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**Interactions of trace elements with
fracture filling minerals from the
Äspö Hard Rock Laboratory**

Ove Landström¹, Eva-Lena Tullborg²

¹ Studsvik Eco & Safety AB

² Terralogica AB

June 1995

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

INTERACTIONS OF TRACE ELEMENTS WITH FRACTURE FILLING MINERALS FROM THE ÄSPÖ HARD ROCK LABORATORY

Ove Landström¹, Eva-Lena Tullborg²

1 Studsvik Eco & Safety AB
2 Terralogica AB

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**INTERACTIONS OF U, Th, REE, Ra, Cs AND Sr
WITH CLAY MINERALS, Fe-OXYHYDROXIDE
AND CALCITE**

**EXAMPLES ON GEOCHEMICAL PROCESSES IN
NATURAL SYSTEMS FROM THE ÄSPÖ HARD
ROCK LABORATORY**

by

Ove Landström¹, Eva-Lena Tullborg²

1 Studsvik Eco & Safety AB

2 Terralogica AB

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Keywords: Trace elements, Natural radionuclides, Groundwater/fracture mineral interaction, Fe-oxyhydroxide, Calcite, Clay minerals, Sorption, Retention processes, Low temperature environment.

ABSTRACT

This report focuses on the distribution of stable elements and natural radionuclides (for example REEs, Th, U, Ra, Sr and Cs) in natural fracture systems. These elements are chemical analogues to or identical with artificial radionuclides occurring in a nuclear waste repository. They have been redistributed by natural processes in the past; mobilisation, transport and deposition of which the latter is manifested as "enrichments" of the elements in fracture fillings. Fracture fillings dominated by Fe-oxyhydroxide, calcite and clay minerals show the highest concentrations. These minerals are thus important in retarding radionuclides and have been studied specifically; sequential extraction has for example been applied to clayish gouge material and fresh Fe-oxyhydroxide/calcite precipitates.

REEs, Sc, Th, U, Ra, Sr and Ba are scavenged by the mixed Fe-oxyhydroxide/calcite precipitates which are deposited at fracture exposures in the galleries of the Äspö Hard Rock Laboratory. Precipitates from different fractures show large variations in concentration levels of trace elements, REE patterns, and activity and activity ratios of natural radionuclides, reflecting variations in physical, chemical and hydrological properties of the fractures. Formation of Fe-oxyhydroxide will occur e.g. in connection to the construction of a repository and at the geosphere/biosphere interface. In connection with the precipitation of Fe-oxyhydroxid radionuclides can be retarded by co-precipitation and/or sorption.

The incorporation of REEs, Sr, Th and U in calcite is significant. The precipitation rate influences (increases) the amount of Sr incorporated and probably other elements as well. Significant precipitation/dissolution of calcite can be expected in the vicinity of a disposal due to the temperature anomaly introduced by the radioactive waste. Uptake/release of radionuclides in connection to these processes should be considered in predictive modelling.

Clay minerals have high sorption capacity and are important in the retention of Cs and Sr (ion exchange) as well as of REEs, Th, U and Ra. The sorption of Cs is characterized by at least two different processes; rapid surface adsorption and slower interlayer sorption. The size of the former, determined in the sequential extraction, is in agreement with that calculated from the Cs concentration in the groundwater and K_d -values determined in batch experiments. REEs and Th seem to be strongly sorbed onto the clay mineral surfaces. Th in such positions will effectively release radium to the groundwater through α -recoil.

The importance of clay minerals in radionuclide retention is emphasized by the results from this study; also small amounts of clay minerals in fractures and fracture zones can significantly influence the radionuclide migration. Accurate determination of quantities and types of clay minerals is therefore very important for radionuclide migration modelling.

ABSTRAKT

Fördelningen i naturliga grundvatten/sprickmineralsystem av stabila ämnen och naturliga radionuklider (t.ex. lantanider, Th, U, Ra, Sr och Cs) har studerats. Dessa element är antingen kemiska analoger till eller identiska med artificiella radionuklider i aktivt avfall. Naturliga processer (mobilisering, transport och deponering) som verkat under lång tid har omfördelat dessa ämnen. Deponering ("uppbromsning") har resulterat i anrikningar på de sprickytor som är i kontakt med grundvattnet. Anrikningar är associerade till sprickbeläggningar som domineras av Fe-oxyhydroxid, kalcit och lermineral vilka följaktligen är effektiva när det gäller att begränsa spridning av radionuklider. De har därför studerats mer ingående; bl.a. genom tillämpning av sekventiell extraktion.

Lantanider, Sc, Th, U, Ra, Sr och Ba tas upp i den blandning av Fe-oxyhydroxid och kalcit som fälls ut där vattenförande sprickor frilagts i tunneln till Äspö berglaboratorium. Utfällningar från olika sprickor visar stor variation i spårelementkoncentrationer, i lantanidmönster och i naturliga radionuklidernas aktiviteter och aktivitetskvoter speglande variationer i sprickornas egenskaper (kemi, hydrologi etc.). Bildning av amorf Fe-oxyhydroxid kan ske exempelvis i samband med byggande av ett slutförvar och i gränsskiktet geosfär/biosfär på grund av kontakt med molekylärt syre. Dessa bildningar kan fördröja radionuklider genom medfällning och/eller sorption.

Inkorporering av lantanider, Sr, Th och U i kalcit kan vara betydande. Hög utfällningshastighet påverkar (ökar) mängden upptaget Sr (och troligen även andra ämnen). Omfattande utfällning/upplösning av kalcit kan förväntas i omgivningen av ett förvar på grund av den temperaturanomali som introduceras genom värmeutveckling från avfallet. Upptag respektive mobilisering av radionuklider vid dessa processer bör beaktas.

Lermineral fördröjer effektivt migrationen av Cs och Sr (genom jonbyte) och migrationen av lantanider, Th, U och Ra. Cs sorptionen karakteriseras av olika processer; en snabb sorption (ytliga positioner) och en långsam sorption ("inter-layer" positioner). Den förra (snabbt reversibel) har bestämts genom sekventiell extraktion och överensstämmer med vad som förväntas från beräkningar baserade på Cs halter i grundvattnet och K_d -värden bestämda i laboratoriet. Resultaten indikerar att lantanider och Th sorberas starkt på lerpartiklarnas ytskikt. Ra kan effektivt frigöras till vattenfasen genom α -rekyl från Th i sådana positioner.

Betydelsen av lermineral för retention av radionuklider understrykes av resultaten från denna studie; även små mängder av lermineral i sprickor och sprickzoner kan signifikant påverka radionuklidmigrationen. Noggrann bestämning av kvantiteter och typ av lermineral är därför mycket betydelsefullt för radionuklidmodellering.

CONTENTS

1.	INTRODUCTION	1
2.	GEOLOGICAL SETTING	5
2.1	GEOLOGY OF THE AREA	5
2.2	GEOLOGY OF THE TUNNEL SECTION 200 TO 1300 M, THE REDOX ZONE AND FRACTURE ZONE NE-1	8
3.	METHODS	13
3.1	MAJOR AND TRACE ELEMENTS	13
3.2	SEQUENTIAL EXTRACTIONS	13
4.	REVERSIBLE/IRREVERSIBLE SORPTION ON GOUGE MATERIAL	15
4.1	CONCEPT	15
4.2	RESULTS	15
4.3	HIGH AND LOW TEMPERATURE ENRICHMENTS OF TRACE ELEMENTS	20
4.4	PARTITION RATIOS FOR Cs	21
5.	STUDIES OF ONGOING PRECIPITATION OF Fe- OXYHYDROXIDE AND CALCITE	23
5.1	CONCEPT	23
5.2	SAMPLING, SAMPLE PREPARATION AND ANALYTICAL METHODS	24
5.3	RESULTS	25
5.3.1	Major and trace elements	26
5.3.2	Radionuclides	35

5.4.	EVALUATION	39
5.4.1	Ra and Ba relationship	39
5.4.2	Retention capacity of calcite and Fe–oxyhydroxide	41
5.4.3	Comparison of precipitate and groundwater data	42
6.	TRACE ELEMENT UPTAKE IN CALCITE	49
6.1	CONCEPT	49
6.2	FRACTURE FILLING CALCITES AT ÄSPÖ – FREQUENCES AND ORIGIN	49
6.3	CALCITE SAMPLES	51
6.4	RESULTS	52
7.	SUMMARIZING DISCUSSION	57
7.1	BEHAVIOUR OF DIFFERENT ELEMENTS	58
7.1.1	Rb and Cs	58
7.1.2	Sr and Ba	58
7.1.3	Th	59
7.1.4	REEs	60
7.1.5	Ra	61
7.1.6	U	61
7.2	RETENTION CAPACITY OF DIFFERENT MINERALS	62
7.2.1	Clay minerals	62
7.2.2	Fe–oxyhydroxide	63
7.2.3	Calcite	64
	Acknowledgements	65
8.	REFERENCES	67

1. INTRODUCTION

The basic concept for final storage of Swedish high level radioactive waste is disposal in a repository at c. 500 m depth in crystalline bedrock. Various engineered barriers, e.g. the copper canister and bentonite buffer, are designed to prevent the waste coming in contact with groundwater. However, safety assessment must also consider a possible failure of these barriers and the subsequent release and transport of radionuclides by groundwater from the engineered barrier environment and out into the surrounding fracture systems. It is then important to understand the different retardation mechanisms occurring at the fracture surfaces which will delay the arrival of the radionuclides to the biosphere e.g. physical and chemical sorption, co-precipitation and diffusion into interconnected pore systems in the host rock.

Fracture surfaces are usually covered by a complex mineral assemblage (so called fracture minerals) i.e. the fresh host rock is seldom exposed. These fracture minerals can either constitute a coating (thin or thick) on the fracture wall or a complete filling of the fracture. Terms like fracture coatings and fracture fillings are used for these mineral assemblages. Loose material, that may be contained in the fracture zones, is called gouge, here defined as unlithified rock and mineral fragments of different grain sizes.

In the Precambrian crystalline bedrock, repeated tectonism and circulation of hydrothermal fluids, followed by low temperature alteration can be recognised in many fractures and fracture zones. This means that fracture mineral assemblages (and their element contents) result from different processes, including tectonism, alteration/weathering and precipitation/mineralisation that have been active during the history of the fracture.

Earlier studies of fracture fillings and gouge material from fractures and fracture zones at Klipperås and Äspö revealed significant enrichment of certain elements relevant to nuclear waste disposal, e.g. Th, U, REE, Ba and Cs (Landström and Tullborg, 1990, 1991 and 1993). These enrichments are the final result of a redistribution of elements by natural processes which have operated over long periods of time and in varying geochemical environments (including hydrothermal events and other extremes). Similar processes (except for hydrothermal events) can be expected to affect the distribution of leached radionuclides within the next 0.1–1 Ma, the time frame usually considered by repository safety assessment.

Redistribution of U, Th and REEs resulting in enrichments in fracture fillings and altered wall rocks have been shown in other investigations and are mostly explained by hydrothermal activity or burial metamorphism (Brewer and Atkins 1989; Leroy and Turpin 1988, Griffault et al., 1993; Kamineni 1989) but also by low temperature processes (Kamineni, 1989 and Griffault et al., 1993).

A realistic measure of the retardation capacity of different fracture filling minerals would be the portion of an enriched element which has been taken up from the fluid phase ("net gain"). To estimate these portions we have applied the immobile element method (cf. Nesbitt, 1979), assuming Zr, Hf and Ti as being immobile, and treating the fracture filling/wall rock system as analogous to a weathering profile (i.e. assuming alteration of an originally fresh rock surface through different water/rock interactions). Such an approach is not without problems (e.g. possible mobility and heterogeneous distribution of the immobile elements) but has given a worthwhile insight into the effectiveness of different minerals in retarding radionuclides.

It turned out that the common low temperature minerals calcite, clay minerals and Fe-oxyhydroxide showed the highest uptake of trace elements from the fluid phase. These minerals are important as they are frequent in water conducting fractures and fracture zones and thus constitute a large active surface for interaction with elements transported by the groundwater.

A direct interpretation of sources and migration paths of the enriched elements, paleo-chemical environments, sorption processes, sequence of alteration events, etc. is difficult or impossible due to a lack of additional data. However, for the models predicting future radionuclide migration it is important to distinguish between low-temperature and hydrothermal enrichments. Complementary studies aiming to elucidate and better understand the enrichment processes in particular were therefore initiated. They follow two main lines:

1. Sequential extraction; main purpose is to determine:
 - a) the distribution of elements in different mineral phases
 - b) reversibly and irreversibly sorbed fractions
 - c) distribution factors from the reversibly sorbed fraction and corresponding groundwater data.

These experiments are focused on important groups of fracture fillings such as those dominated by clay minerals (including chlorite) but have also been applied to Fe-oxyhydroxide and calcite precipitates.

2. Studies of on-going retardation processes in connection with the formation of Fe-oxyhydroxide and calcite. These minerals are often suggested to be important scavengers of REE, Ra, Th and U and this is also strongly indicated by this present study. Precipitation of Fe-oxyhydroxide and calcite on the walls of the Äspö underground laboratory offer unique possibilities for such studies since the environmental conditions can be observed directly and supporting data from other studies are available. Furthermore, these precipitates obviously represent solely low-temperature processes.

This report focuses on reversible/irreversible sorption on clay minerals and

on the roles of the Fe-oxyhydroxide, calcite and clay minerals in the retardation of radionuclides. Sequential extraction on clay minerals, Fe-oxyhydroxide/calcite precipitates and fracture calcites, respectively, are treated in separate chapters and are followed by a summarizing discussion.

The samples discussed in this report are from the Äspö Hard Rock Laboratory (HRL) located about 30 km north of Oskarshamn on the Swedish east coast (Fig 1). The material has been sampled from drillcores and at exposures of fractures and fracture zones in the access tunnel of HRL. For description of the Äspö Hard Rock Laboratory cf. SKB TR 91-22.

