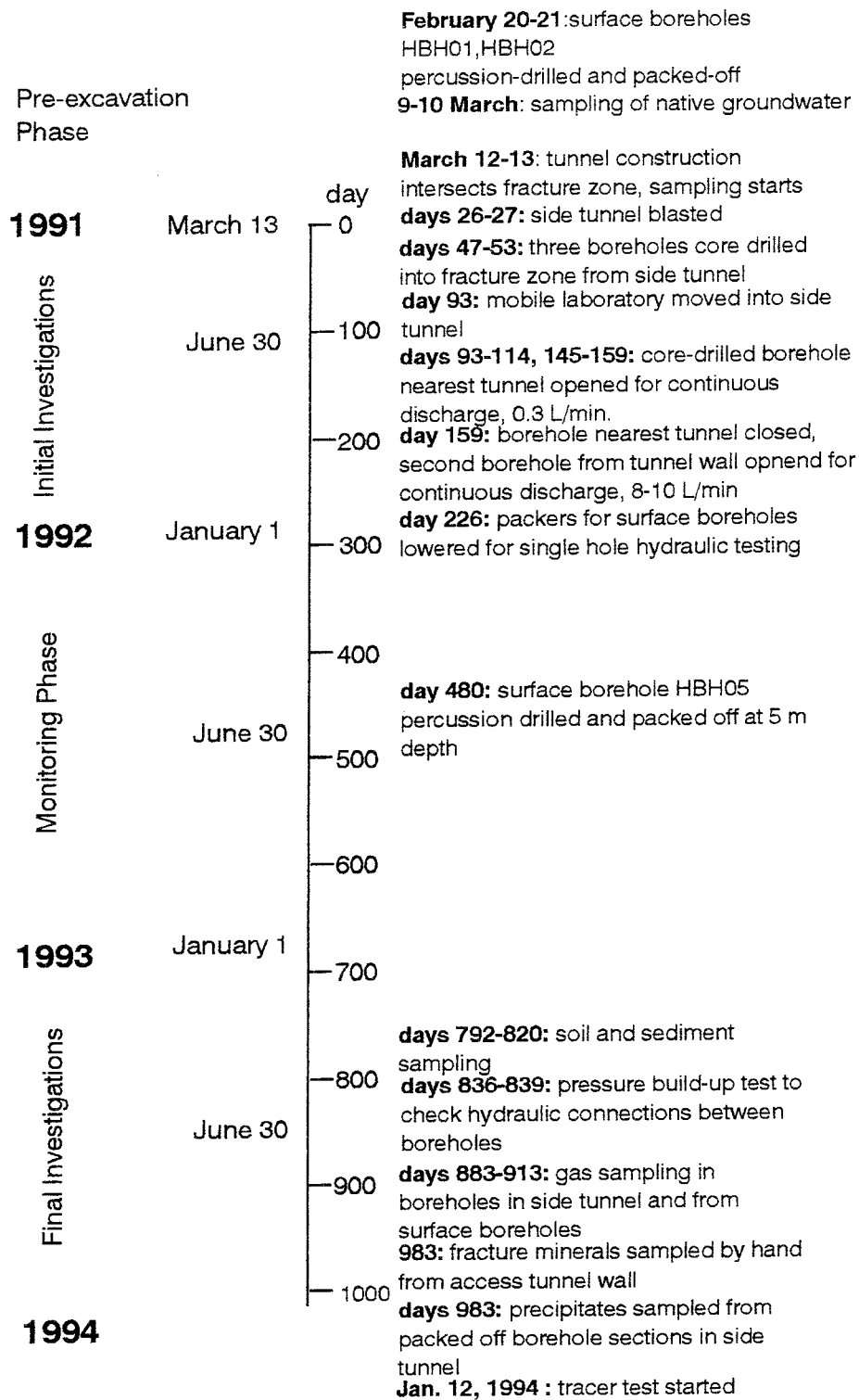
We divided the main experimental activities into 4 time periods; pre-excavation sampling, initial characterization of the fracture zone, the monitoring phase, and final investigations. Figure 5 shows the sequence of events during the project.

#### 3.2 SAMPLING LOCATIONS

Figure 6 shows the location of the boreholes sampled in this study. Two boreholes were percussion-drilled from the surface of Hälö island and intersected the fracture zone at depths of 15 and 45 meters. Four days before intersection of the fracture zone, a borehole was drilled forward from the face of the access tunnel construction zone. Groundwater from the fracture zone was sampled and analyzed for chemical composition (see Table 2). This borehole was subsequently destroyed by tunnel construction. When construction intersected the fracture zone, samples were immediately taken from an inflow point in the roof of the access tunnel.

Four weeks after intersection of the fracture zone, a side tunnel was blasted into the wall of the access tunnel to create a working area for this project. Three weeks later three boreholes were core-drilled horizontally into the fracture zone and packed off. A mobile field laboratory, equipped for continuous on-line monitoring of pH, Eh, conductivity and temperature was then parked in the side tunnel and the bore hole nearest the access tunnel wall (KR0012B) was opened for continuous discharge and monitored. After two months, borehole KR0012B was closed and the second borehole from the access tunnel wall (KR0013B) was opened. This borehole remained open throughout the remainder of the experiment.

Marine sediment core samples were taken from locations marked "A" and "B" in Figure 1. Soil core samples were taken from the surface of the fracture zone directly above the access tunnel. Drillcores from the three boreholes in the side tunnel were characterized regarding fracture zone mineralogy and stable isotope composition of fracture calcites. Suspended solid precipitates were sampled from the packed-off sections of the three boreholes in the side tunnel. Dissolved gases and microbial populations were sampled from all boreholes.



**Figure 5.** Sequence of field investigations during the Äspö Redox Experiment in Block Scale. The time scale is given as both calendar year dates and experimental days from the time tunnel construction intersected the fracture zone. The experiment is divided into 4 stages; pre-excitation, initial investigations, monitoring, final investigations. Intensive periods of activity occurred early and late in the experiment. The monitoring phase was used to evaluate results from the initial investigations.

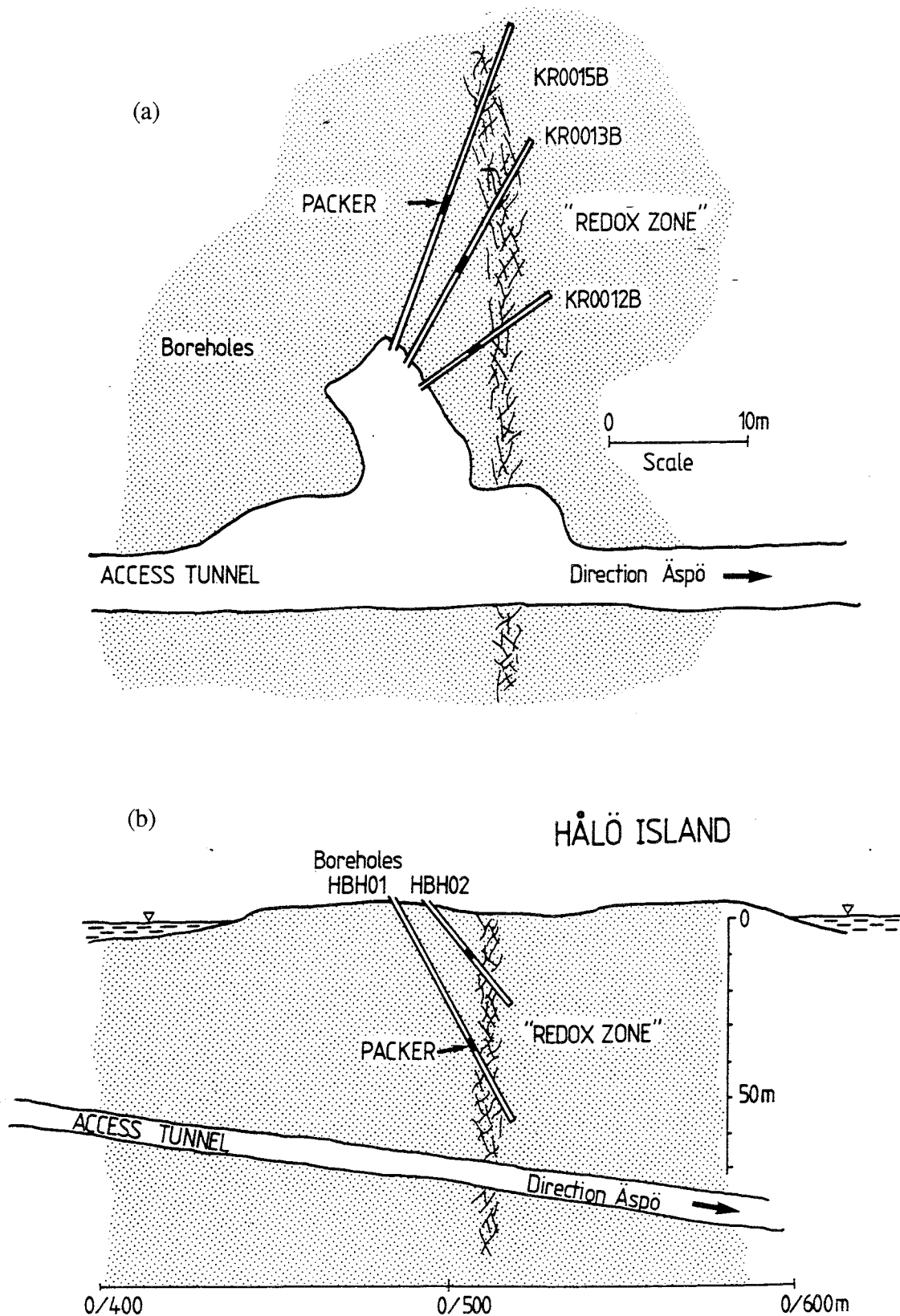


Figure 6. (a) Plan view of the side tunnel and the three horizontally core-drilled boreholes. (b) Section view of the access tunnel, fracture zone, and the location of the sampling boreholes drilled from the surface of Hålö.

#### 4. RESULTS - SITE MODEL AND MAIN EXPERIMENTAL EVIDENCE

Figures 7a and 7b represent the site model for reactive element dynamics before and after start of tunnel construction. Table 3 lists the proposed transport and reaction processes and the experimental evidence for each process. Table 4 lists results from an estimate of the maximum annual turnover of elements in the fracture zone. These results, and a critical evaluation of the site model, are discussed in the following sections.

**Table 3. Summary of Transport and Reaction Processes Observed During the Experiment and Discussed in More Detail in Sections 4.1 - 4.2.**

PROCESS	EXPERIMENTAL EVIDENCE
Vertical Recharge	<ol style="list-style-type: none"> <li>1. Chloride Dilution,</li> <li>2. Vertical movement of Natural Deuterium and <math>^{18}\text{O}</math> spike from surface</li> </ol>
Lateral Flow	<ol style="list-style-type: none"> <li>1. Chloride dilution much greater than recharge from island surface</li> </ol>
Anaerobic Respiration of Carbon	<ol style="list-style-type: none"> <li>1. elevated <math>\text{PCO}_{2(\text{g})}</math></li> <li>2. <math>^{13}\text{C}</math> <math>\text{CO}_2</math> with biogenic signature</li> <li>3. anoxic conditions</li> <li>4. elevated <math>[\text{HCO}_3^-]</math></li> <li>5. steadily increasing <math>^{14}\text{C}</math> activity in <math>\text{HCO}_3^-</math> with 98% modern C in DOC and steady <math>[\text{HCO}_3^-]</math> during final year</li> <li>6. extensive viable counts of anaerobic bacterial populations</li> <li>7. DNA sequences for anaerobic bacteria species commonly found</li> </ol>
Biological Iron(III) Reduction	<ol style="list-style-type: none"> <li>1. significant <math>\text{Fe}^{2+}</math> concentrations</li> <li>2. elevated viable counts of iron-reducing bacteria</li> <li>3. DNA sequences for iron-reducing bacteria found frequently</li> <li>4. anoxic conditions</li> <li>5. <math>[\text{NO}_3^-]</math>, <math>[\text{NO}_2^-]</math>, <math>[\text{NH}_4^+]</math> below detection limits</li> <li>6. no Mn(III,IV) minerals found</li> <li>7. no evidence of sulfate reduction (see below)</li> <li>8. calculated and measured redox potentials for <math>\text{Fe}(\text{OH})_{3(\text{s})}/\text{Fe}^{2+}</math> consistent and greater than for <math>\text{CO}_{2(\text{g})}/\text{CH}_2\text{O}</math></li> </ol>
Biogenic Methane Production	<ol style="list-style-type: none"> <li>1. elevated <math>\text{PCH}_{4(\text{g})}</math></li> <li>2. <math>^{13}\text{C}</math> <math>\text{CH}_4</math> with biogenic signature</li> <li>3. DNA sequences for methane-producing bacteria found</li> </ol>

Table 3 Continued

PROCESS	EXPERIMENTAL EVIDENCE
Sulfate/Bicarbonate Anion Exchange	<ol style="list-style-type: none"> <li>1. increasing sulfate concentrations correlate with increasing bicarbonate input</li> <li>2. no dissolved sulfide found</li> <li>3. relatively small changes in <math>^{34}\text{S}</math> signature of dissolved sulfate which suggests little fractionation due to redox reactions</li> <li>4. the amount of sulfate increase, predicted by anion exchange with increasing bicarbonate input, correlates well with observed hydrochemistry (Bruton and Viani, 1995)</li> <li>5. almost no reduced sulfur found in fracture minerals</li> <li>6. sulfate reduction ruled out by isotope and microbiology studies</li> </ol>
Na <sup>+</sup> /Ca <sup>2+</sup> Cation Exchange	<ol style="list-style-type: none"> <li>1. increasing [Na<sup>+</sup>] upon dilution of groundwater</li> <li>2. decreasing [Ca<sup>2+</sup>] upon dilution of groundwater</li> <li>3. quantitative trends in [Na<sup>+</sup>], [Ca<sup>2+</sup>] concentrations predicted by ion-exchange</li> <li>4. clay minerals found in fracture fillings</li> <li>5. clay minerals very abundant in soils and sediments</li> </ol>
Net Calcite Precipitation	<ol style="list-style-type: none"> <li>1. decreasing [Ca<sup>2+</sup>] during experiment</li> <li>2. groundwater slightly oversaturated with respect to calcite</li> <li>3. increasing <math>^{14}\text{HCO}_3^-</math> activity with steady <math>[\text{HCO}_3^-]</math> during final year</li> <li>3. <math>^{13}\text{HCO}_3^-</math> consistent with biogenic source</li> <li>4. Ca<math>^{13}\text{CO}_{3(s)}</math> signature for fracture calcites not reflected in <math>^{13}\text{HCO}_3^-</math></li> </ol>
Fe(II) Mineral Precipitation	<ol style="list-style-type: none"> <li>1. groundwater maintained near <math>\text{FeCO}_{3(s)}</math> saturation</li> <li>2. no increase in dissolved Fe(II) to correlate with evidence for Iron(III) reduction during anaerobic respiration</li> </ol>

# HÅLÖ ISLAND - Vertical

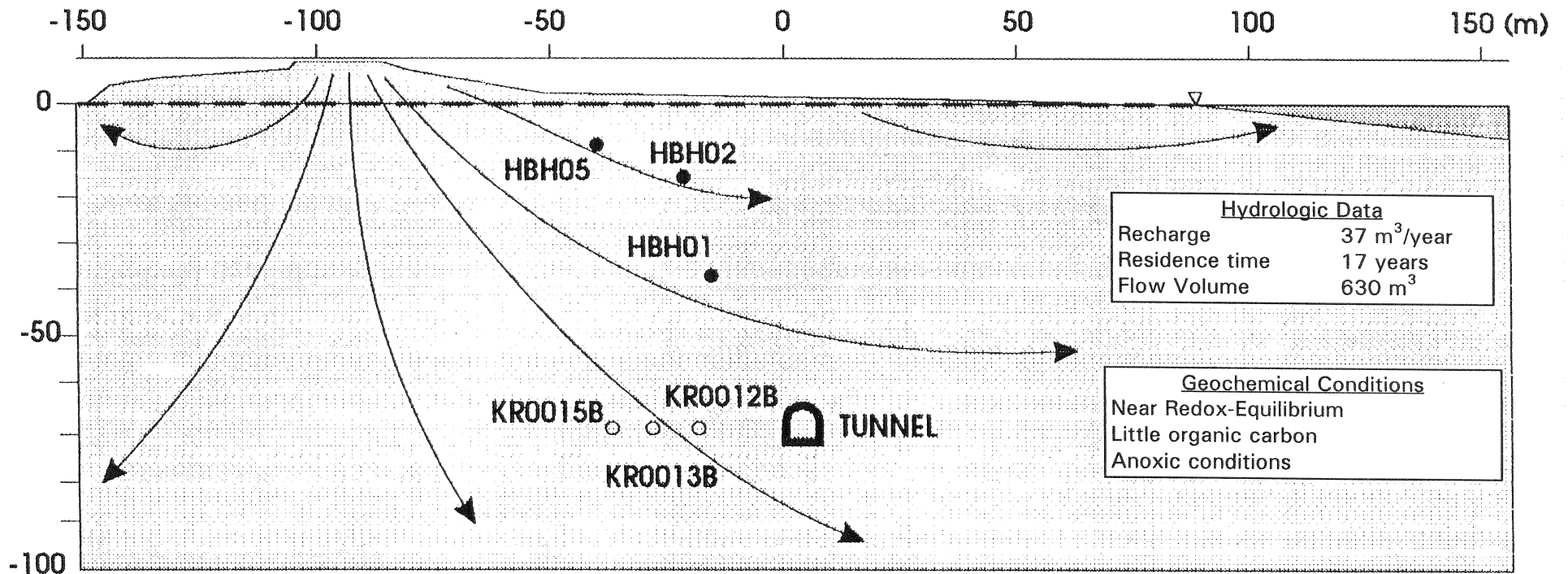
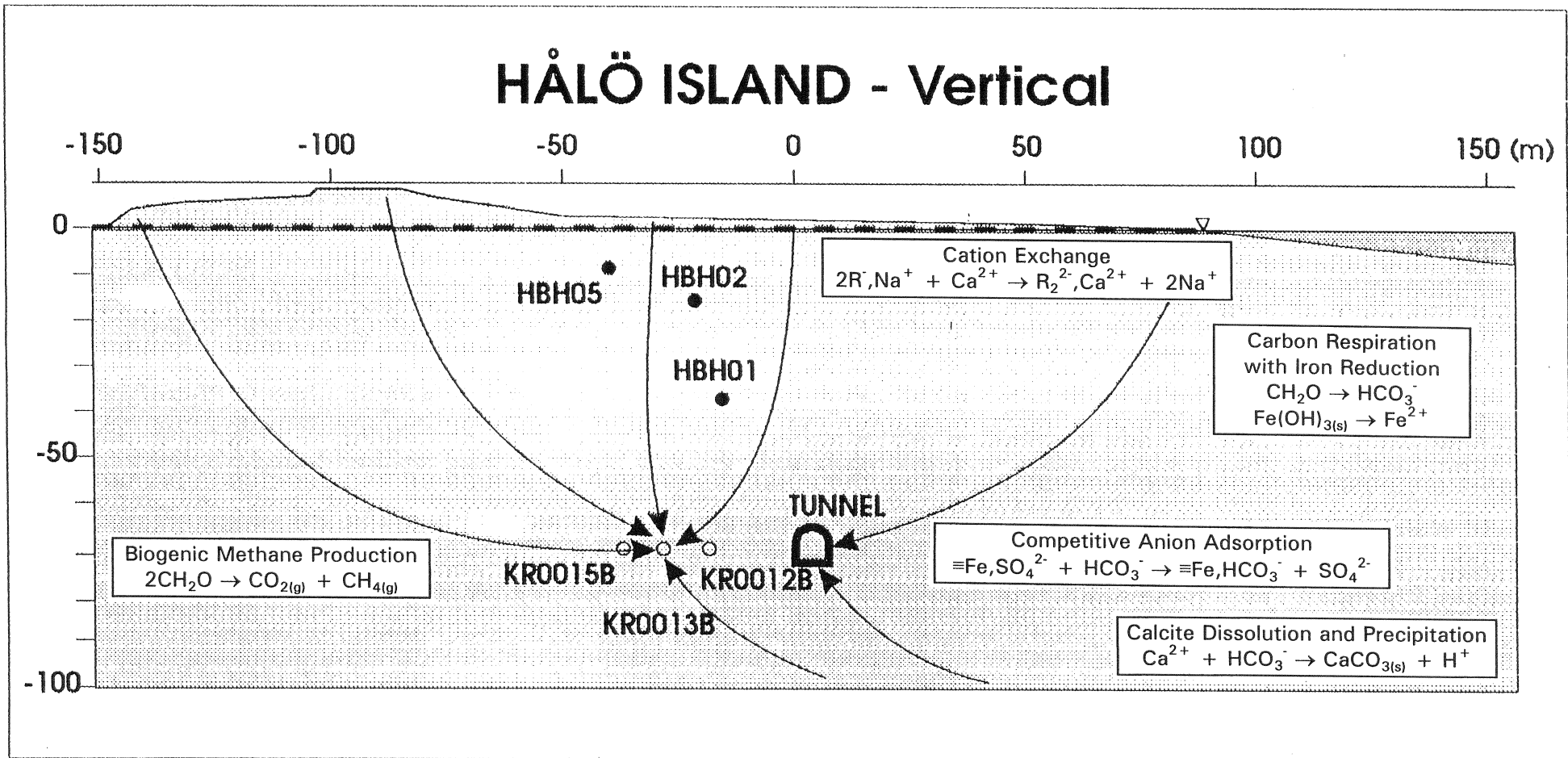


Figure 7a. Conceptual site model for undisturbed system.

**Figure 7b.** Site model for reactive element dynamics after tunnel construction. These processes were identified by investigation results listed in Table 3. Table 4 demonstrates one quantitative estimate of element turnover.

Hydrologic Data	
Total discharge	5260 m <sup>3</sup> /year
Recharge	4050 m <sup>3</sup> /year
Residence time	8 months
Flow Volume	2700 m <sup>3</sup>



**Table 4. Maximum Annual Element Turnover Assuming all Carbon Undergoes Respiration with Iron Hydroxide as Electron Acceptor. In reality, fermentation and methanogenesis take place and decrease the estimated Fe turnover accordingly.**

<b>Process Stoichiometry</b>				
<u>Anaerobic Respiration</u> $4\text{Fe}(\text{OH})_{3(s)} + \text{CH}_2\text{O} + 7\text{H}^+ = 4\text{Fe}^{2+} + \text{HCO}_3^- + 10\text{H}_2\text{O}$				
<u>Secondary Fe Mineral Formation</u> $\text{Fe}^{2+} + 2\text{Fe}(\text{OH})_{3(s)} = \text{Fe}_3\text{O}_{4(s)} + 2\text{H}_2\text{O} + 2\text{H}^+$				
<u>Calcite Precipitation</u> $\text{Ca}^{2+} + \text{HCO}_3^- = \text{CaCO}_{3(s)} + \text{H}^+$				
<u>Cation Exchange</u> $2\text{R}_2, \text{Na}^+ + \text{Ca}^{2+} = \text{R}_2^2, \text{Ca}^{2+} + 2\text{Na}^+$				
<u>Anion Exchange</u> $>\text{Fe}, \text{SO}_4^{2-} + \text{HCO}_3^- = >\text{Fe}, \text{HCO}_3^- + \text{SO}_4^{2-}$				
<u>Resulting Mass Balances:</u> $\Delta[\text{CaCO}_{3(s)}] = -\Delta[\text{Ca}^{2+}] - \frac{1}{2} \Delta[\text{Na}^+]$ $\Delta[\text{CH}_2\text{O}] = -\Delta[\text{SO}_4^{2-}] - \Delta[\text{HCO}_3^-] - \Delta[\text{CaCO}_{3(s)}]$ $\Delta[\text{Fe}_3\text{O}_{4(s)}] = -4 \Delta[\text{CH}_2\text{O}]$ $\Delta[\text{Fe}(\text{OH})_{3(s)}] = 4 \Delta[\text{CH}_2\text{O}] - 2\Delta[\text{Fe}_3\text{O}_{4(s)}]$				
<b>Sources and Sinks for Solutes</b>				
	$\Delta[\text{Na}^+]$ mM	$\Delta[\text{Ca}^{2+}]$ mM	$\Delta[\text{SO}_4^{2-}]$ mM	$\Delta[\text{HCO}_3^-]$ mM
KR0012B	8.79	-1.95	1.14	3.99
KR0015B	9.76	-1.32	1.11	5.68
<b>Annual Element Turnover (Kg per year)</b> based on Atomic Weight of Element				
Element and Reservoir	KROO12B		KROO15B	
Na: $\text{Na}^+$	838		931	
Ca: $\text{Ca}^{2+}$	324		219	
S: $\text{SO}_4^{2-}$	151		147	
C: $\text{HCO}_3^-$	198		283	
C: $\text{CaCO}_{3(s)}$	122		177	
C: $\text{CH}_2\text{O}$	377		515	
Fe: $\text{Fe}_3\text{O}_{4(s)}$	*7,023		*9,589	
Fe: $\text{Fe}(\text{OH})_{3(s)}$	*21,068		*28,767	
*Values for Fe turnover assume that all organic carbon is oxidized via Fe(III) reduction. Investigations from this fracture show substantial fermentation and methanogenic activity. All carbon cycled through those pathways would not contribute to Fe turnover, and the very high values shown here would decrease accordingly. These calculations actually provide evidence that much carbon must cycle through these alternative pathways.				