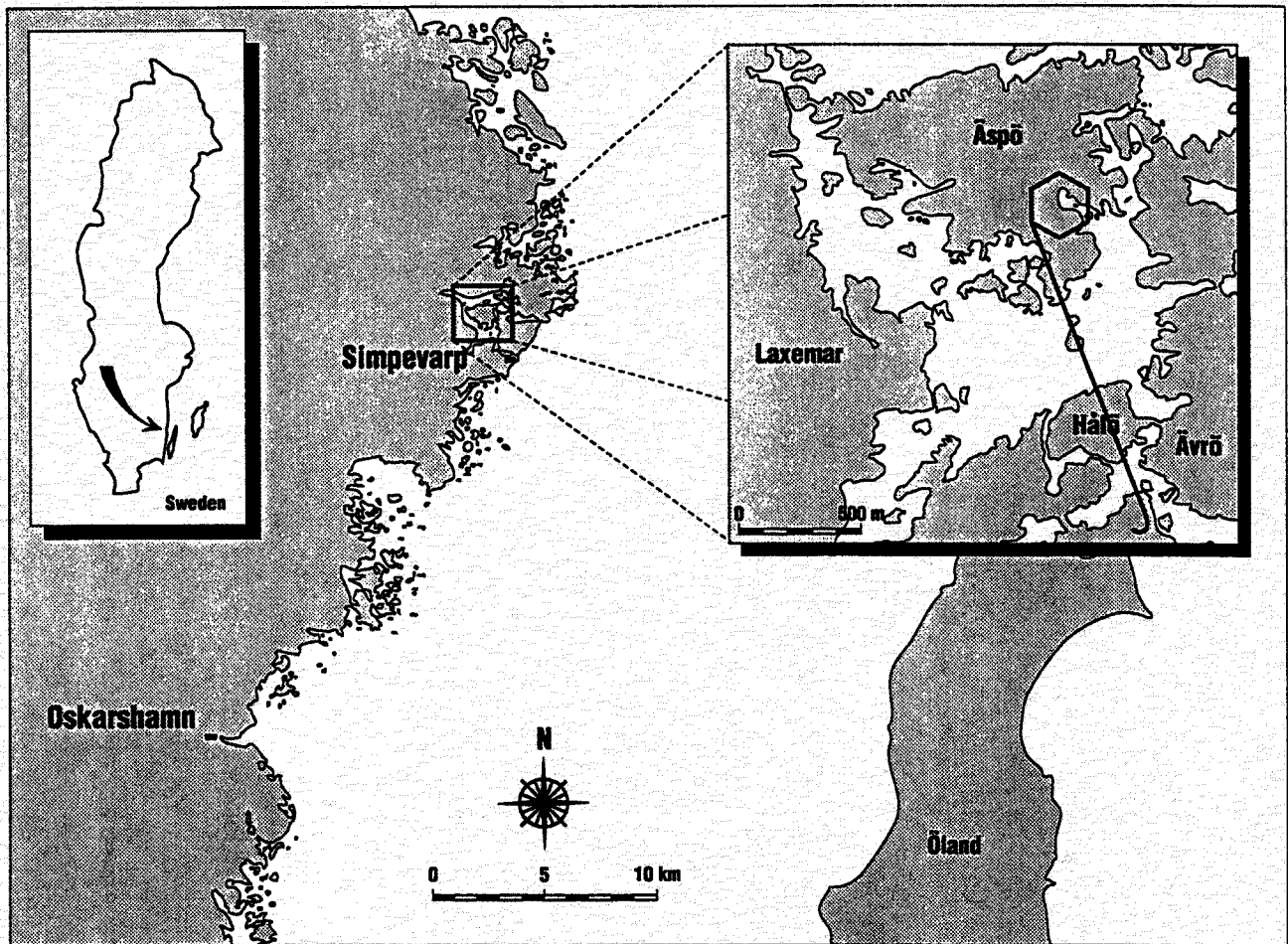


Figure 1. Location of the Äspö Hard Rock Laboratory.

2. GEOLOGICAL SETTING

2.1 Geology of the area

A detailed description of the rocks in the area of the island of Äspö has been presented by Kornfält & Wikman (1988). Based on their report, a summary of the regional and local geology is given below.

According to Gorbatshev (1980) (cf. also Gáal & Gorbatshev, 1987) the rocks belong to the Transscandinavian igneous belt (TIB). The granitoids of the TIB (dominated by so called Småland–Värmland granitoids) are regarded as late- to postorogenic in relation to the Svecofennian orogeny. In the Äspö area, Småland granitoids ranging from granites to monzodiorite dominate. Xenoliths of basic to intermediate metavolcanics occur in the granitoids. The Äspö monzodiorite was dated to 1804 \pm 3 Ma by use of U–Pb multiple zircon technique (Wikman & Kornfält, 1995).

Fine-grained alkali granites post-date the Småland granitoids and are present as lenses and dikes. Most of the fine-grained granites are closely related to the Småland granitoids and show similar ages of approximately 1800 Ma (Wikman & Kornfält, 1995) whereas others show distinct contacts and some of them might be associated with the 1400 Ma anorogenic Götömar granite present in outcrops c. 2 km north of Äspö.

A sequence of deformations in the area has been proposed by Munier (1993). The earliest fabric in the granitoids of Äspö is a penetrative planar foliation generally trending ENE. Subsequent strain was increasingly localised to block boundaries developing gneissic zones. Later mylonites segmented the region into rock blocks. The Götömar granite does not show any regional deformation, in contrast to the Småland granitoids and some of the fine-grained granites. The original foliation is reorientated and intensified in the mylonites. Brittle deformation caused fragmentation of the rocks resulting in the observed sets of lineaments (N–S, E–W, NE and NW; Tirén & Beckholmen, 1987; Nisca, 1987). Most of these faults and fractures are superimposed on older zones of intense foliation and/or mylonite zones. Major fracture zones of the area are shown in Figure 2.

Hydrothermal alteration of the host rock close to the fracture edges is frequently observed (e.g. Eliasson 1993; Banwart 1994 a). This alteration has resulted in a breakdown of biotite which is replaced by chlorite/epidote; magnetite has been oxidised and hematite/Fe–oxyhydroxide has been formed. Plagioclase is usually more altered (showing saussuritisation) close to the fracture edges. This kind of alteration is also found in rock fragments in for example, the Redox zone.

Relative ages of fracture mineralisations have been determined on textural grounds e.g. by cross-cutting relations and a "tectonic history" for the granitoids (Table 1) has been suggested (cf. Landström & Tullborg 1994).

Table 1. Sequence of tectonic events and fracture mineralisations.

Formation of the Småland granitoids	c. 1800 Ma (a)
1) Regional deformation resulting in E-W to ENE-WSW foliation.	
2) Mylonitisation; formation of fine-grained epidote, muscovite and recrystallisation of quartz.	
3) Reactivation of mylonites and formation of idiomorphic epidote and fluorite.	Intrusion of the anorogenic Götömar intrusion c. 1400 Ma. (b)
4) Growth of idiomorphic quartz, muscovite, hematite, fluorite, calcite and spherulitic chlorite.	Post-magmatic hydrothermal circulation.
5) Prehnite, laumontite, calcite, chlorite and fluorite.	c. 1100 Ma? (c)
6) Illite dominated mixed-layer clay, calcite, chlorite?	c. 300 Ma (d)
7) Calcite, Fe-oxyhydroxide, clay minerals?	Recent

(a) Åberg & Persson 1984, 1986; Johansson, 1988, (b) Åberg et al., 1984; Smellie & Stuckless, 1985, (c) Wickman et al., 1983, (d) Maddock et al., 1993.

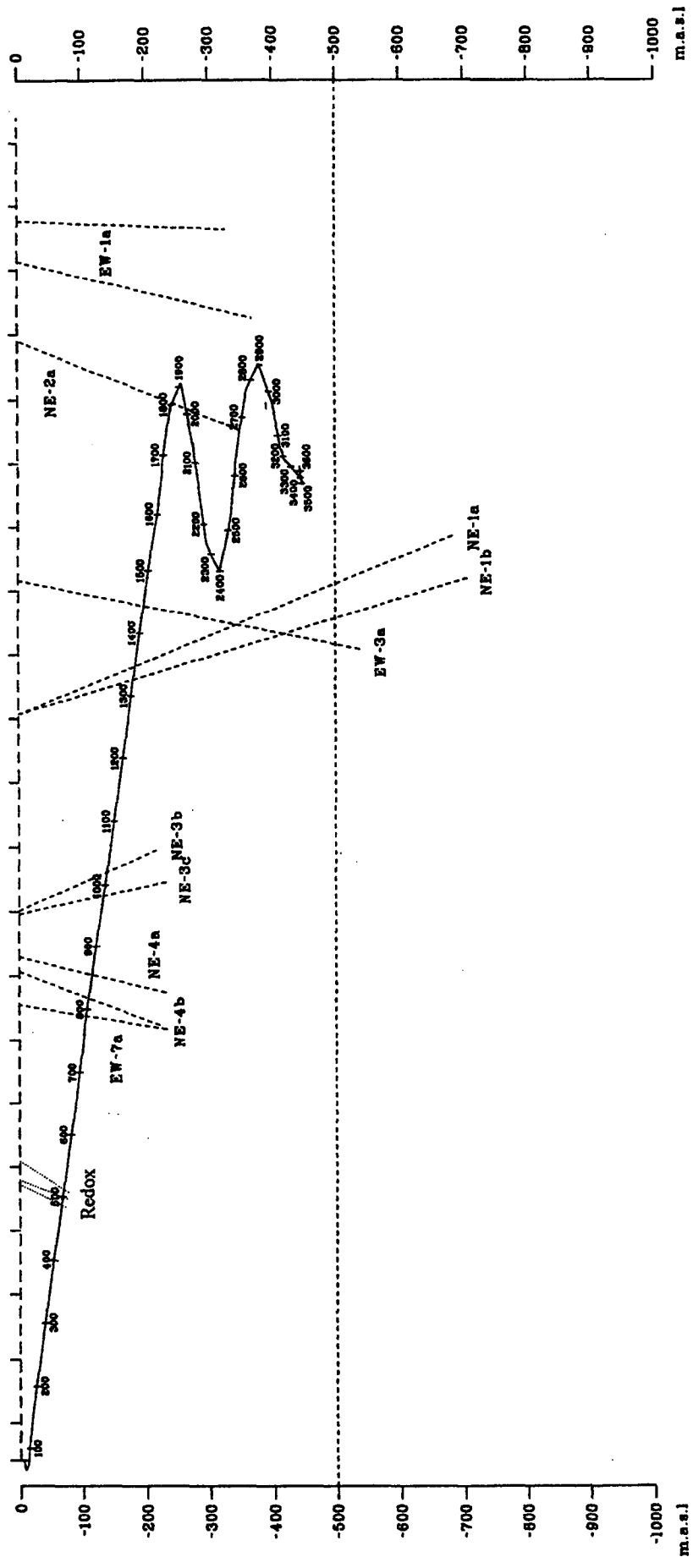


Figure 2. Major tectonic zones, including fracture zone NE-1 and the Redox zone, present in the Hälö-Åspö area.

2.2 GEOLOGY OF THE TUNNEL SECTION 200 TO 1350 M, THE REDOX ZONE AND FRACTURE ZONE NE-1

Lithology, fracture zones and sampling sites in the tunnel section from 200 to 1350 m are shown in Fig 3. The lithology gradually changes along the tunnel from monzogranite ("Småland granite" dominating the 200 to 1000 m interval) to quartz monzogranite ("Äspö diorite"). Both the Småland granite and the Äspö diorite contain granodioritic parts.

Fine-grained alkali granites occur in the 900 to 1000 m section and in lenses (a few metres thick) in sections 430 to 460 m and 1130 to 1320 m. The fine-grained granite is often associated with major fracturing; two of the regional water-bearing zones within this tunnel section are situated in this type of granite (NE-1 and NE-3 in Fig. 3). The fracture zones EW-7 and NE-4 (at about 670 and 850 m, respectively, Fig. 3) and the Redox zone (510 m) are, however, located in Småland granite. Minor fracture zones occur at 1150 m (gently dipping NW) and at 1200 and 1250 m (moderately dipping N).

In general, chlorite and calcite dominate the fracture coatings but epidote and Fe-oxyhydroxide are frequently observed. Clay minerals, epidote and Fe-oxyhydroxides are more frequent in fracture zones than in single fractures.

Two of the fracture zones (NE-1 and the Redox zone) have been studied in detail in other investigations (Landström & Tullborg 1993 and Banwart et al, 1994 a,b,c). Since the present work has concentrated to these zones, they are more thoroughly described below.

2.2.1 THE REDOX ZONE

A subvertical fracture zone intercepted by the Äspö access tunnel at a vertical depth of 70 metres was chosen for the large scale Redox experiment and was then called the "Redox zone". This zone (Fig. 3) is originally a semiductile (Precambrian) deformation zone in the Småland granite. Deformation is associated with hydrothermal alteration of the host granite resulting in breakdown of biotite and magnetite (forming chlorite and hematite/Fe-oxyhydroxide) in association with the saussuritisation of plagioclase (Plagioclase = albite + epidote and sericite). Subsequent brittle deformation has created the present water conducting fracture zone which contains blocks and rock fragments of hydrothermally altered granite. The fragments, of centimetre to decimetre size, are surrounded by unlithified, fine-grained gouge material ranging from millimetre down to micrometer in size. The material, which consists of quartz, K-feldspar, chlorite,

illite and mixed-layer clay, calcite and FeOOH form the water/rock interaction surface of the main hydraulic pathways in the zone (Banwart et al., 1994 c).

Intersection of the Redox fracture zone (by excavation of the tunnel) caused a sharp breakthrough of dilute water in the access tunnel after three weeks (Banwart et al., 1994a). The total disappearance of dissolved Fe indicates arrival of an oxidising front. Subsequently saline water and reducing conditions returned followed by a long term increased inflow of shallow dilute water rich in organic material. Analyses of groundwater, collected in boreholes penetrating the zone (at 70 m below the ground surface; Fig 4), shows that the original salinity c. 5000 mg/l has now decreased to 1000 mg/l Cl. Mixing of shallow water and native saline water explains general trends in the distribution of major elements except for the addition of Na and HCO_3^- and depletion of Ca (Banwart et al., 1994 a). Anaerobic respiration of organic material is believed to be the main source of the alkalinity and the high partial pressure of CO_2 . Fe(III)- bearing fracture minerals are possible electron acceptors for the organic respiration; Fe reducing bacteria have been identified in the zone.

2.2.2 FRACTURE ZONE NE-1

Zone NE-1 (Fig. 3) is originally a ductile/semiductile zone hosted in mylonitised fine-grained granite. The latest reactivation of the zone resulted in the gouge formation, subsequent precipitation of calcite and pyrite, as well as the formation of mixed-layer clay with a high illite content. The fine-grained granite is an alkali granite with a relatively high SiO_2 content (c. 75 weight%). The gouge material is also rich in quartz, and its content of calcite and clay minerals is significantly lower than in the gouge material of the Redox zone.

The hydrochemistry in the NE-1 zone during relatively undisturbed conditions (pre-excavation) characterised by saline water with c. 5700 mg/l Cl, 3300 mg/l Na and 900 mg/l Ca (Wikberg & Gustafsson, 1993). The excavation of the tunnel has influenced the hydraulic conditions leading to a decrease in chlorinity from 5700 mg/l to 4300 mg/l. The oxygen isotope signature indicates that marine water (probably present Baltic) enters the NE-1 zone; in contrast to the situation in the Redox zone the component of shallow non-saline water is very low. The HCO_3^- content remains relatively high (c.280 mg/l) whereas SO_4^{2-} is low, indicating that respiration by sulphate reduction has modified the water composition. This is also supported by Pedersen (1994) who reports the identification of sulphate reducing bacteria in water from this zone.