## 4.1 SUMMARY OF INVESTIGATION RESULTS

### 4.1.1 Hydrochemistry and Geochemical Modeling

Figure 8 shows the evolution of fracture zone salinity during the experiment. Results from Kriging, using the spatial distribution of chlorinity, allow visualization of salinity gradients within the fracture, and how they changed in time.

Figure 9 shows the evolution of some dominant ion concentrations during the experiment. Three weeks after intersection of the fracture zone by tunnel construction, a sharp dilution front arrived in the entrance tunnel. This appeared as a sudden decrease in chloride and base cation concentrations in the inflow water. A short time later, dissolved iron concentrations decreased to near zero for a period of a few weeks. This may have resulted from arrival of an oxidation front in the tunnel.

After this time the fracture zone became increasingly saline until the middle borehole in the side tunnel was opened for continuous discharge on day 159. After about day 50, significant dissolved Fe(II) concentrations at all sample locations, and measured redox potentials in the range  $-200 < Eh < -100$  indicated prevailing anoxic conditions.

Bicarbonate and sulfate concentrations and calculated  $PCO_2(g)$  increase significantly during the experiment. Dissolved organic carbon concentrations were in the range  $10-30 \text{ mg L}^{-1}$  at all sampling locations. Chloride, oxygen-18, and deuterium were used as natural conservative tracers. Comparison of other groundwater solutes with these tracers indicated significant sources of bicarbonate, sulfate, and sodium to the groundwater. There was a significant sink for calcium. Considering the anoxic conditions in the zone, we proposed that anaerobic respiration of organic carbon was a likely pathway for production of alkalinity and  $CO_2$ .

There was no evidence of sulfide production and sulfate concentrations increased during the experiment. Based on the results from isotopic and microbiological studies, there was no evidence for sulfate reduction. The only other dominant electron acceptor observed was iron(III) hydroxide minerals observed in the drillcores taken from the side tunnel.

Chemical speciation calculations showed the groundwater sampled in the side tunnel to be significantly undersaturated with respect to oxidative dissolution of iron sulfides;  $FeS_2(s)$  and  $FeS(s)$ . These could be the source of sulfate to the groundwater although results from the sulfur isotope studies showed little change in isotopic composition during the experiment. This makes oxidative dissolution of iron sulfide unlikely. The conservative tracers indicated no significant input of Baltic water, and thus marine sulfate, to the fracture zone.

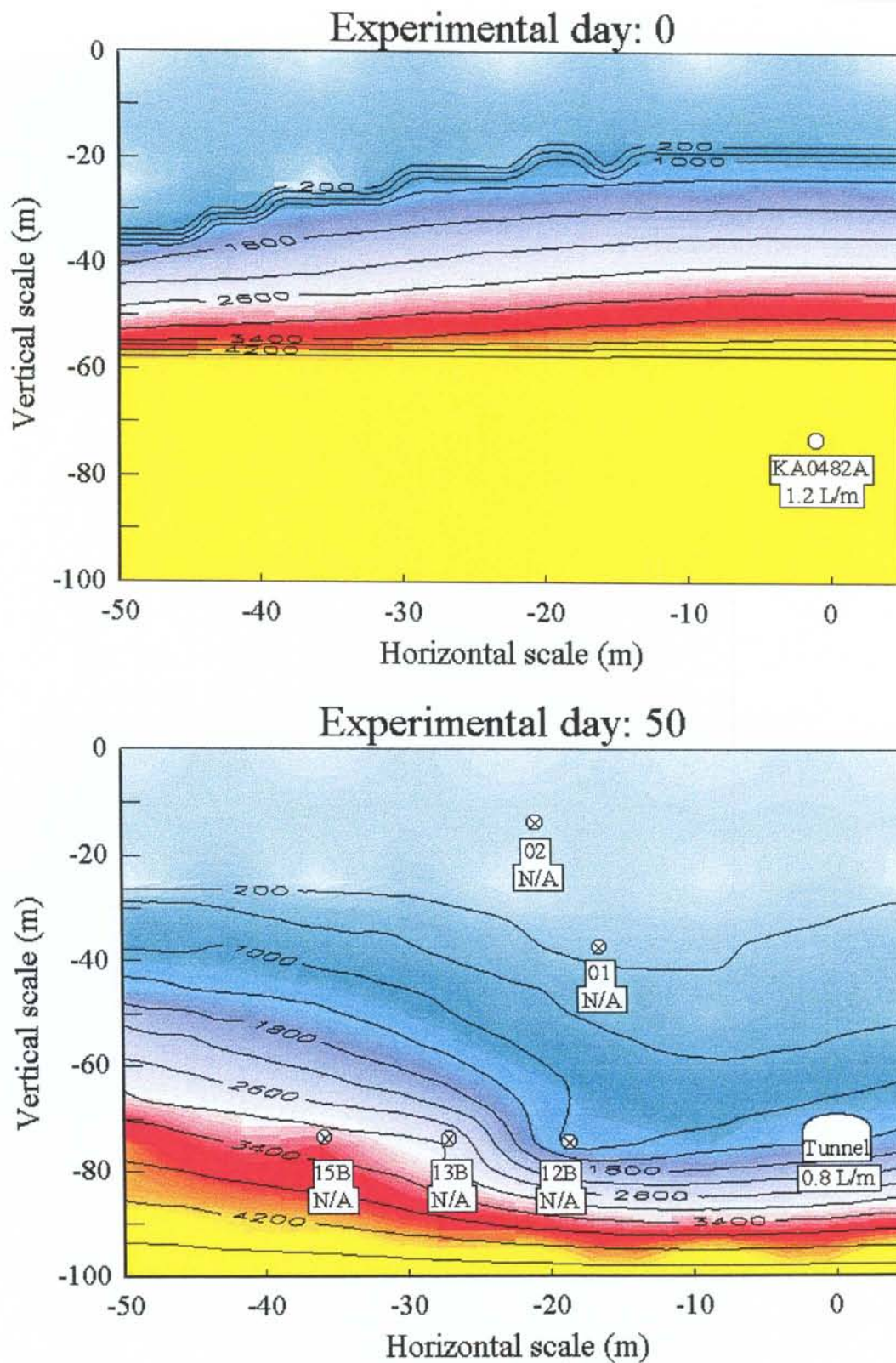


Figure 8. Evolution of groundwater salinity during the experiment. Isoconcentration lines for  $[Cl^-]$ , mg/L, were constructed using Kriging for interpolation from  $[Cl^-]$  in samples from the boreholes. The flow values (L/minute) are measured in connection with hydro- and tracer-tests. N/A = no water flow measurements,  $\otimes$  = normally closed borehole but opened during sampling,  $\circ$  = continuously open borehole. 01=HBH01, 02=HBH02, 12B=KR0012B, 13B=KR0013B, 15B=KR0015B. Taken from Laaksoharju et al., 1995, in SKB Progress Report 25-95-06, Chapter 2.

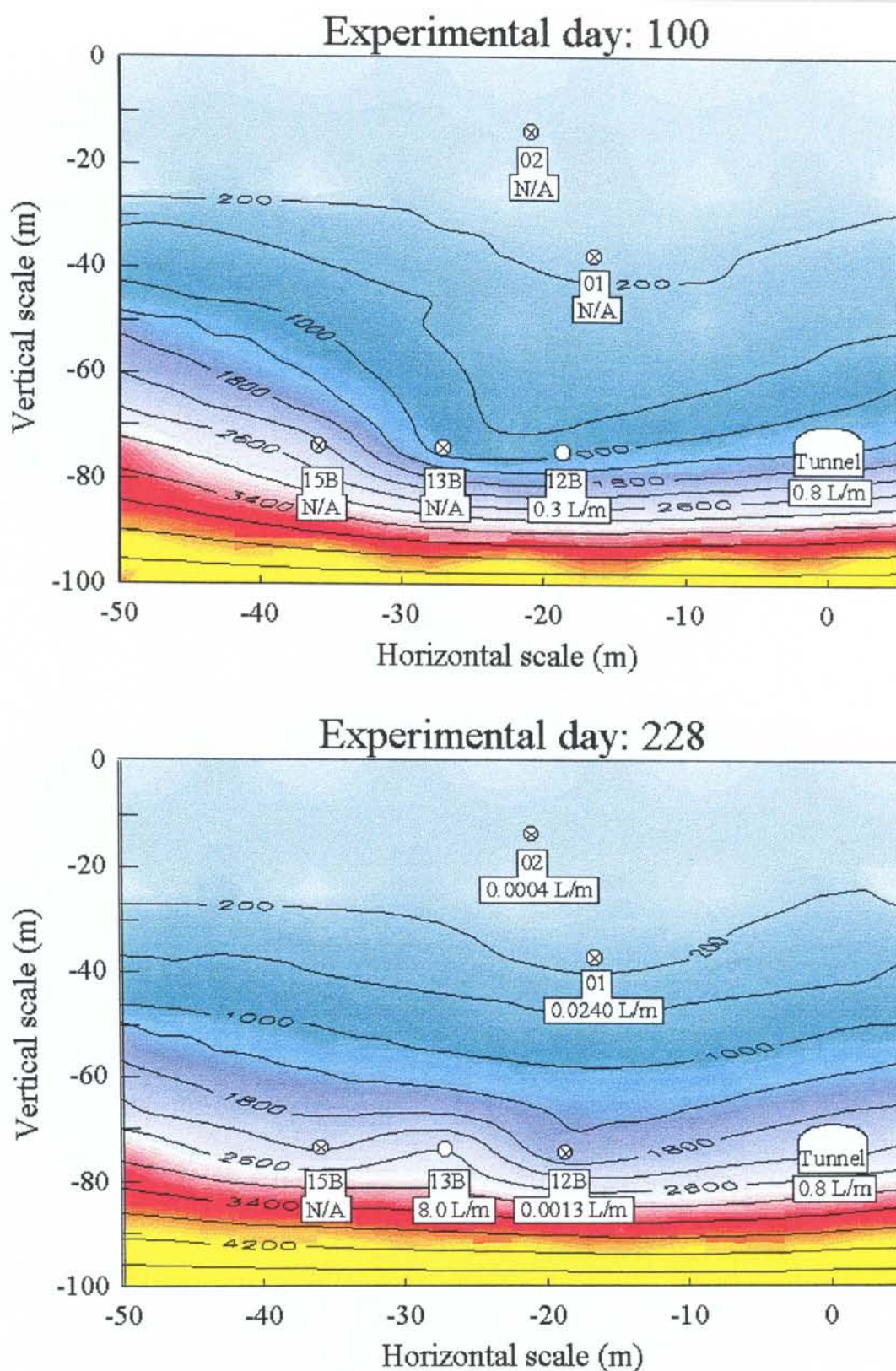


Figure 8. (Continued). Evolution of groundwater salinity during the experiment. Isoconcentration lines for  $[Cl^-]$ , mg/L, were constructed using Kriging for interpolation from  $[Cl^-]$  in samples from the boreholes. The flow values (L/minute) are measured in connection with hydro- and tracer-tests. N/A = no water flow measurements,  $\otimes$  = normally closed borehole but opened during sampling,  $\circ$  = continuously open borehole. 01=HBH01, 02=HBH02, 12B=KR0012B, 13B=KR0013B, 15B=KR0015B. Taken from Laaksoharju et al., 1995, in SKB Progress Report 25-95-06, Chapter 2.

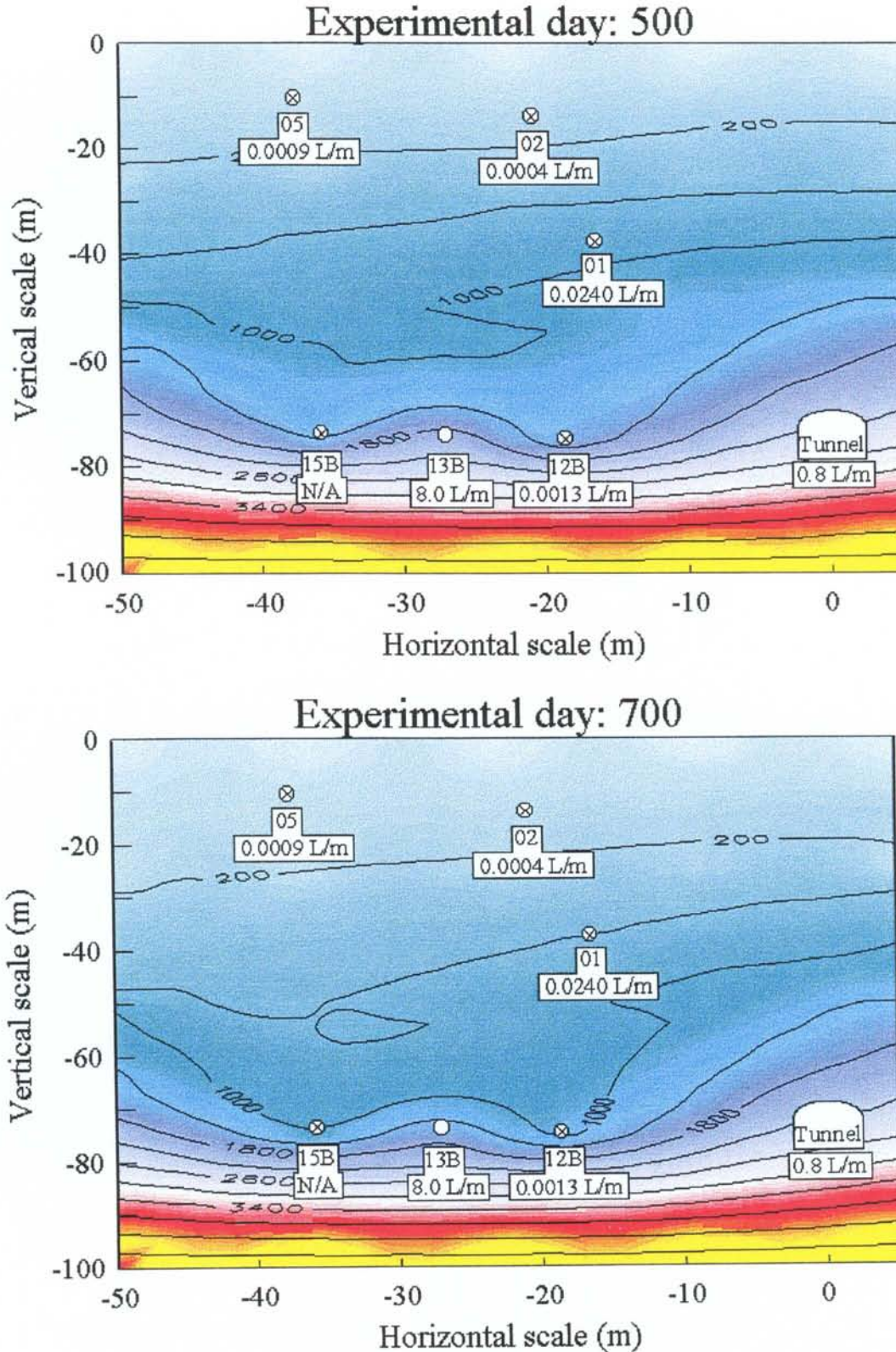


Figure 8. (Continued.) Evolution of groundwater salinity during the experiment. Isoconcentration lines for  $[Cl^-]$ , mg/L, were constructed using Kriging for interpolation from  $[Cl^-]$  in samples from the boreholes. The flow values (L/minute) are measured in connection with hydro- and tracer-tests. N/A = no water flow measurements,  $\otimes$  = normally closed borehole but opened during sampling,  $o$  = continuously open borehole. 01=HBH01, 02=HBH02, 12B=KR0012B, 13B=KR0013B, 15B=KR0015B. Taken from Laaksoharju et al., 1995, in SKB Progress Report 25-95-06, Chapter 2.

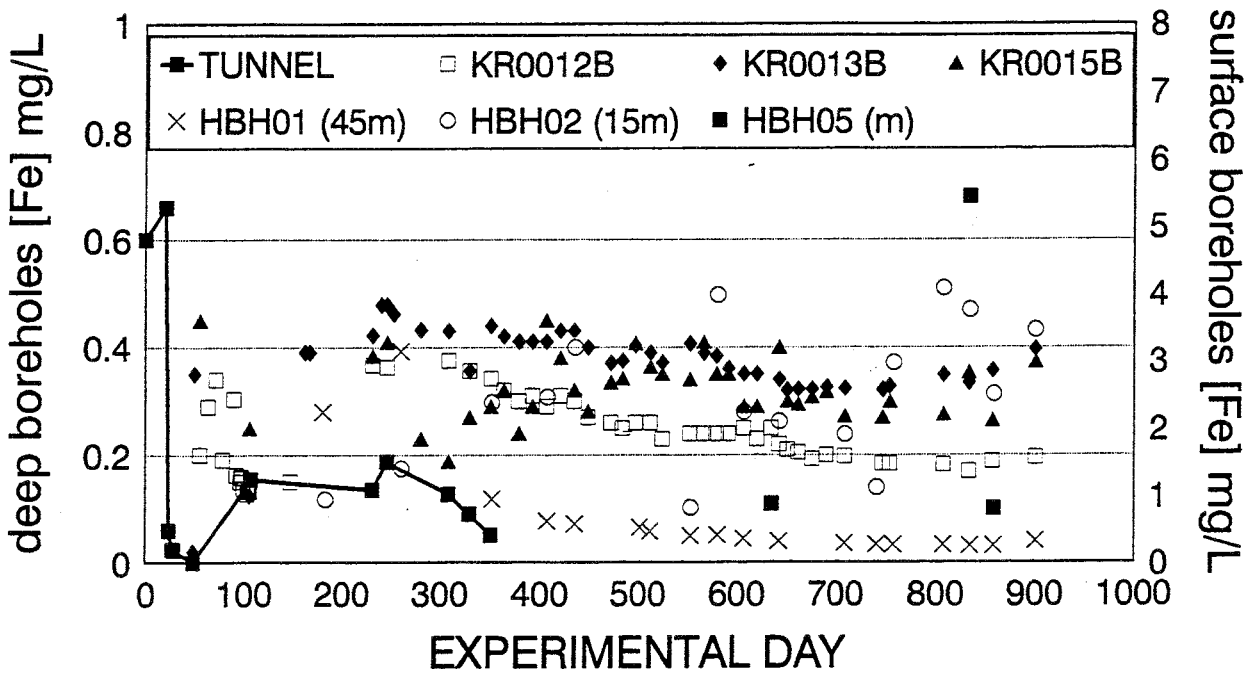
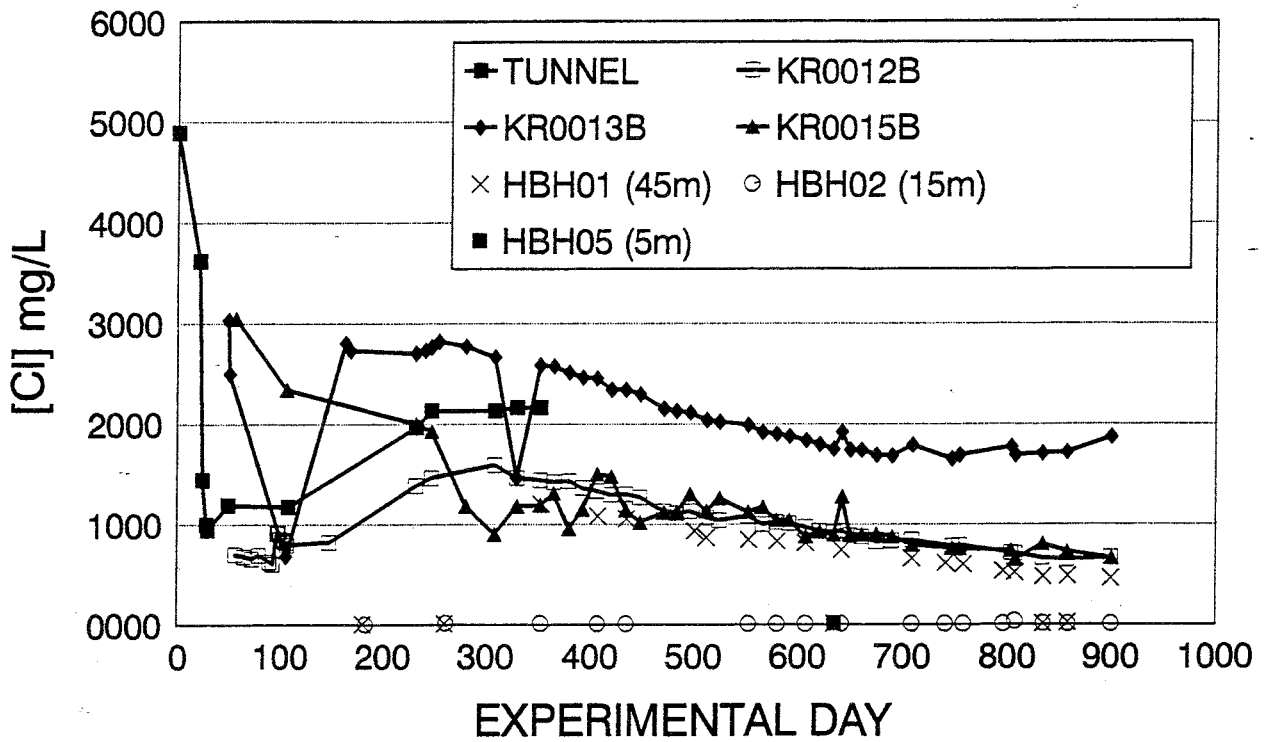


Figure 9. Change in groundwater composition during the experiment. The salinity dropped sharply at day 20. There was a subsequent decrease in dissolved Fe concentration in the inflow to the access tunnel. After this time, dissolved iron increased again, as did sulfate and bicarbonate concentrations. Taken from Banwart et al., 1995, SKB Progress Report 25-95-06, Chapter 3.