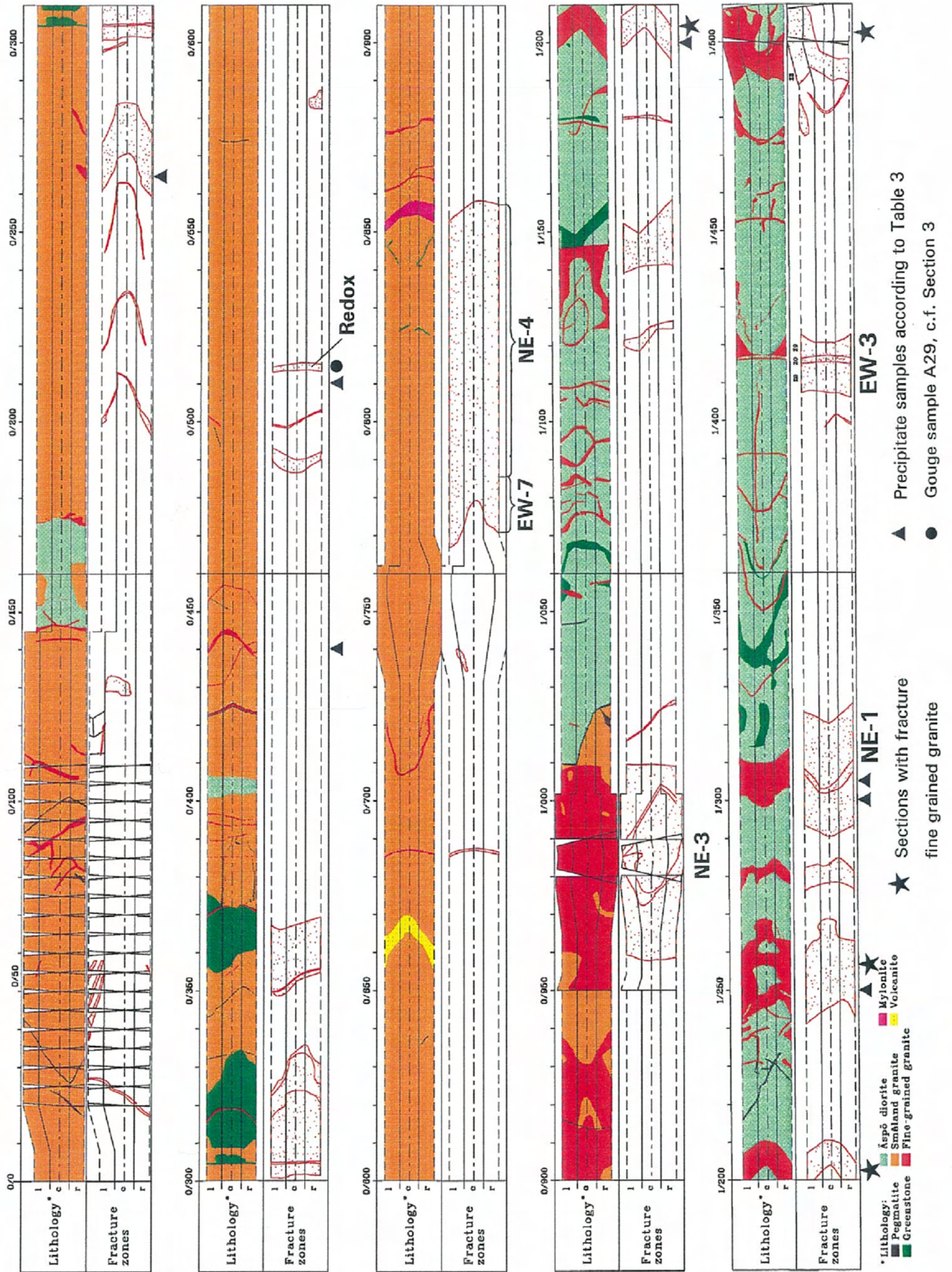


Figure 3. Lithology of the Äspö tunnel, section 0–1500 m.

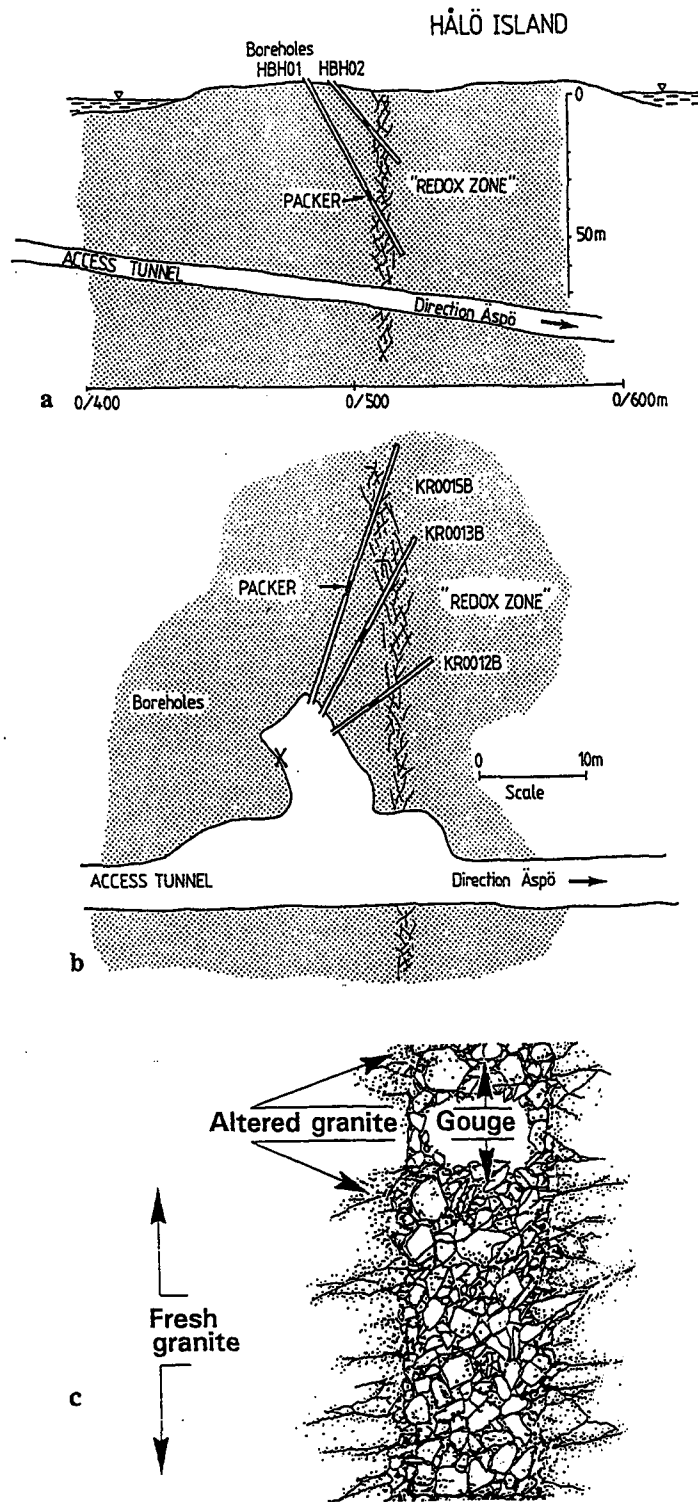


Figure 4 (a) Section and (b) plan views of the access tunnel, the Redox fracture zone and intersecting boreholes. The plan view shows the side tunnel used for instrumentation, from which three sampling boreholes are core-drilled horizontally into the fracture zone at a depth of 70 m. (c) close-up of the gouge filling from the zone (sample A 29). Sample location for the fresh precipitate, YR 0010-A is marked in figure b. (Modified from Banwart et al., 1994a).

3. METHODS

3.1 MAJOR AND TRACE ELEMENTS

Major and trace elements, including Th and U were determined using INAA ("Instrumental Neutron Activation Analysis"). ^{226}Ra , ^{228}Ra and ^{228}Th isotopes were determined using gamma ray spectrometry. All INAA and gamma spectrometry analyses were made on dried material.

3.2 SEQUENTIAL EXTRACTIONS

The amount of fracture coatings available on drillcores is often too small to allow, for instance, elemental analysis, XRD and sequential extractions on sub-samples. There is also a need for studying a large number of samples in order to identify and confirm general trends in the behaviour of trace elements. To overcome these problems we have tried a combination of INAA and sequential extractions; briefly:

- The sample is irradiated by neutrons in a reactor.
- Sequential extractions are applied to the irradiated ("radioactive") sample.
- The distribution and concentration (INAA) of elements in the different extraction phases is determined using gamma ray spectrometry.
- The residue (e.g. clays and mineral particles) can be investigated in more detail by, for instance microscopy, SEM and radioactivity measurements on individual grains to determine elemental compositions.

A prerequisite is that the radionuclides measured are formed by (n, γ) reactions i.e. reactions producing the same radionuclide from other elements must be insignificant. Some benefits of this combination of methods are that the elemental analysis and sequential extractions are carried out on the same sample, contamination problems in the extractions largely eliminated and losses in the extraction steps easily controlled by radioactivity measurements. The amount of sample can be fairly small (20 – 50 mg).

Possible errors caused by Szilard–Chalmers effect was checked by comparison with extractions applied to stable elements. No significant difference in element distribution was obtained. Although the technique for practical reasons is restricted to elements which form long-lived radionuclides ($T_{1/2} > 2-3$ days) when irradiated, most elements (or groups of elements) of interest can be studied conveniently. Exceptions are Th and U which form too short-lived radionuclides by the (n, γ) reactions. INAA analysis of Th and U are usually based on

measurements of ^{233}Pa and ^{239}Np , respectively. These radionuclides are carrier-free and at least ^{233}Pa seems to quickly sorb onto the solid phase in the extraction process. One way to determine the Th and U distributions is to re-irradiate the extracts and apply INAA. However, extractions of Th and U are usually combined with refined measurements of Th and U isotopes (using alpha-spectrometry). It is our intention to apply this technique on selected samples (of which sufficiently large amounts are available).

In a first step we have tested the applicability of these combined techniques on some representative samples. No effort was then spent on development or adjustment of the extraction procedure. An extraction scheme (including seven fractions), described and applied to soil samples by Salbu et al., 1992 and Riise et al., 1990, was adopted in this first step. The seven fractions are: "water soluble" (F1), "exchangeable" (F2), "carbonates" (F3), "easily reducible Fe/Mn oxides" (F4), "oxidizable organic matter" (F5), "acid digestible" (F6) and "residue" (F7). The reactants used in the different fractions are H_2O (F1), 1 M NH_4Ac (F2), 1 M $\text{NaAc}+\text{HAc}$ (F3), 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% (v/v) HAc (F4), 30% H_2O_2 (+3.2 M NH_4Ac) (F5) and 7 M HNO_3 (F6). In a second step the extraction procedure will be shortened (if possible) and adjusted to the relevant samples and elements.

4. "REVERSIBLE/IRREVERSIBLE" SORPTION ON CLAYISH GOUGE MATERIAL

4.1 CONCEPT

Fracture fillings containing clay minerals generally have high Rb and Cs concentrations. From calculations based on the "immobile element method" it seems clear that large parts of these concentrations are due to deposition from the water phase (Landström & Tullborg, 1991). If reversibly sorbed this would imply an unrealistically high distribution coefficient (K_d). Because of this, it is likely that a major proportion of the sorbed Rb and Cs is situated in "irreversible" positions of the clay minerals.

This is supported by studies of Cs-137 from the Chernobyl accident (Riise, et al., 1990; Carbol, 1993). Carbol (1993) showed that Cs-137 was preferentially sorbed on the smallest size fraction of the soil (<0.125 mm, "silt-clay"). He also concluded that Cs-137 was "strongly bound" (i.e. occurred to a large extent in the residual fraction of a sequential leaching procedure applied to soil samples) just 2 years after deposition.

For repository safety assessments it is important to clarify the extent to which Cs (and Rb) is reversibly or irreversibly sorbed, when migrating in natural fracture systems, as it directly influences the use of K_d -values determined in laboratory batch experiments. Our approach to this problem is sequential extraction of fracture fillings containing clay minerals.

The sequential leaching experiments presented below have been carried out on a "gouge" sample from the Redox zone (for site description see section 2.2). The sample is a mixture of fine-grained material which consists of K-feldspar, quartz, chlorite, epidote, clay minerals (dominantly illite rich mixed-layer clay), calcite and FeOOH, and small, hydrothermally altered rock fragments (in 1-10 mm scale) which are partly coated with a thin layer of Fe-oxyhydroxide (Fig 4c). The sample represents the solid material which is in contact with the water of the Redox zone (cf. Banwart et al., 1994c). The sample was collected about one year after the zone was intercepted, which means that sulfide minerals originally present in the zone have probably been oxidised. This may also be valid for U-bearing minerals.

4.2 RESULTS

INAA analyses of the gouge sample (A 29) and corresponding data for the host rock of the Redox zone are presented in Table 2 and in Figure 5. In the following

interpretation it is assumed that the gouge material originates from the host rock and has formed by different processes e.g. tectonism, alteration/weathering and subsequent formation of secondary minerals. Elements like Zr, Hf and Ti are also assumed to have been largely immobile during these processes and thus their concentrations represent the original host rock.

Table 2 also gives the ratios between the gouge and the host rock concentrations. The gouge values have been normalised to the Hf value of the host rock. Ratios higher than one indicate deposition (or "gain") of the element whereas those less than one indicate elemental loss. Deposition of Ca (as calcite), Fe (probably reflecting the red coloured coatings of Fe-oxyhydroxide), Rb, Cs, Th, U (?), Sc and REEs (especially the light REEs) are interpreted from the ratios in Table 2 (cf. also Fig 5). Loss of Na and Ba is indicated. Besides precipitation as calcite part of the deposited Ca can be due to ion exchange with Na.

The distribution of Cs, Ce, Yb, Th, Hf, and Fe on the different extraction fractions is shown in Figure 6. The water soluble (F1) and the exchangeable (F2) fractions are combined and defined as the "mobile" fraction (according to Salbu et al., (1992) and Carbol (1993)). The residue was separated into a fine-grained and a coarse-grained fraction. The first formed a suspension and thus consists mainly of clay minerals whereas the second contains mineral fragments.

Only a small portion of Cs is found to be in the F1+F2 fractions (1.4%) but as much as 75% occurs in the fine-grained residue and 13% in the coarse-grained one. About 5% of each are associated with the organic matter and the acid digestible phase. Calculations (based on the immobile element approach) shows that of the total 46 ppm (Table 2) about 4 ppm Cs is "inert" (that is original Cs bound to the mineral structure), 0.64 ppm is "reversibly" sorbed (F1+F2) and the rest, about 41 ppm is interpreted as being more strongly bound ("irreversibly" sorbed). Most of this, about 34 ppm, is found in the fine-grained residue (clay). Since the weight of the fine-grained residue is one fourth of the total sample (Fig. 6) the actual Cs concentration in this clay is as high as 134 ppm.

Rb (not shown in the figure) differs from Cs by being present in relatively higher contents in F1+F2 and in the coarse-grained residue (where Rb is probably hosted in K-feldspar, mica and chlorite). Similarly to Cs, part of the Rb is probably more strongly bound in the clay fraction. However, due to low levels of radioactivity, the Rb data are uncertain.

About 30% of the light REEs (represented by Ce in Fig. 6) occur in the two residue fractions, 42-49% in fraction F6 (acid digestible) and the rest equally proportioned between F3, F4 and F5 (Fig.6). The REEs are strongly fractionated as can be seen in Figures 6 and 7 and the table below, which compares Ce/Yb ratios ("ppm/ppm") of the total sample and the different fractions.