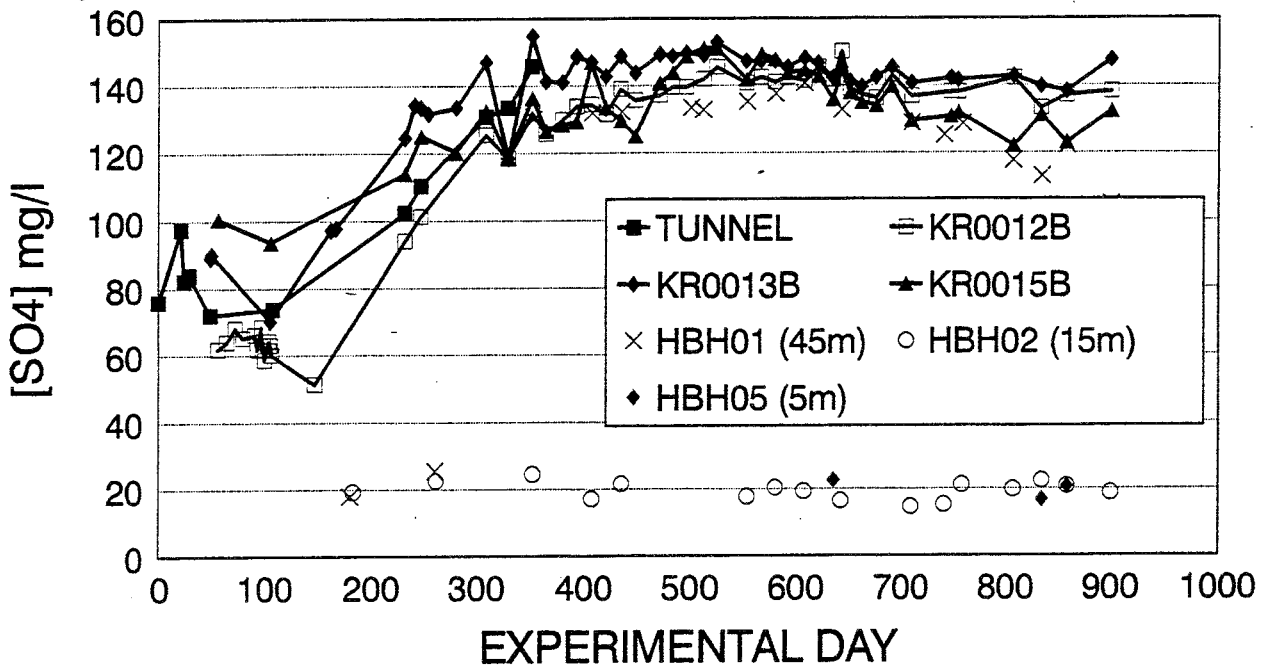
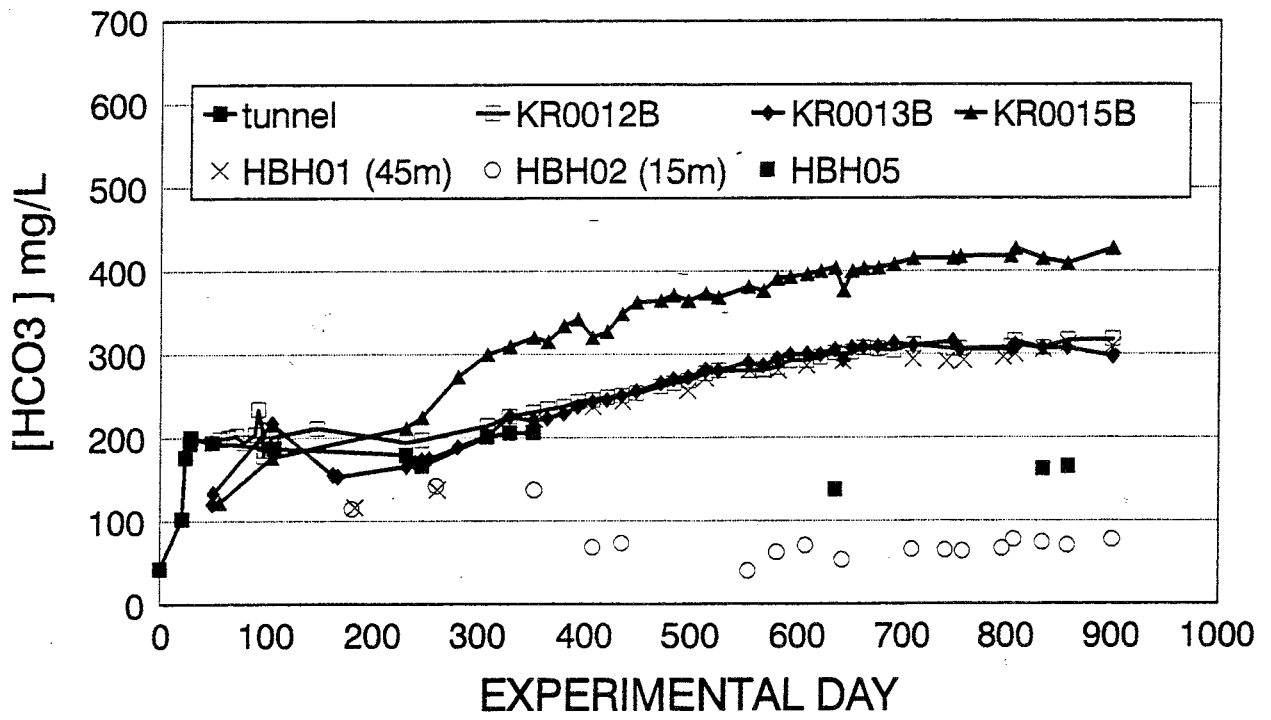
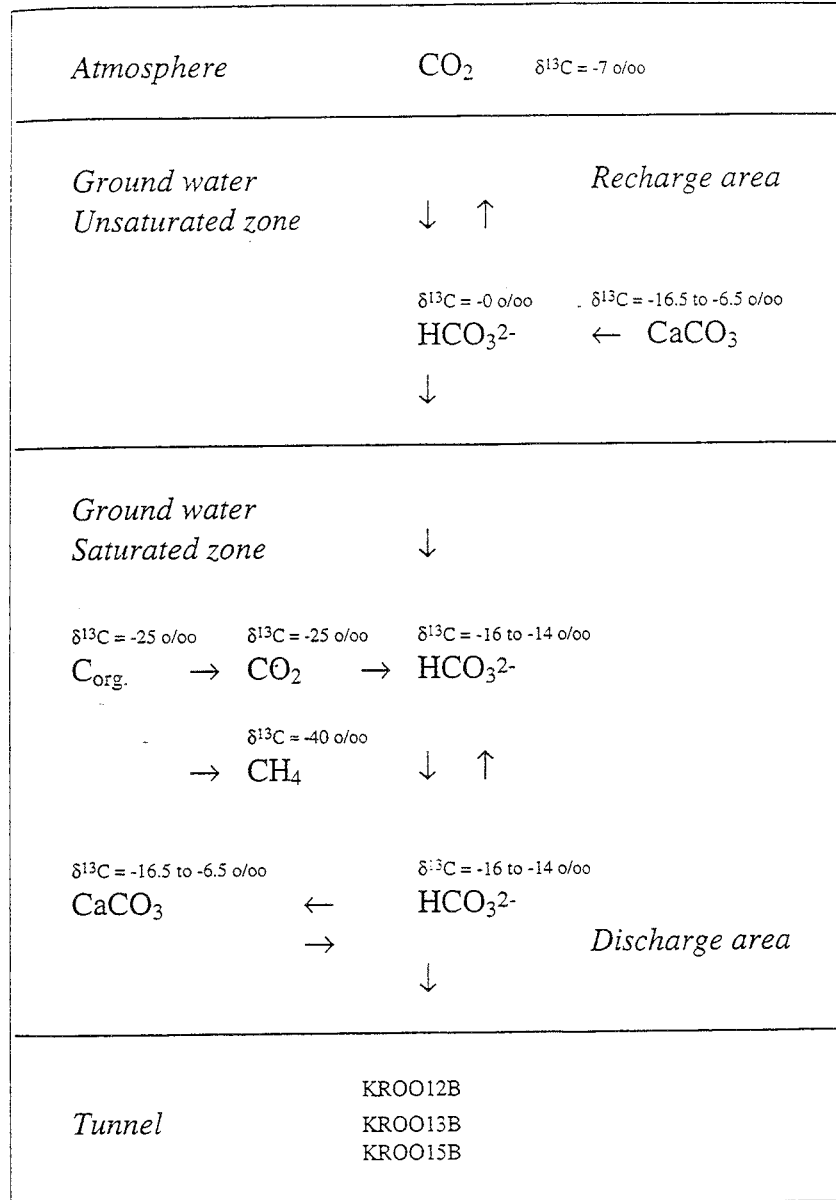


Figure 9. (Continued) Change in groundwater composition during the experiment. The salinity dropped sharply at day 20. There was a subsequent decrease in dissolved Fe concentration in the inflow to the access tunnel. After this time, dissolved iron increased again, as did sulfate and bicarbonate concentrations. Taken from Banwart et al., 1995, SKB Progress Report 25-95-06, Chapter 3.

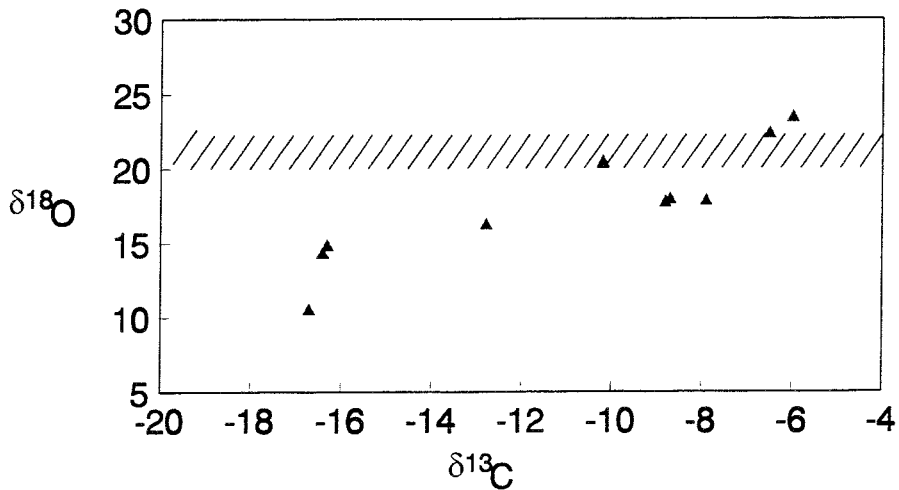
Carbon-13 Analyses

Figure 10 shows the Carbon-13 reservoirs and their isotopic signatures for the fracture zone.



**Figure 10.** Dominant carbon reservoirs and their isotopic composition for the fracture zone. The isotopic signature of fulvic acids isolated from the groundwater ( $\text{C}_{\text{org}}$ ) have an isotopic composition that is the same as that measured in  $\text{CO}_2$  sampled from the groundwater. This value is also predicted by fractionation calculations for dissolved bicarbonate, assuming an open  $\text{CO}_2\text{-H}_2\text{O}$  system for the fracture zone. This isotopic data and the high  $\text{PCO}_{2(\text{g})}$  measured indicate ongoing microbial oxidation of organic carbon. Taken from Wallin, 1995, in SKB Progress Report 25-95-06, Chapter 4.

Because the values for the dissolved bicarbonate (Table 5) fall within a very narrow range, it is unlikely that fracture calcites are the source for dissolved inorganic carbon (Figure 11). The  $\delta^{13}\text{C}$  values in Table 5 are consistent with fractionation equilibrium between dissolved inorganic carbon, biogenic carbon dioxide, and the  $\delta^{18}\text{O}$  of present day groundwater. This supports respiration of organic carbon as a source of  $\text{CO}_2$  to the fracture zone. These results rule out significant input of atmospheric  $\text{CO}_2$ .



**Figure 11.** Isotopic composition of fracture calcites sampled from drillcores taken from the side tunnel (Wallin, 1993). The wide range in  $\delta^{18}\text{O}$  (SMOW) and  $\delta^{13}\text{C}$  (PDB) indicates a variety of conditions during formation of the calcites, and thus different ages. The horizontal hatched area corresponds to  $\delta^{18}\text{O}$  values expected for fracture calcites in equilibrium with present day groundwater



**Table 5.  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  Values for Total Dissolved Inorganic Carbon (data from Wallin, 1993).**

Borehole	Date (1991)	Day	$\delta^{13}\text{C}$ o/oo PDB	$\delta^{18}\text{O}$ o/oo SMOW
KR0013B	May 1	49	-16.2	19.9
KR0013B	May 1	49	-17.4	19.7
KR0012B	June 19	98	-15.8	19.4
KR0012B	June 19	98	-15.8	21.4
KR0012B	June 19	98	-15.9	21.3

The shallow groundwater is significantly undersaturated with respect to calcite. Groundwater from the boreholes in the side tunnel was always slightly oversaturated with respect to calcite. Based on these isotope data, we further proposed that input of carbon dioxide and alkalinity from anaerobic respiration could precipitate carbonate minerals in our system.

Both processes could be occurring, possibly at different locations. Even if calcite was dissolving, it did not necessarily constitute a dominant source of inorganic carbon compared to respiration and fermentation processes.

#### Carbon-14 dating

Table 6 lists results from carbon-14 dating of organic and inorganic carbon. Comparing results from the first and final year of the project confirms a significant input of young carbon to the fracture zone.

The dramatic increase in modern carbon content for both the fulvic acid and the bicarbonate supports our initial conclusions of ongoing respiration of organic carbon. Such carbon must enter the fracture zone with the increased inflow of shallow groundwater.

A likely source of this carbon is soil-derived humic material. Because average  $^{14}\text{C}$  ages for the inorganic carbon decreases strongly during the experiment, we can rule out a significant input from fracture calcites. Because these calcites are extremely old, even a small input would greatly increase the average age of the dissolved inorganic carbon.

**Table 6. Carbon-14 Dating Analyses for Fulvic Acid and Bicarbonate.**

	Carbon-14 Age (Years)	per cent modern carbon
<b>DECEMBER 1991*</b>		
borehole KR0013B		
Fulvic Acid	640	91.8
Bicarbonate	3880	61.4
<b>MAY 1993</b>		
borehole KR0013B		
Fulvic Acid	115 ± 85	98.1
Bicarbonate	1675 ± 80	80.8
borehole KR0012B		
Fulvic Acid	140 ± 85	97.8
Bicarbonate	1565 ± 130	81.9
<b>DECEMBER 1993</b>		
borehole KR0013B		
Bicarbonate	1200 ± 60	85.7
borehole KR0015B		
Bicarbonate	645 ± 70	91.8

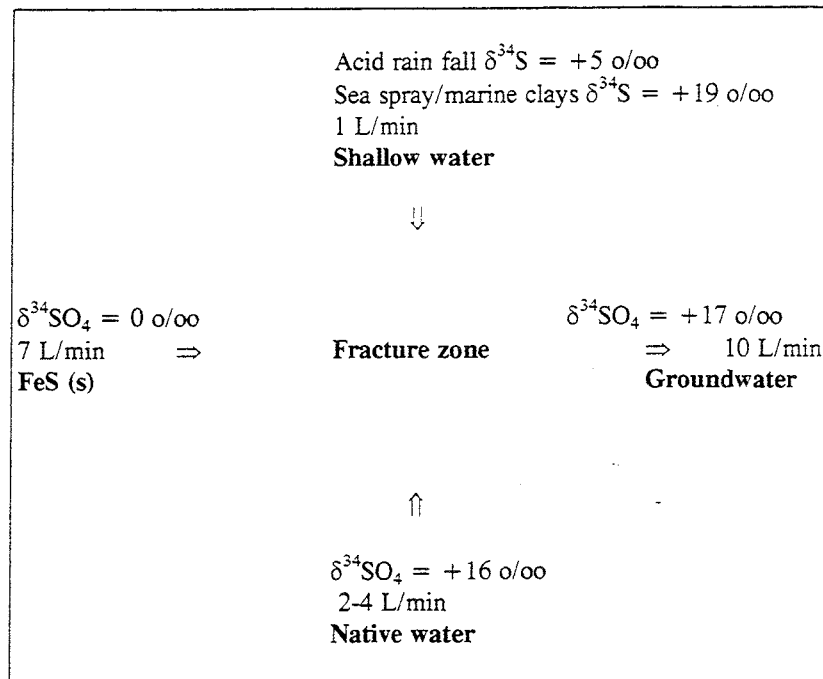
\*values from Pettersson (1992).