	Total	F1+F2	F3	F4	F5	F6	F7a	F7b
Ce/Yb	166	-	94	581	-	281	163	57

Table 2. Trace element composition of gouge and host rock samples from the Redox zone. (analysed by INAA).

Element	Gouge sample A 29	Host rock sample	Gouge*/Host rock
Na %	1,1	3,2	0,27
Ca	4,7	1,6	2,3
Fe	3,1	1,9	1,3
Cr ppm	14	29	0.38
Co	9,2	-	-
Zn	117	-	-
Sb	<0,2	-	-
Rb	280	97	2.3
Cs	46	2	18
Sr	890	660	1.1
Ba	710	930	0.61
Zr	-	-	-
Hf	4,3	3,4	1,0
Ta	0,77	0,85	0,72
Th	27	8,3	2,5
U	5,4	2,5	1,7
Sc	6,9	3,0	1,8
La	170	35	3,9
Ce	280	69	3,2
Nd	96	25	3,0
Sm	10	3.5	2,3
Eu	1,8	0,7	2,0
Gd	-	-	-
Tb	1,0	(0,34)	
Yb	1,7	1,2	1,1
Lu	0,23	0,16	1,1

*The gouge values have been normalised (assuming Hf to be immobile) according to the formula $C_{Hf\ corr} = C_{sample} \times Hf_{host\ rock} / Hf_{sample}$

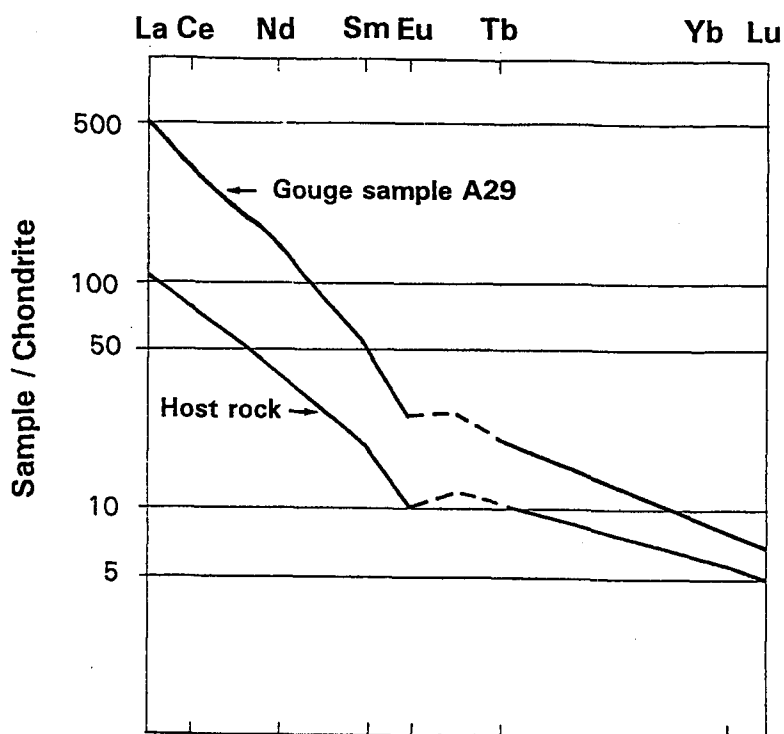


Figure 5. Chondrite normalised REE curves of gouge sample A 29 and host rock of the Redox zone (Småland granite).

The carbonate fraction (F3) and the coarse-grained residue (F7b) have lower ratios than the total sample. Heavy REEs form stronger carbonate complexes than light REEs and this may be reflected in the relative uptake in the carbonate phase. The REE pattern of the coarse-grained fraction resembles that of the host rock (Figs. 5 and 7) indicating that the fragments are largely representative of the host rock. This was verified by microscopy.

Fraction F4 (easily reducible Fe/Mn oxides) and F6 (acid digestible) are fractionated (enriched) in light REEs relative to the total sample (cf the table above and Figs 6 and 7). This may indicate a selective sorption of the light REEs and also some association with Fe; the latter occurs in both these fractions (Fig 6).

Hf and Ta occur in the residue fractions with 80–85% in the coarse-grained one (cf. Hf in Fig 6). This is expected from the fact that these elements usually occur in resistant minerals.

Th which is suggested to be partly deposited from the fluid phase as indicated from the ratio of 2.5 in Table 2, occurs to a large extent (56%) in the acid digestible fraction (F6). This supports the interpretation that Th (and also a large part of the light REEs) is irreversibly sorbed onto the outer grain surfaces which are affected by the HNO₃ treatment. (See also the discussion in chapter 4).

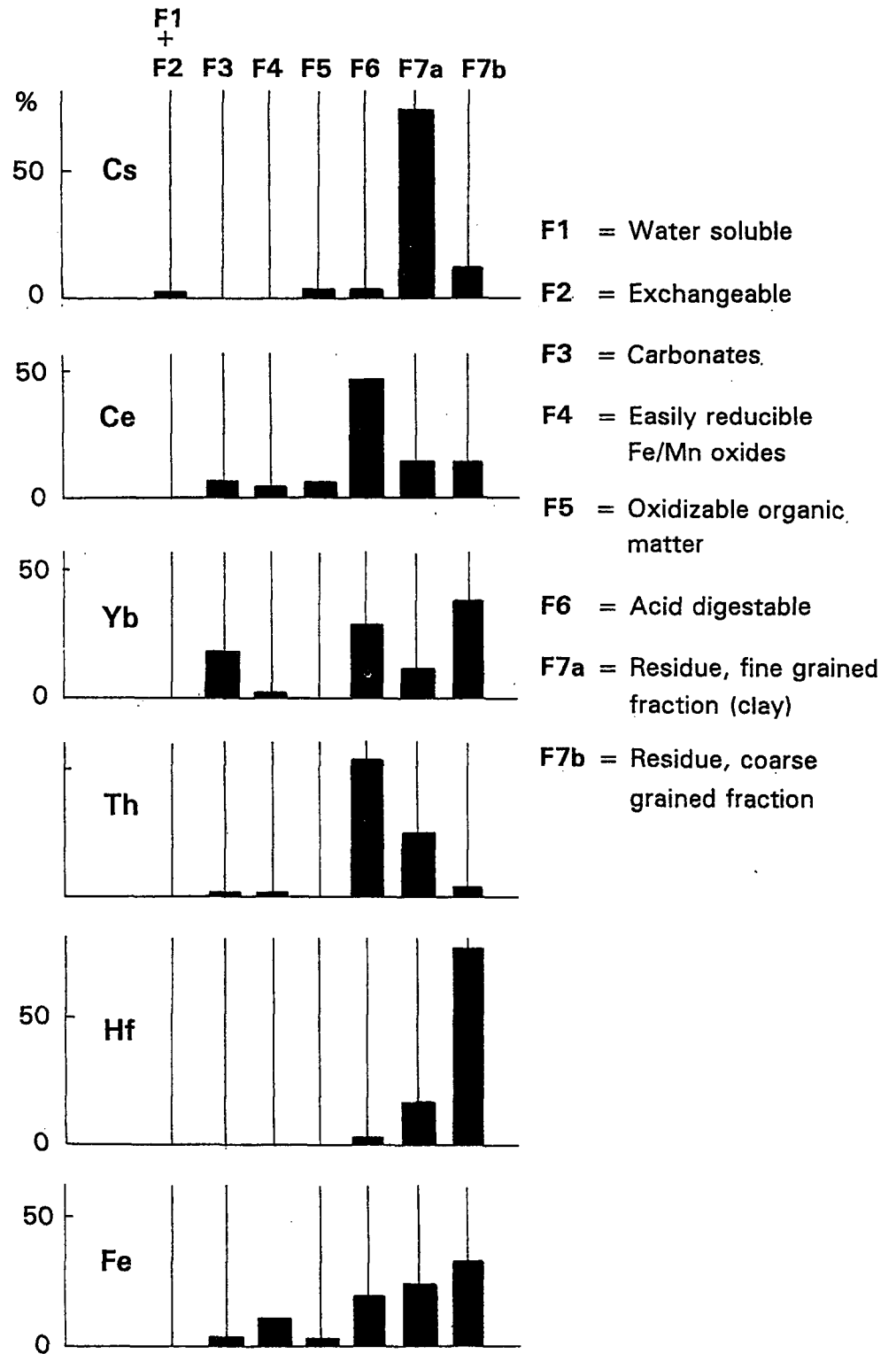


Figure 6 Relative distributions (%) of elements in different fractions of sequential extractions. Sample A29 (gouge material from the Redox zone).

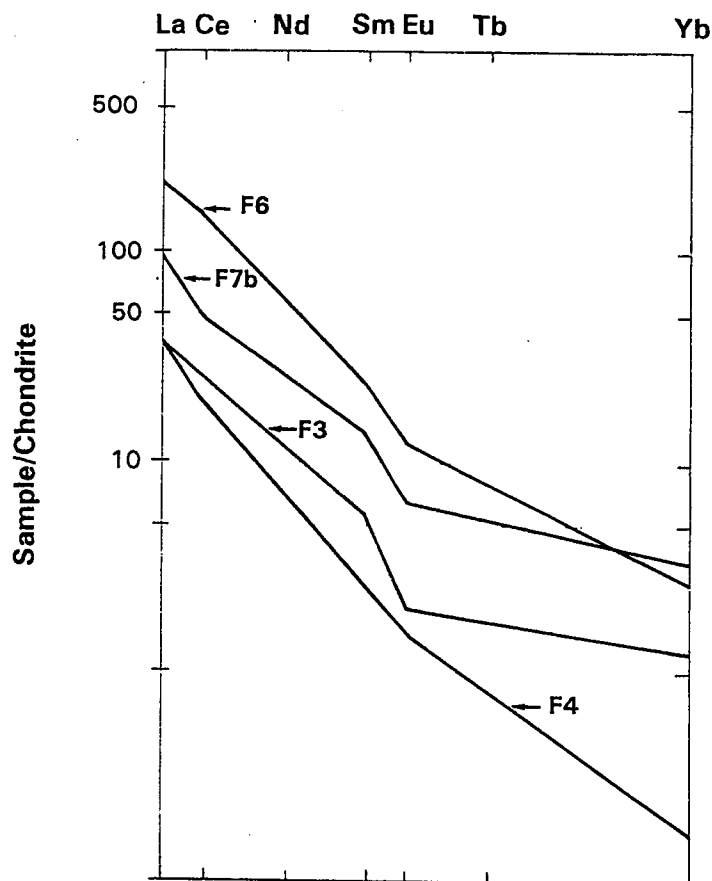


Figure 7. Chondrite normalised REE curves of different fractions of sequential extractions. Sample A 29 (gouge material from the Redox zone).

4.3 HIGH AND LOW TEMPERATURE ENRICHMENTS OF TRACE ELEMENTS

The Redox zone is an originally old (Proterozoic) fracture zone where hydrothermal activity has taken place. In connection to this hydrothermal activity redistribution of trace elements probably has occurred. However, analyses of fresh and altered granite from the Redox zone (Banwart et al., 1995) show that only minor changes in trace element contents have taken place in macro scale (whole rock samples). In detailed scale, trace elements have been redistributed due to mineral transformation and may have been deposited in new accessible positions. This means that part of the trace elements in the pieces of hydrothermally altered granite in sample A 29 is redistributed during high temperature conditions.

Formation of clay minerals is not a very active process in Äspö today. Clays in gouge material from the fracture zone NE-1 and the Redox zone show high illite/smectite ratios which indicate formation temperatures of at least 100°C (Landström & Tullborg, 1993 and Banwart et al., 1994a). Similar authigenic illite dominated mixed-layer clay from fracture zones NE-3 and NE-4 yielded ages of

c. 300 to 400 Ma (Maddock et al.,1993). These data suggest that the clays in the Redox zone and the NE-1 zone are of similar age. The investigated sample A 29 contained mixed-layer clay with high illite/smectite ratio. Portions of the excess trace elements in this sample may have been deposited in connection with the formation of the clay, i.e. during geochemical conditions different from those present and at a temperature around 100°C.

The Fe-oxyhydroxide in sample A 29 can, at least partly, be very young and due to recent oxidation in the tunnel (no pyrite is present in this sample). This means that trace elements associated with the Fe-oxyhydroxide phase may have been deposited from the present low-temperature groundwater.

The calcite phases of sample A 29 occur as discrete grains and as coatings on larger fragments; suggesting different formation conditions for the calcites. Stable oxygen and carbon isotope analyses of two calcites from the same location as sample A 29 (A2 and A3 in Table 12) show equilibrium with the native groundwater and with the present diluted groundwater, respectively. This indicates a dominance of low-temperature precipitate in the carbonate phase in sample A 29 and that trace elements associated with this phase deposited during low temperature groundwater.

Finally, the sequential extraction scheme may give some hints about low-temperature and hydrothermal enrichment. Fractions F1, F2, F3 and F5 should represent mainly low-temperature enrichments and also fraction F4 is probably dominated by elements involved in low-temperature processes, for example formation of amorphous Fe-oxyhydroxide. Fractions F6 and F7 may contain elements deposited by hydrothermal as well as low temperature processes.

4.6 PARTITION RATIOS FOR Cs

Extensive studies on sorption of Cs on different geological material have been carried out in laboratory batch and column experiments; mainly aimed at determine distribution coefficients (K_d) for use in predictive models. On a geological time scale the interaction between the solid and fluid phase was short in these experiments; usually days or weeks and in exceptional cases up to years.

The distribution of fallout and Chernobyl Cs-137 on different phases of contaminated soil samples have been studied (Riise et al., 1990 and Carbol, 1993). Although they applied slightly different extraction scheme, the results are largely similar; a low portion (10-25%) of total Cs-137 being "mobile" (i.e. exchangeable and loosely attached to mineral surfaces, Fe/Mn oxides, etc) and a large portion (65-75%) strongly bound (occurring in the acid leachable and residue fractions). The strongly bound Cs-137 was associated with fine-grained minerogenic material rich in mica and illite. Extensive isotope exchange (Cs-137 and Cs-133)

during the three year period after the Chernobyl accident was also observed (Riise et al., 1990).

There is a significant difference between our results and those of Riise et al. (1990) and Carbol (1993). Whereas most "deposited" stable Cs in sample A 29 is found in the clay residue fraction and only a minor portion in the acid digestible, about equal amounts of Cs-137 (and also Cs-133) were found in these phases of extracted soil samples. This may be attributed to different times available for Cs isotopes to reach more inaccessible interlayer positions but also to the different kinds of sample and environment.

The kinetics of the sorption of Cs on illite was studied by Comans et al. (1991) in series of adsorption and desorption experiments. The processes observed were described as an initial rapid adsorption of Cs on surface sites of illite followed by much slower migration towards interlayer sites; within weeks to months or longer. Also the desorption (after 14 days equilibrium time) was initially rapid. It was concluded that Cs was released from rapidly accessible positions but that the slow forward reaction continued. Experiments on K and Ca saturated illites showed that the sorption was strongly dependent on the competing cations. Evans et al., (1983) found that the discrepancy between the sorbed and desorbed portions seems to increase in time scale of years.

These data indicate that the migration into the interlayer sites starts immediately (is observable within days) and continues for long time and that the desorption from these interlayer sites is very slow. The slow kinetics of the interlayer sorption/desorption makes the terms "reversible" and "irreversible" dependent on the time scale of the experiment and of the processes which are modelled. The term "reversible" uptake used in this report is based on the element content extracted in fractions (F1+F2) with a contact time of <1day and does not include release of Cs from the interlayer positions.

The groundwater in contact with sample A29 is represented by water from borehole KR0012 which has a Cs content of 0.64 $\mu\text{g/l}$ (Table 10). For comparison, a Cs value of 3.0 $\mu\text{g/l}$ for the native groundwater has been estimated from the Cs-Na plot (Fig 12a). Relating these concentrations (0.64 and 3.0 $\mu\text{g/l}$) to the reversibly sorbed ("mobile") fraction of the gouge material (0.64 ppm) give partition ratios of 1.0 and 0.22 m^3/kg , respectively. These are similar to K_d -values obtained in batch experiments; Andersson (1983) gives general values between 0.1–1.0 m^3/kg for crushed rock and rock forming minerals. Comans et al., (1991) give K_d -values for K-saturated illite and fresh water (Ca-HCO₃-type) of approx. 10 m^3/kg (and much higher values for Ca-saturated illite). Byegård et al., (1994) give values of 0.0035 m^3/kg as a measure of "reversible" K_d for chlorite and values of the same order for crushed granite. Saline groundwater (Cl=5600 mg/l) was used in their experiment. As the investigated sample (A 29) constitutes a mixture of minerals of different grain sizes, it would be more relevant to compare the partition ratios with K_d 's obtained in batch experiments on the same gouge material and with groundwater from borehole KR0012.

5. STUDIES OF ONGOING PRECIPITATION OF Fe-OXYHYDROXIDES AND CALCITE

5.1 CONCEPT

In laboratory batch experiments actinides (Np) and REEs (Pm) were shown to strongly sorb on goethite and hematite (Vannerberg, 1994). Studies of fracture coatings containing hematite and Fe(III)-oxyhydroxide have also indicated enrichment of REE, Th and U in these phases (Landström & Tullborg, 1990 and 1991). It is ambiguous whether this enrichment occurred mainly during hydrothermal conditions, sustained for a very long period or is active today. When groundwater emerges from exposed fractures into the Äspö tunnel, Fe(III)-hydroxide and calcite precipitate due to oxidation of Fe (II) and release of CO₂, respectively. The Fe-oxyhydroxides are subsequently formed by dehydration of the Fe(III)-hydroxide. Preliminary analyses revealed uptake of Sr, Ba, Ra, REEs, Sc, Th and U; either co-precipitated or sorbed onto already formed precipitates. This offers a unique possibility for detailed studies of the retention of these elements by Fe-oxyhydroxide and calcite during present low-temperature conditions.

Precipitation of amorphous Fe(III)-hydroxides is common in many Swedish mines and large quantities can be formed. Landström (1978) measured very high concentrations of ²²⁶Ra and ²²⁸Ra (as high as 8x10⁵ Bq/kg of ²²⁶Ra on a dry weight base) in Fe/Mn hydroxides from a small mine in central Sweden. In fact, the large amounts of these hydroxides constituted a significant radon source within the galleries. However, to our present knowledge, no systematic investigations have been carried out concerning the uptake of trace elements in Fe-oxyhydroxide precipitates in deep mines.

In a similar way Fe-oxyhydroxide and calcite may form in nuclear waste repositories during construction; not only in the excavations but possibly also within fractures close to their exposures. This may change the properties of the fractures and hence influence the conditions for radionuclide migration.

In this present study Fe and Ca precipitates from different fracture zones were studied and specific retention capacities for the two minerals Fe-oxyhydroxide and calcite were measured. The study has focused on how the element and radionuclide patterns of precipitates are related to the composition of the contact groundwater and the properties of the associated fracture zones.

5.2 SAMPLING, SAMPLE PREPARATION AND ANALYTICAL METHODS

Samples of precipitates were taken at exposures of different interesting fractures along the tunnel. Sampling sites are marked in Figure 3 and data about these sites are listed in Table 3. No systematic sampling to study variations with time has been made. The precipitates were sampled with a plastic spoon, centrifuged and dried at 105 °C.

At fractures with low groundwater flow only relatively thin layers of precipitate were formed (e.g. sites YA 0440 A and YR 0010 A). These precipitates were, to some extent, mixed with rock and mineral fragments which had been released in connection with the blasting operation and remained as a thin layer on the tunnel wall surface. Before the analysis, large pieces of contaminating fragments were removed. The contribution to the elemental concentrations from the remaining particles was corrected for in two ways (cf. section 5.3). In the highly water conducting NE-1 zone rather thick (10–15 cm) ridges of precipitates were formed; samples taken from the outer part of these ridges contained no rock and mineral particles.

To test the homogeneity of the precipitates (considering the elemental composition), two samples from the NE-1 area (NE-1 X and NE-1 Y) were taken about 1 m apart. At the YR 0010 A fracture two samples were taken from the same location but at an interval of about one year.

The samples are dominated by Fe(III) precipitates which range from Fe-hydroxide to amorphous (and possibly also some crystalline) Fe-oxyhydroxide; these phases are termed Fe-oxyhydroxides in the following. All samples contained approximately 10–15% calcite, which is usually extremely fine-grained, due to rapid precipitation in connection with degassing of CO₂ when the water enters the tunnel. The calcite grains mostly form aggregates which are mixed with the Fe-oxyhydroxide. However, in samples YR-0010A-1 and NE-1Y small calcite crystals could be hand-picked and were analysed separately. Sample YR-0010A-1 also contained magnetite, probably formed by Fe(III) reducing bacteria; such bacteria have been identified in groundwater samples from the Redox zone (Pedersen, 1994).

Major and trace elements, including Th and U were determined using INAA ("Instrumental Neutron Activation Analyses") and ²²⁶Ra, ²²⁸Ra and ²²⁸Th isotopes using gamma ray spectrometry. All INAA and gamma spectrometry analyses were made on dried material. Sequential extraction was applied to one precipitate sample (NE-1 Y). For details about methods, see chapter 3.

Table 3. Data on sampling sites for Fe–oxyhydroxide and calcite precipitates along the Äspö tunnel.

Sample flow**	Tunnel length (m)	Date of sampling	Date of latest activity*	Dominating host rock	Water
YA 0263B	263	921008	910516	Småland granite	w
YA 0440A	440	921008	910900	–"/ Fine–grained gr	w
<i>The Redox zone</i>					
YR 0010A–1	510	921008	910315	Småland granite	w
YR 0010A–2	–"	931110	–"	–"	w
OL	c. 1200	920512	–	–	w
<i>Fracture zone NE–1</i>					
1250 B 1250	930605	–	–	Fine–grained granite	s
NE–1 X	c.1300	930605	–	Fine–grained granite	s
NE–1 Y	–"	–"	–	–"	s
1306	1306	930728	–	–"	s

* e.g. time of blasting, cleaning etc.

** w = weak, s = strong.

5.3 RESULTS

Results of the INAA analyses and of the sequential extractions are presented in Tables 4 and 5 and activity and activity ratios of U, Ra and Th isotopes are presented in Table 6. Th and U are treated both in the trace element chapter and in the radionuclide chapter.

Corrections of contributions from contaminating rock fragments

Samples taken from thin precipitate layers were usually contaminated by rock and mineral fragments which contributed to the total elemental composition of the

sample. To obtain the specific concentrations of the precipitates these contributions had to be corrected for. This was carried out in two ways for sample YR 0010 A-1:

1. Microscopy showed that the contaminating fragments were fresh pieces of host rock (in this case Småland granite). Assuming 1) that all Hf in the sample was associated with the rock fragments, and 2) that the latter had the same elemental composition as the host rock, the concentrations of the fragments were calculated and subtracted from the total values (Table 4a).
2. A large part of the Fe-oxyhydroxide in this sample has been transformed to magnetite; Fe(III) probably reduced by bacteria. Using a strong magnet it could be removed. Although the separation was not as effective as desired the fraction of rock fragments was reduced in the separate. The separated magnetite was analysed with INAA (Table 4a).

Although both these corrections are imprecise they are supported by a reasonable agreement between them (Table 4a) and also by low or zero concentrations of Na, Al, Rb and Cs (elements present in the host rock and in clay particles but not likely to accumulate in Fe-oxyhydroxide and calcite).

Contamination of the NE-1 samples by rock and mineral fragments is considered insignificant and has been neglected. This is supported by microscopy, low contents of Hf, Ta, Rb and Cs (Table 4b) and the absence of a residual phase in the sequential extraction (Table 5).

5.3.1 MAJOR AND TRACE ELEMENTS

Fe and Mn:

The Fe content of some samples (e.g. YR 0010 A) are 10–20% lower than that of the NE-1 samples due to dilution by contaminating rock fragments. The sequential extraction of sample NE-1 Y (Table 5) shows a partition of Fe between fractions F4 (easily reducible Fe-oxide) and F6 (acid digestible) of 65% and 35% respectively. This may be interpreted as a gradual change into more crystalline forms of Fe-oxyhydroxide. The concentration of Mn is low (< 0.25% in the two samples analysed).

Table 4a. Elemental concentrations in precipitates from the Redox zone area.

	YR 0010A-1				YR 0010A-2
	Total	Corr*	Magnetite*	Calcite**	Total
Na%	0,39	-	0,22	0,73	-
Ca	5,7	6,9	4,1	39	6,8
Al	0,79	-	-	-	-
Fe	35	45	43	1,4	31
Mn	0,14	-	-	-	-
Cr ppm	10	4,0	11	25	14
Co	1,5	-	1,3	5,0	1,0
Zn	-	-	<10	-	-
Sb	0,18	-	<0,5	1,3	0,18
As	-	-	3,9	<2	-
Rb	29	8,4	<20	<50	20
Cs	0,65	-	<0,2	<2	0,64
Sr	1890	2250	2400	1660	1280
Ba	1210	1300	1520	710	1150
Hf	0,79	-	0,55	<0,3	0,45
Ta	-	-	<0,2	-	-
Th	3,0	1,4	2,3	<0,3	2,8
U	1,8	1,6	2,4	1,5	1,6
Sc	1,6	1,2	1,3	0,98	1,2
La	109	131	125	78	148
Ce	175	207	194	91	206
Nd	83	100	110	30	122
Sm	15	18	17	4,0	19
Eu	3,2	4,0	4,0	0,88	4,0
Tb	2,6	-	2,5	-	2,6
Yb	7,5	9,4	7,7	0,91	8,7
Lu	1,1	1,3	1,2	0,14	1,4

YR 0010A-1 is sampled 921008

YR 0010A-2 is sampled 931119

* see text for explanation

** calcite crystals hand-picked from YR 0010A-1

Table 4b. Elemental concentrations in precipitates from NE-1 zone area.

	1250B	NE-1 X	NE-1 Y	Calcite*	1306
Na%	0,48	0,49	0,41	0,0014	0,55
Ca	5,5	11,2	6,6	35,4	5,8
Al	-	-	-	-	-
Fe	42,9	40,6	39,4	2,4	43
Mn	-	-	-	-	-
Cr ppm	9,3	8,3	7,4	7,6	6,0
Co	3,3	2,4	2,6	0,72	2,3
Zn	-	7,0	8,0	7,7	2900
Sb	<0,3	<0,3	<0,3	0,32	0,14
As	-	-	-	-	2,6
Rb	<15	<15	<15	-	<15
Cs	<0,25	<0,25	<0,25	-	<0,25
Sr	1220	2030	1320	1570	2740
Ba	680	860	850	440	1010
Hf	<0,25	<0,25	<0,25	-	<0,25
Ta	<0,2	<0,2	<0,2	-	-
Th	0,82	0,91	0,27	-	<0,2
U	5,8	4,7	4,4	3,8	2,3
Sc	2,1	2,2	2,0	0,22	0,42
La	29	22	17	0,94	10
Ce	51	37	26	1,0	16
Nd	31	23	-	-	10
Sm	8,1	6,0	4,2	0,43	2,3
Eu	1,1	0,89	0,66	-	0,37
Tb	2,3	1,9	1,6	-	0,50
Yb	14,6	13,1	11,6	0,77	2,0
Lu	2,4	2,1	1,8	-	0,32

* Calcite crystals hand-picked from precipitate NE-1Y (only 2 mg).

Table 4c. Elemental concentrations in precipitates from different fractures.

	YA0263 B 263 m	YA0440 A 440 m	OL c. 1200 m
Na%	0,58	1,0	-
Ca	5,5	8,0	6,8
Al	0,06	-	-
Fe	36	27	43,6
Mn	0,21	-	-
Cr ppm	3,4	9,7	3,1
Co	0,23	2,8	0,92
Zn	230	-	-
Sb	0,11	-	0,67
As	9,2	-	-
Rb	14	43	<10
Cs	0,10	0,5	<0,5
Sr	1710	1660	1860
Ba	390	400	330
Hf	-	1,7	<0,1
Ta	-	0,33	<0,1
Th	0,21	3,1	<0,2
U	2,5	2,8	<0,5
Sc	0,24	2,0	0,37
La	28	48	15
Ce	41	75	18
Nd	-	37	7,0
Sm	5,4	5,0	1,3
Eu	1,1	1,1	0,29
Tb	1,6	0,86	0,27
Yb	2,1	3,3	1,1
Lu	0,29	0,57	0,2

Table 5. Total concentrations of elements and their relative distributions in the different extraction fractions. Sample NE-1 Y.

Element	Concentrations (INAA)	Relative distributions in %						
		F1	F2	F3	F4	F5	F6	Residue
Ca	6,6 %	<2	30	68	-	-	-	-
Fe	39,4	-	-	2	58	4	36	-
Sr	1320, ppm	1	21	78	-	-	-	-
Ba	850	-	2	34	64	-	-	-
Hf	0,47	-	-	-	-	-	100	-
Th	0,27	-	-	-	-	-	100	-
U	4,4	-	3	39	39	16	3	-
Sc	2,1	0,1	0,2	17	46	11	26	-
La	17	-	-	9	38	21	32	-
Ce	26	-	-	9	30	16	45	-
Nd	-	-	-	-	-	-	-	-
Sm	4,2	-	-	9	29	13	49	-
Eu	0,66	-	-	11	26	16	47	-
Tb	1,6	-	-	13	35	16	36	-
Yb	11,6	-	-	11	26	12	51	-
Lu	1,8	-	-	11	26	14	49	-

F1 = Water soluble
 F2 = Exchangeable
 F3 = Carbonates
 F4 = Easily reducible Fe/Mn oxides
 F5 = Oxidizable organic matter
 F6 = Acid digestible

Ca and Sr:

Ca ranges from 5.5 to 11% and Sr from 1200 to 2000 ppm. Ca and Sr are both confined to fractions F2 and F3 of the sequential extraction procedure (Table 5) with the main proportions (68 and 78%, respectively) associated with the carbonate phase (F3) and 30 and 21% exchangeable (F2). From microscopy and tests with HCl it is clear that the carbonate phase consists of calcite. The Ca/Sr ratios of the precipitates (on average 41) are similar to or slightly lower than those of the Äspö groundwaters, indicating co-precipitation of these elements. However, the Ca/Sr ratio of small hand-picked calcite crystals is higher by a factor of 5 (on

average 230) and the Ca/Sr ratio of calcite dominated fracture fillings still higher (ranging from 450–6000). This large span indicates an influence on the Ca/Sr ratio of the high precipitation rate as discussed in chapter 6.