### Sulfur-34 Analyses

Figure 12 shows the reservoirs of sulfur and their  $\delta^{34}\text{S}$  values. By mass balance considerations, we concluded that there is a significant sulfur source within the fracture zone.

None of the observed sulfur pools can adequately explain both the high sulfate concentrations of up to  $150 \text{ mg L}^{-1}$  and the associated  $\delta^{34}\text{S}$  values of +17 ‰ observed in the groundwater during the experiment. Mono-sulfide minerals sampled from shallow marine sediments showed  $\delta^{34}\text{S}$  values near 0 ‰, sulfate in acid deposition is expected to have values of 0 to +5 ‰ and intermediate depth (200-400 m) Äspö groundwaters show  $\delta^{34}\text{S}$  values ranging between +15 and +20 ‰.

The most puzzling result is that the isotopic composition of dissolved sulfate did not change very much, in spite of a very large increase in sulfate concentration during the experiment.



**Figure 12. Dominant reservoirs of Sulfur, and their isotopic composition, in the fracture zone and connected systems. Taken from Wallin, 1995, SKB Progress Report 25-95-06, Chapter 6.**

Another explanation has been postulated by Bruton and Viani (in The Proceedings of the 2nd Äspö International Groundwater Geochemistry Workshop, M. Laaksoharju and B. Wallin, eds, Äspö International Cooperation Report in preparation). They show that increasing bicarbonate concentrations can displace adsorbed sulfate from mineral surfaces due to competitive adsorption of bicarbonate. We refer to this process as Anion Exchange in the site model.

This model is appealing because if the adsorbed sulfate is in dynamic equilibrium with the groundwater, then adding sulfate to solution through competitive adsorption of bicarbonate would not alter the isotopic composition of dissolved sulfate. This explanation resolves the problem of a large change in sulfate concentration without a corresponding change in isotopic signature.

#### 4.1.3 Microbiology

Table 7 shows results from sampling of attached growth bacteria from artificial surfaces exposed to borehole discharge, and from sampling of groundwater in the fracture zone or access tunnel inflow. These results show the absence of sulfate reducing bacteria in samples taken from the fracture zone. They also qualitatively demonstrate significant iron reducing activity for samples taken throughout the zone.

**Table 7. Total numbers of bacteria on surfaces exposed to flowing groundwater from different boreholes, results from enrichments for iron reducing and sulfate reducing bacteria and numbers of sulfate reducing bacteria determined with viable counts in agar shakes in water samples from different boreholes in the fracture zone and the Äspö tunnel area. Results from Pedersen et al.,1995, SKB Progress Report 25-95-06, Chapter 7).**

Position (depth) flow ml/min	Total number of bacteria cm <sup>-2</sup>	Sulfate- reducing bacteria enrichment	Sulfate- reducing bacteria ml <sup>-1</sup> ml <sup>-1</sup>	Iron- reducing bacteria
	921202-930207	921202	930207	930207
<b>Fracture zone</b>				
HBH 02 (10 m) pump	-	no	<20	yes
HBH 01 (40 m) pump	-	no	<5	yes
KR 0012 B (68 m) 500 ml	-	-	<10	yes
KR 0013 B (68 m) 605 ml	470,000	no	<5	yes
KR 0015 B (68 m) 1460 ml	-	-	<5	yes

These results support our previous conclusions that sulfate reduction was not a dominant process in the fracture zone, and that iron(III)-bearing fracture minerals may be important electron acceptors for organic carbon respiration. It is important to note that samples from deeper in the access tunnel (SA 0813B, 112 m depth) show significant numbers of sulfate reducing bacteria in enrichment cultures (M. Laaksoharju, ed., SKB Technical Report on Biological Sulfate Reduction in preparation).

#### 4.1.4 Fracture Minerals

We sampled fracture minerals by hand from the access tunnel wall. This material was washed, dried, and size fractionated. A key result from these investigations was identification of the smallest diameter size fraction

(<2mm) as mixed-layer clays. Table 8 summarizes the chemical composition of this size fraction, and the estimated ion-exchange capacity for the fracture zone based on the abundance of this mineral.

Calcium-Sodium ion-exchange reactions, and their possible influence on groundwater chemistry, have been modeled by Viani and Bruton (1994). Their results indicate that the increasing dilution of the native groundwater causes preferential uptake of calcium ions. This provides a sink for Ca and a source for Na to the groundwater.

An open question regarding investigations in granitic aquifers is the quantity of clay minerals hosted in fracture zone. Drilling operations probably remove much of the fine particle size fraction due to flushing by drill water.

**Table 8. Summary of Clay Mineral Abundance and Associated Ion-Exchange Capacity for Fracture Material Excavated by Hand**

size fraction	<2mm									
weight %	0.67%									
mineral type	illite, mixed layer clays									
mineral abundance	5.7 g clay Kg <sup>-1</sup> rock									
ion-exchange capacity*	0.20-1.4 mole Kg <sup>-1</sup> clay									
fracture zone porosity	0.1%									
fracture zone rock density	2800 Kg m <sup>-3</sup>									
clay mineral : water ratio	0.140 Kg L <sup>-1</sup>									
fracture zone exchange capacity	0.004 - 0.03 mole L <sup>-1</sup>									
SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	MnO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>	
%	%	%	%	%	%	%	%	%	%	%
50.4	21.01	2.09	9.52	7.02	3.48	0.11	0.95	0.19	0.36	

\* range in cation exchange capacity for illite (0.2-0.4 mole Kg<sup>-1</sup>) and chlorite-smectite mixed layer clays (0.33-1.4 mole Kg<sup>-1</sup>) taken, respectively, from reviews by Barnhisel and Bertsch (1989) and Fanning et al.(1989).

Results from this hand excavation of fracture-filling material shows a relative abundance of clay minerals. These can have a strong influence on the chemistry of base cations (Viani and Bruton, 1994) and possibly dissolved Fe(II) (Banwart et al., SKB Progress Report 25-95-06, Chapter 9) in this system.

The amount of iron hosted in this material is significant. Although the iron content is reported here as Fe<sub>2</sub>O<sub>3</sub>, the iron(II) content is relatively high (~50% of total iron). We propose above that iron(III) fracture minerals

may be reduced to iron(II) during anaerobic respiration. In this case we must conclude that there is a large in situ sink for iron(II), because no iron is mobilized from the fracture zone. Speciation calculations showed that the groundwater is near saturation with respect to siderite ( $\text{FeCO}_3(\text{s})$ ) and greatly oversaturated with respect to magnetite ( $\text{Fe}_3\text{O}_4$ ). In addition to these simple carbonate and oxide minerals, clay minerals should be considered as an important reservoir for Fe(II) within the fracture zone flow path.

#### 4.1.5 Colloid Chemistry

Table 9 summarizes the results of colloid sampling in the fracture zone, and compares these results with those from Äspö groundwaters (Laaksoharju et al., 1995, SKB Progress Report 25-95-06, Chapter 8). These results show that groundwaters sampled during this experiment show higher colloidal concentrations of Fe, S and Si than those sampled from Äspö waters. Lower concentrations of Mn, Al and Ca are observed. Because the groundwater  $\text{PCO}_{2(\text{g})}$  was much greater than atmospheric, calcite precipitation during sampling may have contributed to the Ca values.

Thermodynamic calculations show that Al is in equilibrium with respect to Aluminum hydroxide or kaolinite. Equilibrium with other clay mineral phases may also be possible. Iron is in equilibrium with respect to both iron hydroxide (goethite) and iron carbonate, according to calculated redox potentials and the thermodynamic model of Grenthe et al. (1992). Malmström et al. (1995, SKB Technical Report 95-01) propose that dissolved iron(II) may also be in equilibrium with ferrous clay minerals.

Groundwaters are always slightly oversaturated with respect to calcite. Due to the problem of  $\text{CO}_{2(\text{g})}$  degassing during sampling, the calcium content of the colloids does not provide definitive proof of in situ calcite precipitation.

The groundwater is greatly undersaturated with respect to iron sulfide phases, but is greatly oversaturated with respect to elemental sulfur. Precipitation of elemental sulfur may explain the high sulfur content of the colloids. This explanation helps resolve the problem that the sulfur content in the colloids was too high, compared to iron, to account for pyrite as a colloidal phase. Groundwaters are in equilibrium with Barite, although Ba concentrations are so low that barite formation would not influence the total sulfur content of the colloids.

**Table 9. Results of element concentrations as colloidal material, and comparison with data obtained from Äspö groundwater. Results of element concentrations as precipitates in horizontal boreholes at the 70 m depth.**

Sample No. concentration units filter pore size:  Element Analysis	Sample #2 ppb 50-400 nm	Sample #3 ppb 50-400 nm	Sample # 4 ppb 50-400 nm	Äspö ppb 50-400 nm
Al	2.87	6.62	2.02	6
Ca	47.40	27.5	83.23	319
Fe	13.44	3.72	4.15	2
Mn	0.07	0.10	0.03	1
Si	5.37	7.03	7.45	3
S	57.42	32.07	64.99	26
Sum	127	77	162	356
<b>Calculated Colloid Phases:</b>				
Ca as calcite $\text{CaCO}_3$	118.3	68.7	207.8	796
Fe as amorphous Goethite $\text{FeOOH}$	25.7	7.1	7.9	3
S as pyrite $\text{FeS}_2$	214.9	120.0	24302	96
Si as chalcedony $\text{SiO}_2$	11.5	15.0	15.9	6
Mn as pyrolusite $\text{MnO}_2$	0.1	0.2	0.1	1
Al as K-Mg-Illite clay, pyrophyllite $\text{K}_{0.6}\text{Mg}_{0.25}\text{Al}_{2.3}\text{Si}_{3.5}\text{O}_{10}(\text{OH})$	40.8	94.1	28.8	85
Phase Sum, 50-400 nm size	411	305	504	988
*[Coll]	1174	871	1438	2819
Sum omitting Calcite precipitation	836	675	845	545
*[Coll] = (Phase Sum/max-min filter pore size)*(1000-1) nm				
<b>Precipitates from Packed-Off Borehole Sections at 70m Depth</b>				
Element	Atomic%		Weight%	
C	19.45		13.25	
Na	1.01		1.32	
Mg	0.51		0.71	
Al	4.25		6.50	
Si	7.50		11.95	
Cl	0.41		0.83	
K	1.03		2.29	
Ca	0.48		1.08	
Fe	1.23		3.89	
O	64.13		58.19	
Total	100		100	

Solids were also sampled from the horizontal borehole sections in the tunnel. Their chemical composition (Table 9) showed elevated Ca, S and Fe concentrations in these solids. The Al and Si contents indicated these precipitates to have a similar composition as the clay minerals in the colloidal phases. The Fe and Mn content of these precipitates were higher than for the colloidal phases, but could be due to oxygen contamination, rather than evidence of *in situ* mineral formation.

There is a relatively high carbon content in the precipitates. There are insufficient amounts of cations in the samples to account for carbonate phases. This suggests that much of the carbon is organic. The general conclusion is that clay minerals are the dominant inorganic phases in both the colloid and precipitate samples, and that significant amounts of organic material was present in the precipitate samples.

## 4.2

### CRITICAL DISCUSSION OF SITE MODEL

The site model is based on the preliminary analysis presented in SKB Progress Report 25-95-06 (Banwart et al., 1995, SKB Progress Report 25-95-06, Chapter 9). New hydrochemistry modeling results by Bruton and Viani, more recent flow modeling results of Nordquist and Gustafsson, in the Proceedings of the 2nd Äspö International Groundwater Geochemistry Workshop (Laaksoharju and Wallin, eds., Äspö International Cooperation Report in preparation) are included in the site model given in Figure 7 and Table 4.

Modeling based on major element behavior resulted in several possible reaction processes, or hydrochemical reservoirs that could explain element mass balances equally well. Combining these models with isotopic and microbiological information further constrained the possible explanations. This proposed site model provides the best consistent explanation for all hydrochemical tracers considered, including bacteria.

The greatest uncertainty in this system is the enormous heterogeneity of this groundwater system. The fracture zone and tunnel lie at the interface between four environments: atmosphere, soil, bedrock and marine. The highly fractured bedrock is spatially heterogeneous with regard to its hydraulic and geochemical properties. In spite of this heterogeneity, we assume that the hydrology of this fracture zone is represented primarily by mixing between recharge water and brackish groundwater.