Rb and Cs:

Rb and Cs are low in all precipitates, for example < 15 and < 0.25 ppm, respectively, in the NE-1 samples. Considering the relatively high Rb and Cs concentrations in the Äspö groundwaters (21–41 and 1.1–3.2 µg/l (cf. Table 10 and Landström & Tullborg, 1991) these low values demonstrate the insignificant retention capacity of Fe-oxyhydroxide and calcite for these elements in the current geochemical environment.

Ba:

Precipitates from the Redox and the NE-1 zones have the highest Ba concentrations, 800 ppm–1000 ppm. According to the sequential extraction most Ba (64%) is associated with Fe in fraction F4 (easily reducible Fe-oxide) and about 33% with carbonate in fraction F3 (Table 5 and Fig. 9). However, being less frequent (about 10–15% of the sample weight) calcite shows a retention capacity for Ba which is a factor of 3 higher than that of Fe-oxyhydroxide. The Ra-Ba relationship is discussed separately.

Co, Cr, Zn, Sb and As:

Co, Cr, Zn and Sb are low in most samples. Exceptions are high values of Zn in samples YA 0263 B and 1306 A. The cause of this has not been clarified but contamination due to different activities in the tunnel (e.g. grouting of the NE-1 fracture zone at 1306 m) should be considered. Only a few analyses of As have been made but the results indicate an enrichment of this element.

REEs and Sc:

The REEs vary significantly between different fracture sites, both in concentration level and in chondrite normalised patterns (Table 4 and Fig. 8). Samples from the NE-1 area are characterised by low La/Yb ratios (2–5), high concentrations of heavy REEs and pronounced negative Eu anomalies. Since contamination of these samples by rock and mineral fragments is negligible it is suggested that the REEs have been deposited from the groundwater phase.

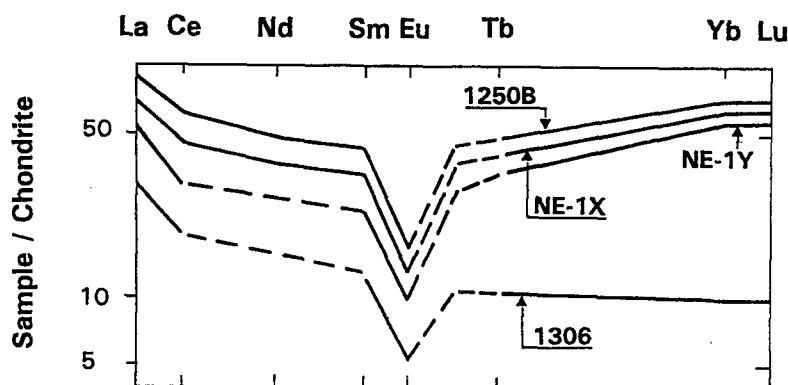
The two YR 0010 A samples from the Redox zone area contrast with higher La/Yb ratios (14–16), 3 to 5 times higher concentrations of light REEs and smaller Eu anomalies than in the NE-1 samples. It is clear from the high REE values of the corrected sample YR 0010 A-1 (Table 4) and the separated magnetite that the REEs are associated with the precipitates and thus deposited from the groundwater phase.

In the sequential extraction of sample NE-1 Y (Table 5) about 10% of the total REEs are found in the carbonate phase F3, 15–20% in the organic phase F5 and the main portion (about 70%) partitioned between fractions F4 and F6 (easily reducible Fe-oxide and acid digestible, respectively). However, the ratios of REEs

to Ca and Fe, indicate an approximately equal retention capacity of calcite and Fe-oxyhydroxide for REEs (cf. section 4.4). Compared to total REEs, the REEs of the different fractions are slightly fractionated (see the table below showing Ce/Yb ratios), suggesting a somewhat stronger association of heavy REEs with fractions F3 and F6 (carbonate and acid digestible) and of light REEs with fractions F4 and F5 (easily reducible and oxidizable organics, respectively).

	Total	F1+F2	F3	F4	F5	F6
Ce/Yb	2.2	-	1.7	2.6	3.0	1.9

A



B

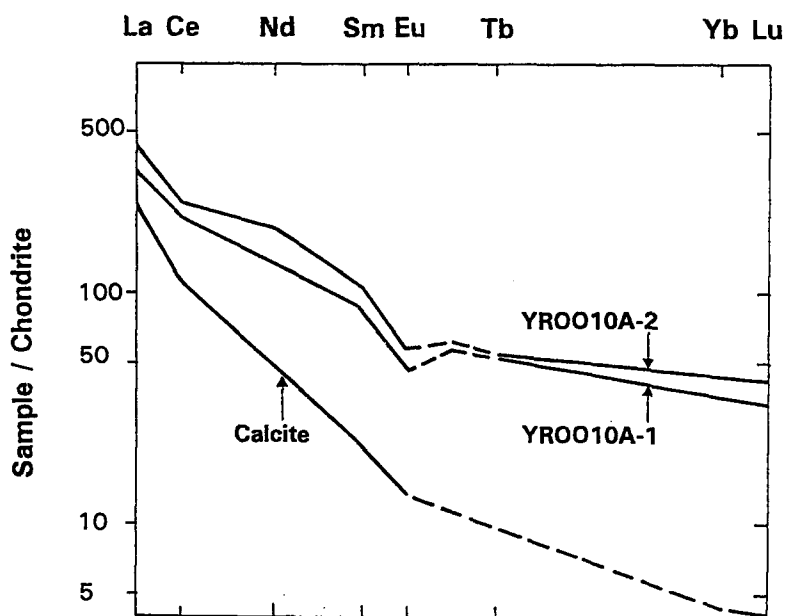


Figure 8. Chondrite-normalised REE curves of precipitates from the NE-1 (a) and Redox zones (b) and a calcite separate from sample YR0010-A-1 (b).

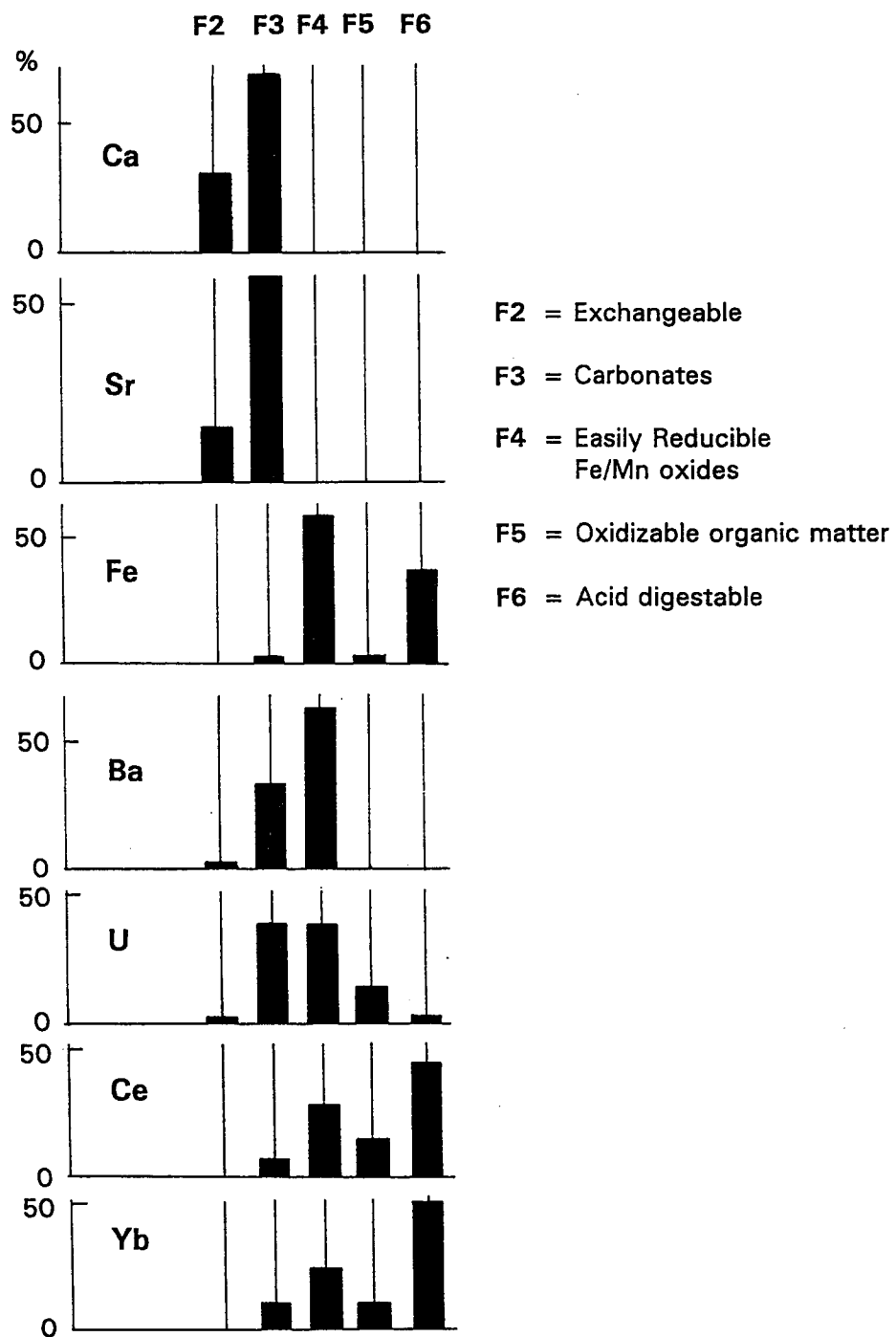


Figure 9. Relative distribution (%) of selected elements in different fractions of sequential extractions. Sample NE-1 Y.

The small calcite crystals which were hand-picked from sample YR 0010 A-1 show strong fractionation in light REEs, with a La/Yb ratio of 81 (Table 5 and Fig 8). This suggests that the accumulation process may be controlled by the similar size of the Ca and La ionic radii. However, the corresponding calcite crystals from sample NE-1Y show very low La/Yb ratios, 1.2, which seem to be of the same order as the ratio of the supplying water (cf section 5.4.3.).

Sc is generally low in all precipitates but slightly higher in the NE-1 samples than in the YR 0010A samples; the Sc/La ratio is thus a factor of 10 higher in the former. The distribution of Sc in the extraction fractions follows roughly those of REEs (Table 5). Calcite seems, however, to be more efficient in retaining Sc as is apparent from the calculated Sc concentrations in calcite and Fe-oxyhydroxide (Table 9). Similarly to the REEs, it is suggested that Sc has been deposited from the groundwater phase.

Hf, Ta and Th:

Hf, Ta and Th usually occur in resistant minerals (zircon etc). This fact, together with low solubilities have classified them as more or less immobile in low-temperature alteration and weathering processes. Occurrence of these elements in the precipitates would thus indicate contamination by some accessory minerals or rock fragments. Measured concentrations of Hf and Ta can be explained in this way but not Th. 1.4 ppm Th remains in sample YR 0010 A-1 after correcting for contributions from contaminating rock fragments (Table 4a).

Recent studies have demonstrated Th mobility in crystalline rock environments. Release of ^{230}Th from illitic clay to groundwater has been reported by Griffault et al., (1993) and an excess of Th, obviously supplied from the fluid phase has been observed in fracture fillings by Landström & Tullborg, (1990, 1991). Moreover, the disequilibrium of $^{228}\text{Th}/^{228}\text{Ra}$ (with activity ratios significantly exceeding unity) in the YR 0010 A samples indicates an on-going supply of ^{228}Th from the groundwater phase (cf section "natural radionuclides"). Although we cannot present any strong proof of ^{232}Th uptake in the precipitates (mainly due to uncertainties in the corrections for contaminating rock fragments), the deposition of ^{232}Th from the groundwater phase can not be ruled out. Th (as ^{232}Th) has, moreover, been determined in surface water and groundwater from the Redox zone (Table 10).

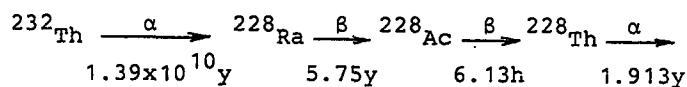
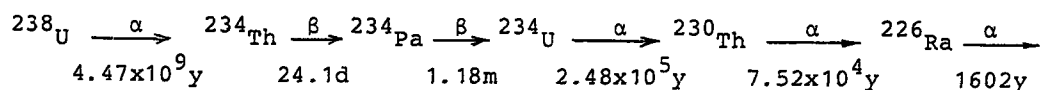
U:

U is generally low with highest values in the NE-1 samples (4-6 ppm, Table 4). The sequential extraction of sample NE-1Y shows a partition of U between fractions F3 (carbonate) and F4 (easily reducible Fe-oxide) with about 39% in each and 16% in the organic phase F5 (Fig. 8). However, the U concentrations in the carbonate and Fe-oxyhydroxide phases (cf. section 5.4 and Table 9) indicate a factor of 9 higher retention capacity of the carbonate phase for U compared to the Fe-oxyhydroxide. This gives a U concentration in the carbonate phase of about 18 ppm (Table 9) However, analysis of hand-picked calcite crystals from the NE-1Y gives only 4 ppm. This difference can have different causes, for example:

- The U uptake may depend on the precipitation rate; i.e. higher concentrations are taken up in rapidly precipitated carbonate aggregates than in the relatively larger calcite crystals. This explanation is suggested for the corresponding difference in the Sr contents (cf the Sr section above).
- Removal of U adsorbed on the Fe-oxyhydroxide phase in connection with the extraction of carbonates (F3). The adsorption of U on Fe-oxyhydroxide is strongly pH dependent and the pH 5 used in the carbonate extraction step may be sufficiently low to allow desorption of U from the Fe-oxyhydroxide phase as well. However, in solutions with high carbonate contents the sorption of U on Fe-oxyhydroxide is very low (Hsi & Langmuir 1985) and this may be the case in the NE-1 zone in which the groundwater has a HCO_3^- content of 354 ppm.

5.3.2 NATURAL RADIONUCLIDES

Below are shown relevant parts of the ^{238}U and ^{232}Th decay chains. In a closed system radioactive equilibrium (which means equal activities of the different members and thus that all activity ratios equal unity) will be attained within 1.5 Ma for the ^{238}U decay chain and about 30 a for the ^{232}Th decay chain. In an open system, like the studied fractured crystalline rocks, the equilibria are usually strongly upset. This is a consequence of different mobilities of the chain members, α -recoil effects and dependence on precursor isotopes.



This study has been focused on Th and Ra isotopes, as their reported behaviour in fractured crystalline rocks are scarce; most importantly their relative half-lives are favourable for disequilibria studies within the time span of construction and operation of the Äspö Hard Rock Laboratory (HRL).

As is clear from Table 6, the precipitates are associated with considerable Ra isotope activity; the highest ^{226}Ra value (950 Bq/kg) is equivalent to about 75 ppm U and the highest ^{228}Ra value (5550 Bq/kg) is equivalent to about 1400 ppm Th.

Table 6. Activity (in Bq/kg, dry weight base) and activity ratios of natural radionuclides

Sample	Th-232*	U-238*	Ra-226	Ra-228	Th-228	$\frac{\text{Ra-226}}{\text{U-238}}$	$\frac{\text{Ra-228}}{\text{Th-232}}$	$\frac{\text{Th-228}}{\text{Ra-228}}$	$\frac{\text{Ra-228}}{\text{Ra-226}}$
YA0263B	0.82	31	950	3500	1430	113	4270	0.41	3.70
YA044A	3.50	< 25	110	450	310	> 4	129	0.69	4.10
OL (c. 1200 m)	<0.80	< 6	843	682	310	>140	>800	0.45	0.81
YR0010A -1 (Redox zone)	11.80	22	362	336	652	17	28	1.90	0.93
YR0010A -2 (Redox zone)	11.00	20	187	178	598	9.4	16	3.40	0.95
1250B (NE-1 zone)	3.20	72	548	2400	689	7.6	750	0.29	4.40
NE-1 X (NE-1 zone)	3.60	58	700	5550	1130	12	1541	0.20	7.90
NE-1 Y (NE-1 zone)	1.10	55	615	5270	952	11	4790	0.18	8.60

*Activities calculated from INAA analyses

$^{226}\text{Ra}/^{238}\text{U}$ and $^{228}\text{Ra}/^{232}\text{Th}$ activity ratios:

In all samples the activities of ^{226}Ra and ^{228}Ra are much higher than their grandparents ^{238}U and ^{232}Th . Such disequilibria of $^{226}\text{Ra}/^{238}\text{U}$ and $^{228}\text{Ra}/^{232}\text{Th}$ can either indicate a higher sorption capacity of the precipitates for Ra than for U and Th, or simply reflect the relative concentrations of these isotopes in the supplying groundwater. In Table 7 the $^{226}\text{Ra}/^{238}\text{U}$ ratios of the YR0010 A precipitates and in groundwater from the Redox zone are compared. The ratios are significantly higher in the precipitates indicating preferential accumulation of ^{226}Ra . The main Redox fracture zone is only a few metres from the YR0010 A fracture (Fig 4b) and its groundwater data are assumed to be representative of the YR 0010A groundwater.

Table 7. Comparison of $^{226}\text{Ra}/^{238}\text{U}$ activity ratios of Redox groundwater and YR0010A precipitates.

	Groundwater				Precipitate	
	KR0012	KR0013	KR0015	HBH02	YR0010A-1	YR0010A-2
$^{226}\text{Ra}/^{238}\text{U}$	0,48	0,71	1,1	<0,68	17	9,4

$^{228}\text{Th}/^{228}\text{Ra}$ activity ratios:

The $^{228}\text{Th}/^{228}\text{Ra}$ activity ratio shows large variation; from 0.18 in NE-1 Y to 3.4 in YR0010 A-2. ^{228}Ra has been deposited from the groundwater, whereas three different sources of ^{228}Th can be identified:

- ^{228}Th confined in contaminating rock fragments. Since the Th content in the (YR 0010 A-2) sample, 2.8 ppm, is equivalent to 11Bq/kg ^{228}Th , this source can be neglected when compared to the measured activities.
- ^{228}Th produced by ingrowth through decay of deposited ^{228}Ra . This activity is significant but difficult to calculate because the time of deposition can not be precisely defined. However, due to the low age of the precipitates (<1-2 years) the ^{228}Th activity can never exceed that of ^{228}Ra unless the latter has been released from the precipitates, which is not probable.
- ^{228}Th deposited from the groundwater phase. This can explain a ratio exceeding unity.

From the above, it is clear that the $^{228}\text{Th}/^{228}\text{Ra}$ ratios in the YR0010 A samples (1.9 and 3.4) strongly suggest that a fraction of the measured ^{228}Th activity has been deposited from the groundwater. ^{228}Th is thus mobile in the present system.

$^{228}\text{Ra}/^{226}\text{Ra}$ activity ratios:

The $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio is about 1 for the YR 0010 A samples from the Redox zone area but as high as 8.6 for the samples from the NE-1 area (Table 6). Since the two Ra isotopes are expected to behave similarly in the sorption process

these ratios reflect those of the supplying groundwater; the latter are only slightly higher (about 10%) due to decay of deposited ^{228}Ra . The large difference between the ratios of groundwater from the YR0010-A fracture and the NE-1 zone is interesting since the ratio depends, in a complex way, on the geological, hydrogeological and geochemical properties of the fracture (and thus could be used as a source of information about these properties). This is exemplified by three alternative interpretations of the cause of the variations in $^{228}\text{Ra}/^{226}\text{Ra}$ ratios:

- 1) The $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio simply reflects the activity ratio of their grandparent (^{232}Th and ^{238}U) in the host rocks i.e. the radium isotopes are released to the groundwater in proportion to their occurrence in the host rock. The $^{232}\text{Th}/^{238}\text{U}$ activity ratio of Småland granite (host rock in the Redox zone) is rather constant and on average 1.1, which is about the same as the $^{228}\text{Ra}/^{226}\text{Ra}$ ratio of the YR 0010 A precipitates. For fine-grained granite (host rock in the NE-1 zone) the ratio varies strongly, between 0.5–2.5, but even the maximum value is much lower than the measured $^{228}\text{Ra}/^{226}\text{Ra}$ ratio of 8.6 for the NE-1 Y sample. This alternative interpretation is thus not valid on its own for the NE-1 precipitates.
- 2) The groundwater $^{228}\text{Ra}/^{226}\text{Ra}$ ratio depends on the fluid/solid contact time. A short contact time (higher groundwater flow rate) favours the release of the short-lived ^{228}Ra ($T_{1/2} = 5.75$ y) relative to ^{226}Ra ($T_{1/2} = 1620$ y) as is clear from the equation (Dickson, 1990).

$$A_t = A_\infty (1 - \exp(-\lambda t))$$

where A_t = Activity of the Ra isotope in groundwater at time t
 A_∞ = Equilibrium activity (in "stagnant" groundwater)
 t = Contact time
 λ = Decay constant of the Ra isotope

The NE-1 fracture zone is characterised by high water flow rates which decreases the fluid/solid contact time. This may thus be one main cause of the high $^{228}\text{Ra}/^{226}\text{Ra}$ ratios in the NE-1 zone precipitates.

- 3) The high ^{228}Ra activities of the NE-1 samples (> 5000 Bq/kg) suggest an effective release of ^{228}Ra to the groundwater. This would be accomplished if the parent ^{232}Th isotope is sited on a solid surface in contact with the groundwater since theoretically 50% of the produced ^{228}Ra isotopes can then be released to the groundwater through α -recoil. Earlier mobilisation of ^{232}Th in connection to alteration processes and subsequent sorption onto the surface of clay particles could thus be another cause of the high $^{228}\text{Ra}/^{226}\text{Ra}$ ratios. Compared to ^{232}Th an earlier mobilisation and redistribution of ^{230}Th (precursor of ^{226}Ra) is insignificant due to its relatively short half-life; it decays within 0.35 Ma. Indications of Th mobility have been reported in this paper and high concentrations of Th have been determined in $< 2\mu\text{m}$ fractions from the Redox zone (Banwart et al., 1994c), both supporting this hypothesis. An interesting observation is the chemically altered, very porous rock ($> 15\%$ porosity) in the NE-1 zone at about 400 m depth (Landström & Tullborg, 1991). Th is rather

high in this rock (65 ppm) and the extensive chemical alteration and possible redistribution of Th may have created sites of Th in close contact with the groundwater. It is possible that this kind of alteration can be found at several places along the fracture zone.

We can not at present give a detailed explanation of the significance of different factors influencing the $^{228}\text{Ra}/^{226}\text{Ra}$ ratio of the groundwaters. However, a better understanding of these factors will certainly aid the characterization of the properties of fractures and fracture zones.

5.4 EVALUATION

5.4.1 Ra AND Ba RELATIONSHIP

Similar behaviour in natural chemical processes can be expected for Ra and Ba because of their analogous chemical properties. However, in contrast to Ba, the Ra isotopes are also affected by a physical process; recoil in connection with α -decay of their progenitors. This process may be important in the release of Ra from the solid phase to the groundwater, and thus indirectly for the mobility and migration of the Ra isotopes.

Combined Ra and Ba analyses can be used to determine the relative significance of the two mechanisms in releasing Ra; chemical processes (like mineral dissolution) which affect both Ra and Ba and α recoil which affects only Ra (Dickens, 1990). This idea is preliminary tested on the present data.

$^{226}\text{Ra}/\text{Ba}$ and $^{228}\text{Ra}/\text{Ba}$ ratios of groundwater, precipitates and host rocks from the Redox and NE-1 zones are illustrated in Table 8. For groundwater, only the $^{226}\text{Ra}/\text{Ba}$ ratios from the Redox zone are available. For ^{226}Ra and ^{228}Ra in the host rocks, values in equilibrium with average ^{238}U and ^{232}Th activities were taken.

From Table 8 the following conclusions can be drawn:

- 1) Approximately similar $^{226}\text{Ra}/\text{Ba}$ ratios in groundwater from the Redox zone and precipitates from sample YR0010-A suggest that these two elements did not fractionate when "sorbed" by Fe-oxyhydroxide and calcite; this indicates similar behaviour of the two elements in these processes.
- 2) Assuming that the $^{226}\text{Ra}/\text{Ba}$ and $^{228}\text{Ra}/\text{Ba}$ ratios of the precipitates are representative of those in the supplying groundwater (see above), the much higher

ratios of the precipitates (and groundwater) than those of the host rocks indicate that in the present environment α recoil is more important in releasing Ra than are chemical processes. However, one must consider that the two elements usually occur in different minerals with variable resistance to weathering/alteration: Ba is usually present in feldspars and biotite and Ra isotopes are often found in accessory minerals and at grain boundaries. Damage of the crystal lattice due to radioactivity may also facilitate the chemical release of Ra.

Table 8. Ra/Ba ratios in groundwater, precipitates and host rock

	$^{226}\text{Ra}/\text{Ba}$	$^{228}\text{Ra}/\text{Ba}$ (Bq/kg/ppm)
<i>The Redox zone</i>		
Groundwater	0,50	–
Precipitates (YR00101)	0,23	0,22
Host rock (Småland granite)	0,032*	0,025*
<i>The NE-1 zone</i>		
Groundwater	–	–
Precipitates	0,69	4,9
Host rock (Fine grained granite)	0,057*	0,057*

* ^{226}Ra and ^{228}Ra calculated from equivalent ^{238}U and ^{232}Th values.

The large difference between the $^{228}\text{Ra}/\text{Ba}$ ratios of precipitates and host rock from the NE-1 zone (a factor of 80 higher in the precipitates) must imply ^{232}Th sites from which ^{228}Ra is efficiently released to the groundwater. This supports the hypothesis of Th redistribution, discussed in the preceding chapter.

The distribution of Ra isotopes on the different mineral phases has not been investigated by sequential extraction. However, the Ba distribution suggests a partition of Ra between calcite and Fe-oxyhydroxide.

5.4.2. RELATIVE RETENTION IN CALCITE AND FE-OXYHYDROXIDES

Since only two mineral phases, calcite and Fe-oxyhydroxide, are present in the precipitates, the Ca and Fe concentrations are approximately proportional to the weights of these minerals. Assuming that the carbonate phase (F3) consists of calcite (CaCO_3) and "Fe-oxyhydroxide" represented by $\text{Fe}(\text{OH})_3$ in fractions F4 and F6, the concentrations of Ba, U, Sc, La, Eu and Yb in the two minerals have been estimated and listed in Table 9. Using these concentrations (weight of element per weight of mineral) as a measure of retention capacity it is clear that calcite is more efficient than Fe-oxyhydroxide in retaining Ba (by a factor of 3), U (by a factor of 6) and Sc (by a factor of 2). For REEs the concentrations in the two mineral phases are about the same.

Table 9. Estimated concentrations of elements in the extracted calcite and Fe-oxyhydroxide phases (ppm).

Element	"Calcite" (F3)	"Fe-oxyhydroxide" (F4+F6)
Ba	2570	720
U	15	2,5
Sc	3,2	2,0
La	14	16
Eu	0,65	0,64
Yb	11	12

5.4.3 COMPARISON OF PRECIPITATE AND GROUNDWATER DATA

Concentrations of major and trace elements in groundwater from the NE-1 and Redox zones are presented in Table 10. The data refer to Nilsson, (1995) where also sampling technique and analytical methods are described.

Groundwater from the NE-1 zone.

From borehole KBH 02 which intersects the NE-1 fracture zone at a depth of 180 m, groundwater was sampled on 930929 for trace element analyses; about three months after the precipitate sampling. Small variations in major element concentration for the period Aug – Nov 1993 suggest that the water composition had stabilized after the evolution from the native composition. Spatial variations are assumed to be small since the high conductivity of the zone should ensure a thorough mixing of the groundwater. Although details about the groundwater evolution from its native composition is not known (successive analyses are incomplete) the data in Table 10 are considered fairly representative of the groundwater being in contact with the precipitates.

The retardation of Sr, Ba, La, Th, U, Rb and Cs by the precipitate NE-1 Y appears from Table 11, column 1, which shows partition ratios (concentration in "total" precipitate, dry weight base, to concentration in contact groundwater). Surprisingly, La is by far the most enriched element with a partition ratio almost as high as Fe and 25–35 times higher than those of Th, U and Ba. The similar values for Sr and Ca suggest analogous behaviour of these elements, probably co-precipitation.

Table 11 column 2 and 3 show specific partition ratios of Ba, La and U for the carbonate (calcite) and Fe(III)-hydroxide phases (calculated from groundwater data and concentrations given for the two mineral phases in Table 9). Both phases retain La more efficiently than Ba and U. The partition ratios of the two phases are similar for La but factors of 2 and 7 higher for Ba and U, in calcite. This probably reflects the speciations of the elements; U mainly occurring as uranyl carbonate complexes and La possibly partitioned between carbonate complexes and colloids, in association with Fe (see below).

Groundwaters from the Redox zone

Groundwater has been sampled from boreholes intersecting the Redox zone at 15 m depth (HBH02) and at 70 m depth (KR0012, KR0013 and KR0015), Fig 4 a and b. The values given are averages of data on groundwater sampled during the period Jun–Nov 1993. The HBH02 samples constitute shallow fresh water whereas the others are results of mixing between native saline water, shallow fresh water and small portions of brackish Baltic Sea water (Banwart et al., 1995)

Table 10. Major and trace element concentrations in groundwater from the NE-1 and the Redox zones.