This requires that these two reservoirs are uniform in composition over a large volume. The shallow groundwater sampled above the tunnel must represent dilute groundwater in the entire recharge area, and the native groundwater must be representative for deeper groundwater input throughout the experiment.



The best justification for these assumptions is that the Oxygen-18 and Deuterium values predicted by the chloride mixing ratios coincide very well with observed values in the discharge borehole throughout the experiment. In addition we note that the composition of the shallow groundwater above the tunnel varies only slightly during the experiment. This is in spite of a large seasonal deuterium peak in precipitation recharge that travels through this groundwater horizon on a time scale of a few months. This shows that the shallow groundwater is not a static reservoir of dilute water, but is a dynamic source of recharge water with remarkably steady composition.

During the entire 3 year project time the concentrations of conservative constituents plot on a mixing line between fresh precipitation and the native groundwater. The composition of the native groundwater is also characteristic for other groundwaters in the Äspö area. The reservoir for this type of groundwater might, in fact, be regional. Compositional changes can be predicted extremely well by dilution of this groundwater type.

There may be "pockets" of groundwater, soil, or marine sediment that interact with lateral flow to the fracture zone. We specifically note shallow boreholes on Ävrö and in the Laxemar area that show relatively high values for sulfate and bicarbonate.

We tested several mixing models that include three, and even four, possible sources to the fracture zone (Laaksoharju et al., 1995, SKB Progress Report 25-95-06, Chapter 2). Some of these models included the possible input of these high sulfate-bicarbonate groundwaters. These calculations indicated that including these high sulfate-bicarbonate waters, or other sources, in the model can affect the relative strength of the sources and sinks. In all cases, there was a significant sink for calcium, and significant sources for sulfate, bicarbonate, and sodium.

This reactive element behavior is not easily explained by in-mixing from a hydrochemical reservoir that we have not considered. The main reason is that the sources and sinks of elements are remarkably steady during the final 2 years of the experiment (Banwart et al., 1995, SKB Progress Report 25-95-06, Chapter 3). If such a reservoir exists, it must be enormous; sufficiently large to explain a steady input for these elements over a period of 2-3 years, for a fracture zone with a  $10 \text{ L min}^{-1}$  rate of discharge into the access tunnel.

In conclusion, we propose the site models presented in Figure 7 as the best explanation for the hydrochemical evolution of shallow groundwater during tunnel construction at Äspö.

## 5. IMPLICATIONS FOR REPOSITORY PERFORMANCE ASSESSMENT

### 5.1 GENERALITY OF THE OBSERVED CONDITIONS

Figure 13 shows the interface between recharge water and saline groundwater for 4 different geological settings. This experiment took place on the island Hälö, in the Baltic Archipelago, which is situated near the coast of S.E. Sweden. The generality of site-specific results is critical to assessing the relevance of this project for generic performance assessment issues. Table 10 summarizes processes that take place at this site and their relevance to performance assessment. These performance assessment issues are discussed further in sections 5.1.2 - 5.3.3.

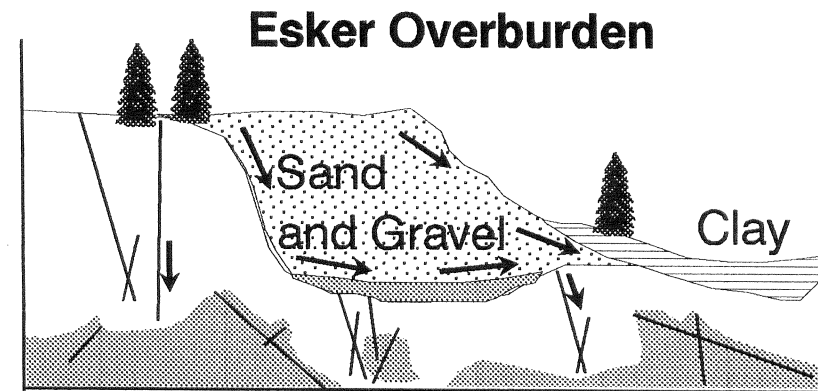
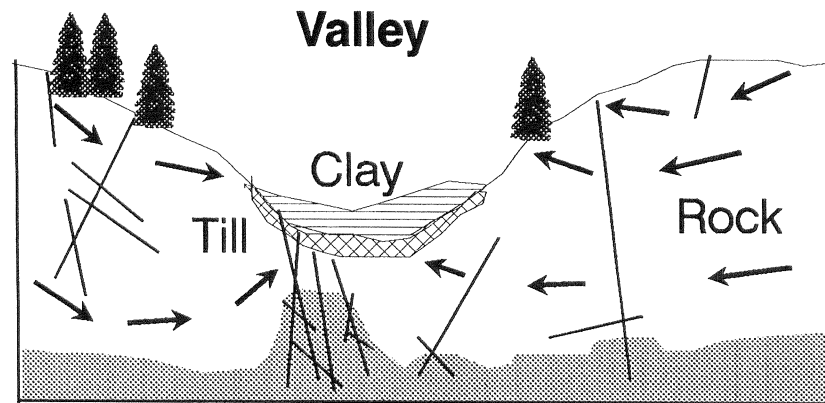
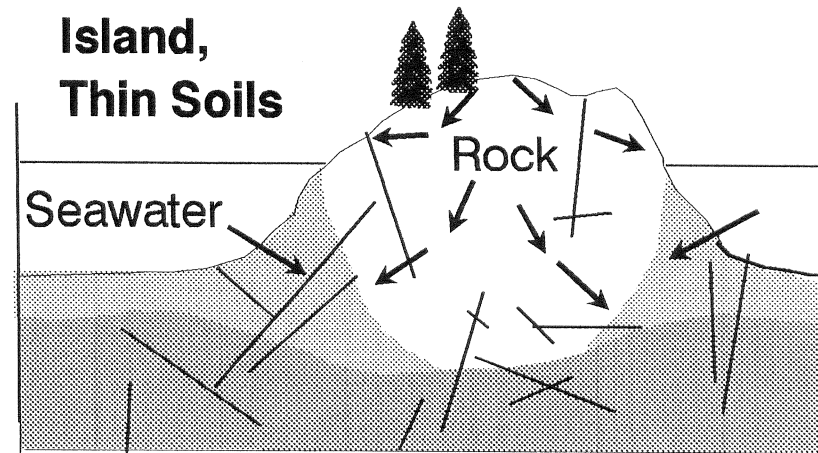
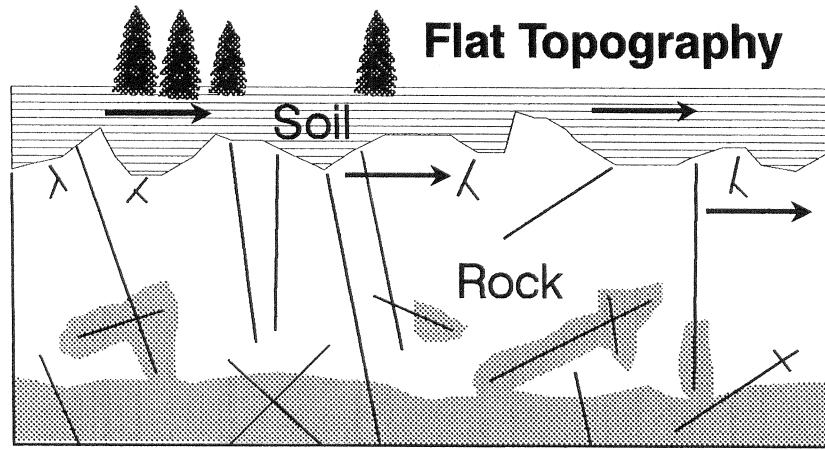
#### 5.1.1 Generality of Fracture Zone Properties

The fracture zone is a minor one regarding physical size (Stanfors et al., 1992). The width of the intensely fractured part ranges between a few dm to one meter and the length of the zone is some hundreds of meters. It was originally a Precambrian semiductile deformation zone in Småland granite which has later been reactivated and suffered brittle deformation causing the present gouge material. This material consists of fragments of hydrothermally altered granite surrounded by unlithified grains of mainly chlorite, calcite, FeOOH and significant amounts of mixed-layer clay. This type of fracture zone is very common regarding local as well as regional scale.

The fracture is seen as a depression on the island's surface, a few meters wide, with outcropping rock on both sides. This depression (up to 5 m deep) is filled with till followed by one meter of glacial clay with a thin layer of organic rich soil on top. Several fracture zones on Äspö island have the same appearance. Recharge to the fracture zone is drawn from a catchment defined by the rock outcrops on either side.

The inflow of groundwater to the tunnel is estimated to be on the order of 1 L/min while the three boreholes drilled into the fracture zone give inflow rates of 0.4, 4 and 10 L/min.

As in many other fracture zones the hydraulic properties vary considerably. There is a marked hydraulic contrast with the surrounding rock which has a typical conductivity of  $5.4 \times 10^{-8} \text{ m s}^{-1}$ . Hydraulic conductivities measured at two points in the fracture zone were  $8.3 \times 10^{-6} \text{ m s}^{-1}$  and  $6.4 \times 10^{-7} \text{ m s}^{-1}$ , respectively. Assigning a single effective transmissivity to the zone gives  $2 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$  and puts the zone in the middle of three classes of low, medium and high conductivity. Within the fracture zone water is flowing between most of the crushed pieces making the contact surface large (Banwart et al., 1994).



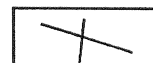
**Saline Groundwater**



**Seawater**



**Groundwater Flow**



**Fractures**

Figure 13. Hydrogeological environments where saline groundwaters interface with recharge waters (after Olofsson, 1994). Repository construction will introduce large amounts of recharge water below the salinity interface. This study showed that even a very soil-poor site like Hålö Island can provide organic carbon to the groundwater during repository construction. This result is expected for any repository site, and would be even more likely at sites with a thicker soil cover, due to the greater pool of available carbon.

**Table 10. Implications of Important Processes for Repository Performance Assessment, Discussed in More Detail in Sections 5.1.2 - 5.3.3.**

Process	Performance Assessment Issue
<b>Dilution</b>	<ol style="list-style-type: none"> <li>1. Salinity changes affect solubility and sorption of radionuclides, particularly those such as Cs and Sr which are sensitive to ion-exchange properties of fracture minerals.</li> <li>2. Increasing dilution enhances colloid stability and thus mobility with groundwater flow.</li> </ol>
<b>Aerobic respiration</b>	<ol style="list-style-type: none"> <li>1. Removal of O<sub>2</sub> in soil and upper bedrock protects the canister from exposure to oxic, corrosive water.</li> <li>2. Maintaining reducing conditions induces low solubility and high sorption for oxygen-sensitive radionuclides; Tc, Np, U.</li> </ol>
<b>Iron Reduction</b>	<ol style="list-style-type: none"> <li>1. Reductive dissolution of Fe(III) hydroxide may possibly cause release of radionuclides sorbed on the Fe(III) minerals.</li> <li>2. Reductive dissolution of Fe(III) minerals releases Fe<sup>2+</sup> which can subsequently consume infiltrating oxygen, thus helping keep reducing conditions (important for Tc, Np, U).</li> <li>3. Formation of new Fe(II) carbonate or clay minerals provides a sink for oxidants that helps preserve reducing conditions.</li> </ol>
<b>Sulfate Reduction</b>	<ol style="list-style-type: none"> <li>1. Production of hydrogen sulfide can cause sulfidic corrosion of canisters.</li> <li>2. The HS<sup>-</sup> ion produced will react with any oxygen in the water, and help keep reducing conditions (important for Tc, Np, U).</li> <li>3. Precipitation of iron sulfide will decrease hydrogen gas buildup, and provide an additional sink for oxidants.</li> </ol>
<b>Methane Production</b>	<ol style="list-style-type: none"> <li>1. Provides an <u>in situ</u> source of organic carbon</li> </ol>

**Table 10 (continued)**

**Fracture Performance During Enhanced Recharge**

<b>Factors affecting Oxygen Intrusion Depth from Surface</b>	<ol style="list-style-type: none"><li>1. Groundwater recharge rate</li><li>2. Oxygen diffusion rate</li><li>3. Relative amounts of reactive reductants (organic C, Fe(II) minerals, sulfides)</li><li>4. Oxygen consumption rate for each reductant</li><li>5. Spatial distribution of flow paths relative to reductants</li></ol>
<b>Conditions for Prevailing Anoxia</b>	<ol style="list-style-type: none"><li>1. Deep, saturated, organic-rich soil layer</li><li>2. No preferential flow paths through soil</li><li>3. Ongoing biomass production</li><li>4. Rapid decomposition of complex biomass</li><li>5. Vertical transport of organic carbon to groundwater</li><li>6. Abundant ferrous and sulfide minerals that rapidly consume oxygen</li></ol>

5.1.2 Dilution Fronts

The native groundwater in the fracture zone had a chloride content of 5000 mg/l, the Baltic Sea 3000 mg/l and surface water less than 100 mg/l. This makes the salinity a suitable tracer, especially for surface water inflow. Changes in the overall chemistry in the fracture zone were dominated by simple dilution of the native groundwater.

By the coast saline groundwater has been frequently observed. Further inland saline water has been observed occasionally at greater depths (several hundred meters). Saline water at greater depths seems to be a common phenomena. Where deep drilling followed by water sampling has been attempted, brines have been found which underlie the normal, well-known non-saline groundwaters.

Salinity fronts have been observed in e.g. Finnsjön (along a subhorizontal fracture zone) while the salinity at Äspö is gradually increasing toward depth. Probably the hydraulic regime governs whether or not a sharp front will exist.

The site model represents processes that occur when saline groundwaters are rapidly replaced or mixed with recharge water. According to Figure 13 an island topography such as for Hälö represents a favorable natural recharge gradient for introduction of fresh water into the bedrock. Even under the favorable recharge conditions implied by this topography, the native groundwater with 5000 mg/l chloride already existed at 70 m depth.

Repository construction at any site, even with unfavorable natural recharge gradients such as shown for a valley in Figure 13, would draw large

amounts of recharge water into the deep environment. This is inevitable given the enormous hydraulic gradients that will be created in the repository. Repository construction will override any site-specific hydraulic conditions while the repository is open. The results observed here are expected for construction at any site and are considered general.

### 5.1.3 Redox Fronts

Dissolved oxygen in the groundwater is rapidly consumed during breakdown of organic material (aerobic respiration) and/or oxidation of Fe(II) present in the soil cover, exposed bedrock and fracture minerals. The formation of Fe(III) is manifested in Fe-oxyhydroxide precipitates (often accompanied by calcite dissolution) observed in the upper tens of meters in the bedrock.

These Fe(III) precipitates can be found down to 100 - 150 meters in recharge areas where the organic content in the soil cover is low. However, in investigations from SKB's different test sites, recent oxidation of Fe(II) at deeper depth has not been found. Hematite in deeper parts of the rock mass has probably been formed at hydrothermal conditions where the water has been reduced, i.e. no molecular oxygen was involved.

In this experiment biological processes are controlling the redox status of the groundwater by maintaining respiration processes at relatively rapid rates. The amount of organic matter in the infiltrating water is of utmost importance. Except for the thin soil layer within the narrow depression, the catchment area for recharge to the fracture zone is almost entirely exposed bedrock; there was almost no soil at the site.

Given the glacial history of the site, and the uplift above sea level only during the past 2-3 thousand years, there has been little opportunity for development of soil and the associated accumulation of organic carbon. In spite of being soil-poor, the fracture zone recharge area provided a significant input of organic carbon, rather than oxygen, to the groundwater.

This result is certainly expected at other sites, particularly those with thicker soils. Such sites would have an even larger soil carbon reservoir available for mobilization into the groundwater. Such sites would also have a longer travel time for recharge water through the thicker overburden, thus allowing more time for oxygen to be consumed, and more organic carbon to be mobilized.

The carbon-14 data presented above, together with the elevated partial pressure of carbon dioxide measured in gas samples, show conclusively that there is intensive respiration of organic carbon during this experiment. The rate of respiration is apparently accelerated by the input of organic carbon with the increased surface inflow under the disturbed hydraulic conditions. Here we consider the effect of bacteria and organic carbon reactions on the performance of a deep repository.

The proposed site model shows that biologically-mediated reactions can affect fracture mineral dissolution and precipitation, and the associated fluxes of sorbing trace elements including radionuclides. The oxidation of organic carbon is coupled to the reduction of other major elements species such as dissolved oxygen, nitrate, nitrite, manganese(III,IV), iron(III) and sulfate. Because proton transfers must accompany electron transfers to maintain charge balance in solution, these reactions influence groundwater alkalinity and pH, as well as the redox status; oxic, anoxic, sulfidic.

Iron(III) fracture minerals are the most likely oxidants for the respiration of organic carbon in this experiment. The fracture zone is persistently anoxic. Results from the investigations conclusively rule out sulfate reduction. Manganese oxide minerals were not found during the mineralogical investigations. Nitrate and nitrite were present in only trace concentrations. This discussion focuses on aerobic respiration, iron reduction, sulfate reduction, and methane production.

### 5.2.1 Aerobic Respiration

Because the fracture zone remains persistently anoxic, we conclude that dissolved oxygen is consumed within the topmost regions of the fracture zone. The increased inflow of surface water adds reducing capacity in the form of organic carbon, rather than oxidizing capacity in the form of dissolved oxygen as expected before this experiment. This additional reducing capacity helps maintain anoxia in the groundwater environment while the repository is open.

There are two implications for oxygen consumption by aerobic respiration:

1. Removal of oxygen in the upper parts of the bedrock results in lower exposure of the canister environment to oxygen. Other sources of oxygen will be the open repository conditions during operation, and radiolysis of groundwater.
2. Maintaining reducing conditions in fracture zones provides a migration barrier to redox-sensitive radionuclides; Tc, Np, U (Grenthe et al.1992). These elements are highly soluble under oxic

conditions, and are thus more mobile. They are only sparingly soluble under reducing conditions.

### 5.2.2 Iron Reduction

We propose that iron(III) oxyhydroxide fracture minerals are the most likely electron acceptor for respiration of organic carbon. Because there is no significant mobilization of dissolved iron(II) from the fracture zone, iron(II)-bearing fracture minerals must form; siderite ( $\text{FeCO}_3$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ), Fe(II)-bearing clays.

Reduction of iron(III) minerals has four implications for the mobility of sorbing radionuclides and intrusion of oxygen:

1. Because iron(III) oxyhydroxide is an efficient adsorbent for trace metals (Dzombak and Morel,1990), its dissolution may result in mobilization of any trace constituents such as radionuclides.
2. The iron(III) reduction will generate  $\text{Fe}^{2+}$  ions which helps to define the redox status of the groundwater. The  $\text{Fe}^{2+}$  ions, pH and Fe(III) minerals define an Eh system which is important for reducing conditions in groundwater. Equilibrium between the aqueous Fe(II) and Fe(III) species and the solid mineral is apparent from redox electrode measurements and hydrochemical analyses of deep groundwaters in Sweden (Grenthe et al.,1992).
3. Formation of Fe(II)-bearing fracture minerals will add reducing capacity and sorption capacity to water-bearing fractures. This can provide a migration barrier to radionuclides.
4. Because iron(II) minerals react rapidly with dissolved oxygen (White and Yee,1985), their formation provides a barrier against future intrusion of oxygen into a fracture zone.

### 5.2.3 Sulfate Reduction

Although we rule out sulfate reduction in this experiment, the results for the microbiological investigations showed sulfate reducing activity at deeper locations along the access tunnel. It is generally observed in the Äspö groundwater environment that sulfate reducing zones are located below iron reducing zones (Smellie and Laaksoharju,1992). Increased input of organic carbon may affect where the transition between iron-reducing and sulfate-reducing zones occurs.

There are three implications for sulfate reduction in the deep repository environment.



1. Sulfate reduction affects canister stability because hydrogen sulfide can corrode copper metal.
2. A positive aspect of sulfate reduction is the generation of HS<sup>-</sup> ions which will rapidly react with any oxygen in the groundwater. In fact, measurable amounts of HS<sup>-</sup> is a clear sign of the absence of O<sub>2</sub> in groundwater.
3. Precipitation of iron sulfide fracture minerals such as pyrite will limit the buildup of hydrogen sulfide in the groundwater, and will provide a reducing migration barrier (Wersin et al., 1994) to redox-sensitive radionuclides.

Further studies of biological sulfate reduction are underway (M. Laaksoharju, ed., SKB Technical Report on Biological Sulfate Reduction in preparation).

#### 5.2.4 Methane Production

Methane production requires intensely anaerobic conditions. Its observation, as in this experiment, demonstrates for at least some parts of the fracture zone that very reducing conditions exist. Methane production also acts as an in situ source of organic carbon in deep environments.

### 5.3 PERFORMANCE OF FRACTURE ZONES UNDER INCREASED GROUNDWATER RECHARGE

We consider the effect of repository construction on the groundwater environment. In this experiment there are two dominant effects from increased groundwater recharge under the disturbed hydraulic conditions created by tunnel construction.

1. increased groundwater recharge causes dilution of the native groundwater
2. increased groundwater recharge adds reducing capacity in the form of organic carbon to the groundwater

#### 5.3.1 Dilution Effects On Fracture Zone Performance

Groundwater salinity affects aqueous speciation and colloid stability through ionic strength effects. Changes in aqueous speciation affect the solubility of mineral phases and the sorption behavior of trace elements. Decreasing ionic strength favors colloid stability and thus transport of colloids and sorbed trace elements. Ion exchange surfaces are increasingly

selective for divalent cations upon increasing dilution. Groundwater dilution and reaction with ion-exchange minerals may therefore result in lower calcium/sodium ratios in solution. This also favors colloid stability and can affect calcite solubility.

### 5.3.2 Conditions for Prevailing Anoxia

Prevailing anoxic conditions are favored in this experiment by the input of organic carbon from the surface, and also by the abundance of Fe(II)-bearing fracture minerals. Iron reduction by organic carbon can produce an even larger reservoir of Fe(II) fracture minerals in the flow path. If organic carbon input from the surface were to stop, this reservoir of mineral reductants would provide a barrier to oxygen intrusion.

Anoxia results in this experiment because there is a net reducing capacity in the subsurface, i.e., more organic carbon and Fe(II) than oxygen, and because reaction of oxygen with these reductants is more rapid than oxygen transport into the fracture zone.

Conditions that favor prevailing anoxia are:

1. A diffusion barrier to atmospheric oxygen; saturated soil conditions and long diffusion paths (thick soils/sediments)
2. No preferential flow paths that short-circuit organic-rich soil sediment layers
3. Sufficient biomass production to create a reservoir of organic carbon.
4. Sufficient decomposition of complex biomass (plant material) to dissolved or colloidal forms that can be hydrodynamically transported.
5. Sufficient infiltration to transport organic carbon into the subsurface
6. A reservoir of reducing fracture minerals that can rapidly consume any oxygen that may intrude the subsurface.

### 5.3.2 Intrusion Depth for Oxidizing Fronts from the Surface

For an infinite supply of subsurface reductants, the depth of oxygen intrusion depends on the relative rates of vertical transport and oxygen reduction. The increased surface water inflow created by tunnel construction can be taken as an extreme case for rapid vertical transport of groundwater. In spite of this, oxygen is rapidly consumed in the very shallow parts of this fracture zone.

Oxygen may be consumed primarily by aerobic respiration of organic carbon. On the other hand, rapid consumption of oxygen by fracture minerals may maintain anoxia, thereby preserving organic carbon for anaerobic respiration at greater depths. In either case, because oxygen consumption is rapid compared to surface water inflow or vertical diffusion of oxygen, oxic conditions do not develop below a very shallow depth.

For this condition of rapid oxygen consumption, the net reducing capacity of the subsurface becomes critical. In the case of limited reducing capacity, i.e., little organic carbon and few reducing minerals, oxygen transport will only be retarded until this small reservoir of reductants is consumed. Oxygen would then be transported with the groundwater flow until a zone containing reductants is reached. In this case, the depth of oxygen penetration is determined by the location of this reducing zone and the time scale for groundwater flow.

We identify two limiting cases for defining the depth of oxygen intrusion:

1. for an infinite subsurface reservoir of reductants, oxygen intrusion depth depends on the rate of vertical oxygen transport, relative to the rate of oxygen consumption along the flow path. A steady-state approximation may be sufficient to assess oxygen intrusion depth.
2. for a limited subsurface reservoir of reductants, oxygen intrusion depth depends on the spatial distribution of reducing zones, the time scale for groundwater flow, and the time scales to consume the reductants in these zones.

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<sup>1</sup> Royal Institute of Technology, Department of Inorganic Chemistry, Stockholm, Sweden

<sup>2</sup> Universidad Politécnica de Cataluña, Departamento de Ingeniería Química, Barcelona, Spain

<sup>3</sup> MBT Tecnología Ambiental, Cerdanyola, Spain  
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<sup>2</sup> Studsvik Nuclear AB, Nyköping, Sweden  
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<sup>1</sup> Göteborg University, General and Marine Microbiology, The Lundberg Institute, Göteborg, Sweden

<sup>2</sup> Swedish Nuclear Fuel and Waste Management Co., Stockholm, Sweden  
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<sup>1</sup> Department of Geology, Earth Sciences Centre, Göteborg University, Göteborg, Sweden  
<sup>2</sup> Geological Survey of Sweden, Earth Sciences Centre, Göteborg, Sweden  
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<sup>1</sup> GeoPoint AB, Sollentuna, Sweden

<sup>2</sup> University of Geneva, Switzerland

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