	NE-1 KBH-02	KR0012	Redox		HBH 02
			KR0013	KR0015	
Cl mg/l	4350	648	1828	818	12
Na	1850	402	799	493	6,4
K	19,4	5,5	4,6	3,6	1,4
Ca	647	121	365	182	26
Sr	9,3	1,83	5,36	2,64	0,065
Mg	158	19,6	55,8	26,5	3,7
HCO ₃ ⁻	354	316	302	410	72
SO ₄	72,7	140	146	129	21
Fe _{TOT}	2,91	0,18	0,37	0,33	3,2
Mn	1,2	0,23	0,38	0,27	0,37
TOC	-	13,7	13	17,9	16
pH	7,0	7,5	7,4	7,4	6,2
Rb µg/l	42	7,6	8,5	7,8	1,8
Cs	4,0	0,64	1,3	0,90	0,040
Ba	527	64	69	59	35
Hf	-	0,016	0,016	0,034	0,070
Th	0,17	0,037	0,050	0,091	0,44
U	1,85	6,3	3,4	1,1	1,1
Sc	-	0,031	0,036	0,054	0,22
La	0,29	-	-	-	8,8
Ce	-	0,40	0,44	0,64	17
Nd	-	-	-	-	7,6
Sm	-	-	-	-	1,5
Eu	-	0,011	0,017	0,021	0,23
Tb	-	0,011	0,018	0,021	0,20
Yb	-	0,058	0,070	0,11	0,51
Lu	-	0,013	0,014	0,020	0,093
Y	1,0	-	-	-	-

KBH 02 sampled 930929

The Redox values are averages for samples taken during June–Nov 1993.

Methods for major element analyses, see Banwart et al., (1995).

Trace elements in the NE-1 samples were analysed using ICP.

Trace elements in Redox samples were analysed using INAA.

A characteristic difference between the shallow fresh water and the saline groundwater is a factor of ten higher concentrations of REEs, Th and Sc in the shallow water. Also the chondrite normalised REE patterns differ significantly; with Ce/Yb ratios of 33 and 6–7 for shallow freshwater and saline groundwater, respectively (Fig.10). The correlations of Th with REEs (represented by Yb), Sc, Hf and Fe (Fig. 11) indicate similar behaviour for these trace elements and an association with Fe.

The trend of the U content is opposite to that of Th, resulting in U/Th ratios varying from 2.5 (HBH02) to 170 (KR0012). Cs correlates with Na (Fig 12 a) and the Rb/Cs ratios show characteristic values for the three saline groundwaters and correlate with the corresponding Na/Ca ratios (Fig 12). This has been discussed in section 3.5.

Table 11. Partition ratios (concentrations in solid phase, dry weight base, to the corresponding concentration in groundwater) for "total" precipitate NE-1 Y and for the extracted "calcite" and "Fe-oxyhydroxide" phases of the same sample.

Element	Total precipitate m ³ /kg	"calcite" m ³ /kg	Fe-oxyhydroxide"* m ³ /kg
Fe	135,		
Ca	0,10		
Sr	0,14		
Ba	1,6	4,9	1,4
La	58	47,	55,
Th	1,6		
U	2,4	8,2	1,3
Rb	<0,36		
Cs	<0,06		

* Values for the solid phase taken from Table 9.

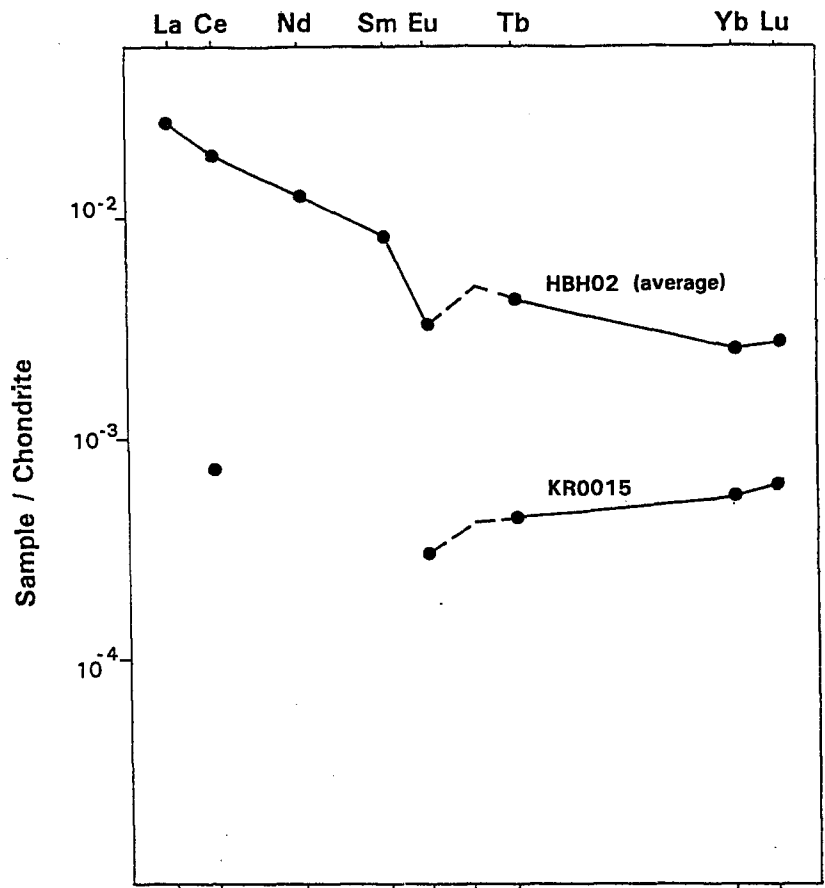


Figure 10. Chondrite normalised REE pattern for shallow fresh water (HBH 02) and groundwater (KR0015) from the Redox zone.

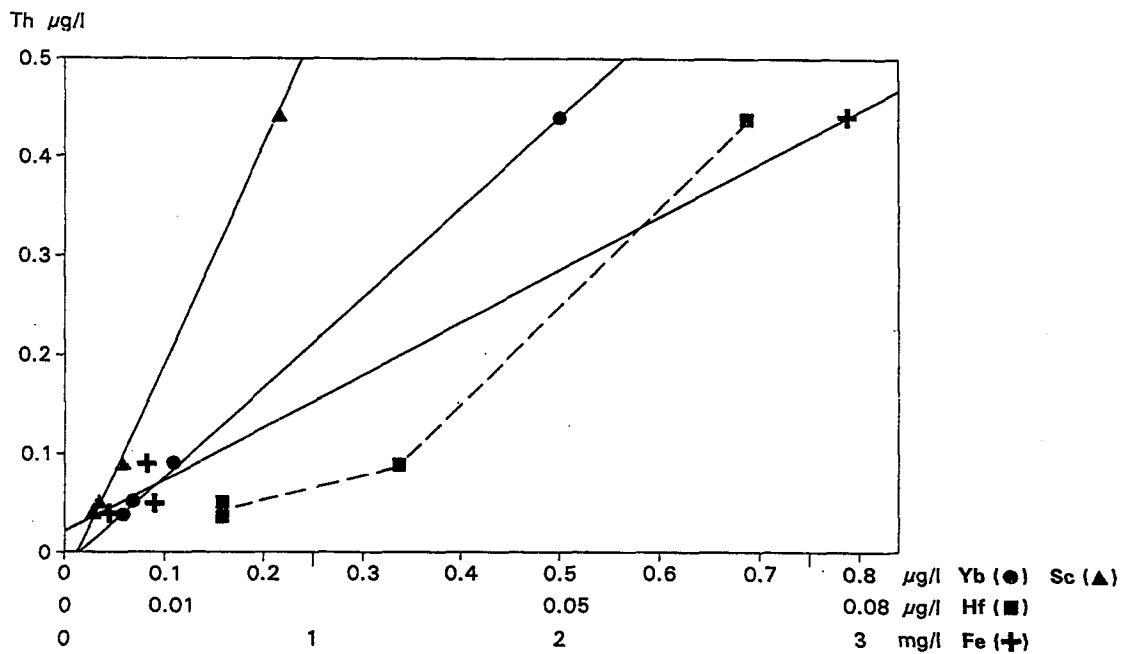


Figure 11. Th versus Yb, Sc, Hf and Fe for groundwater from boreholes HBH02, KR0012, KR0013 and KR0015 from the Redox zone.

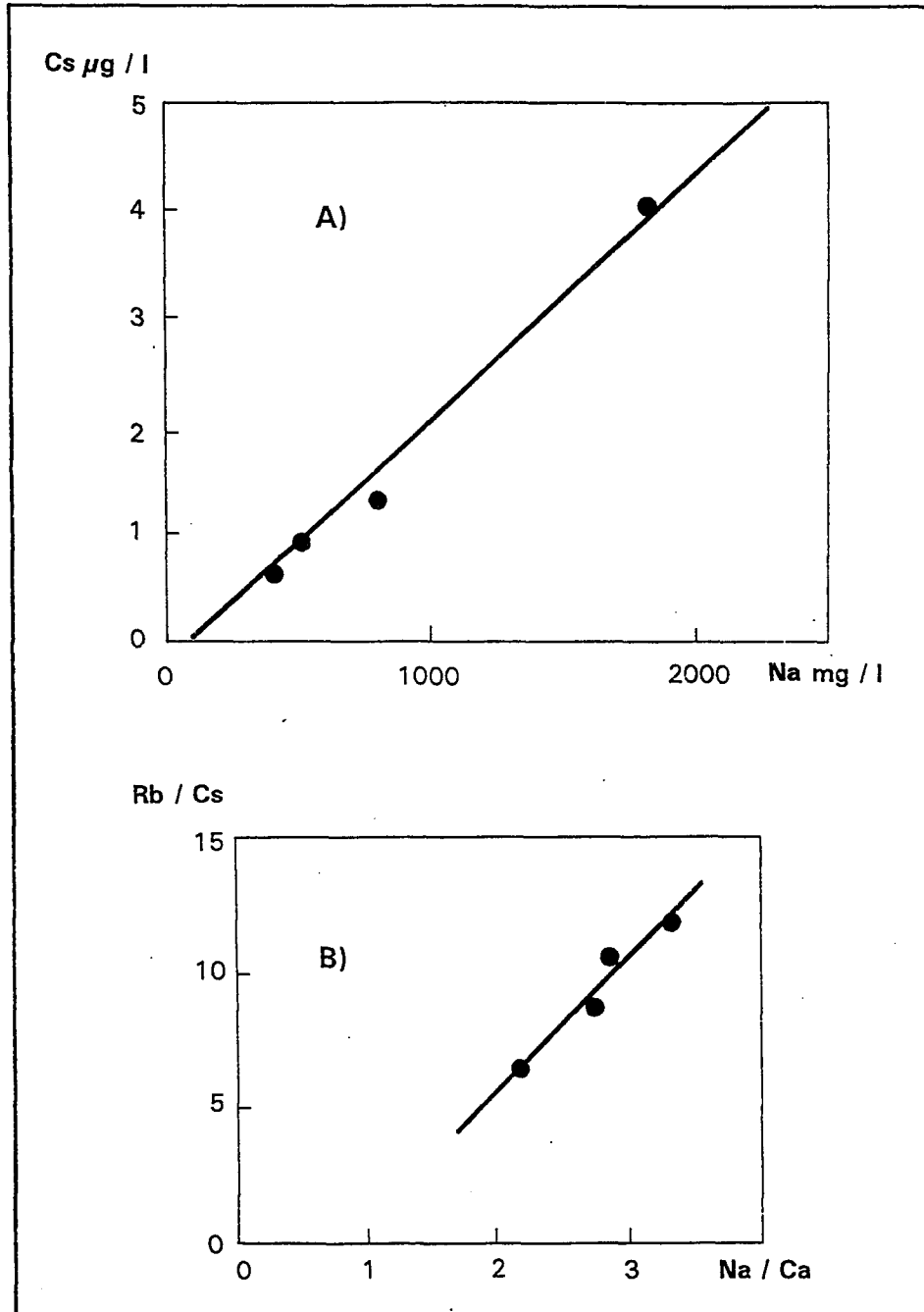


Figure 12. a) Na versus Cs for groundwaters from the Redox and NE-1 zones.
 b) Rb/Cs ratios versus Na/Ca ratios for groundwaters from the Redox and NE-1 zones.

Fractionation of REEs – a clue to speciation and processes?

The fractionation of REEs is a result of their different susceptibility to geochemical processes; in turn dependent on the regular changes in chemical properties from light through heavy REEs (ionic radius, etc). This study has shown distinct fractionations of the REEs; exemplified by high La/Yb ratios of gouge and calcite samples from the Redox zone and large variations in the REE patterns of fresh precipitates from different fractures.

Fractionation can occur because of differences in speciations (for instance increasing stability of complexes from La through Lu), ionic radius (preferential substitution of light REEs for Ca in calcites) and in affinity for sorption onto the solid phases involved. Studies of fractionation processes will thus aid to the understanding of the behaviour of individual REEs (and indirectly of their actinide analogues) in a natural environment. In the following some observed fractionation trends are discussed; focusing on fresh precipitation but including also earlier processes for comparison.

Figure 13 shows REE curves for samples of gouge material (A29), calcite (A2 and A3) and groundwater (KR0015) from the Redox zone. In this case the REEs have been normalised to those of the host rock ("Småland granite") which in a broad sense is the original source of the mobilised REEs. The REE patterns of the gouge and calcite samples (in which most REEs have been deposited from the groundwater) are mirror images to that of the associated groundwater, indicating preferential sorption of light REEs on the solid phases and a corresponding depletion in the groundwater phase. The higher proportion of heavy REEs in the groundwater phase can be explained by stronger complexation of heavy REEs (for instance in carbonate complexes). The REE patterns of figure 13 may illustrate general long term fractionation trends caused by earlier hydrothermal as well as later/present low-temperature processes. Whether these patterns are representative of other fracture zones cannot be established since adequate groundwater REE data are not available. However, earlier studies of fracture fillings from Äspö usually indicate preferential uptake of light REEs (Landström & Tullborg, 1991, 1993).

Sequential extractions of a fresh Fe-oxyhydroxide/calcite precipitate (Sample NE-1Y) showed the following fraction trends, relative to the "total" REEs; preferential uptake of heavy REEs in the carbonate (calcite) and crystalline Fe-oxyhydroxide phases and of light REEs in the amorphous Fe-oxyhydroxide and organic phases. These fractionations may be controlled (at least partly) by the speciation of REEs in the groundwater; e.g. carbonate complexation of heavy REEs and a possible dominance of light REEs in organic complexes and iron colloids. Transformation of amorphous Fe-oxyhydroxide to more crystalline forms may also modify the relative REE concentrations; decreasing La/Yb ratios is indicated.

Some of the described trends in the fresh precipitate (NE-1 Y) are supported by the results of the sequential extraction of the gouge sample A 29. Relative to "total" REEs, heavy REEs are enriched in the carbonate phase and light REEs in the amorphous Fe-oxyhydroxide and organic phases.

Y and of the REEs only La have been analysed in the NE-1 groundwater (Table 10). Estimation of Yb from the Y value (based on the average Yb/Y ratio of host rock samples)

gives 2.9 for the La/Yb ratio of the NE-1 groundwater. This is of the same order as the La/Yb ratio of the NE-1 Y precipitate sample, suggesting that the opposite fractionation trends observed in the different phases may largely balance each other.

In several precipitate samples negative Ce anomalies are indicated. Oxidation of Ce(III) to the "immobile" Ce(IV) may have occurred in sites through which the groundwater have passed. Dissolved REEs are then depleted in Ce and when scavenged by Fe-oxyhydroxide/calcite precipitations negative Ce anomalies may form. However, this must be confirmed by accurate analyses of the REE patterns in corresponding groundwater samples.

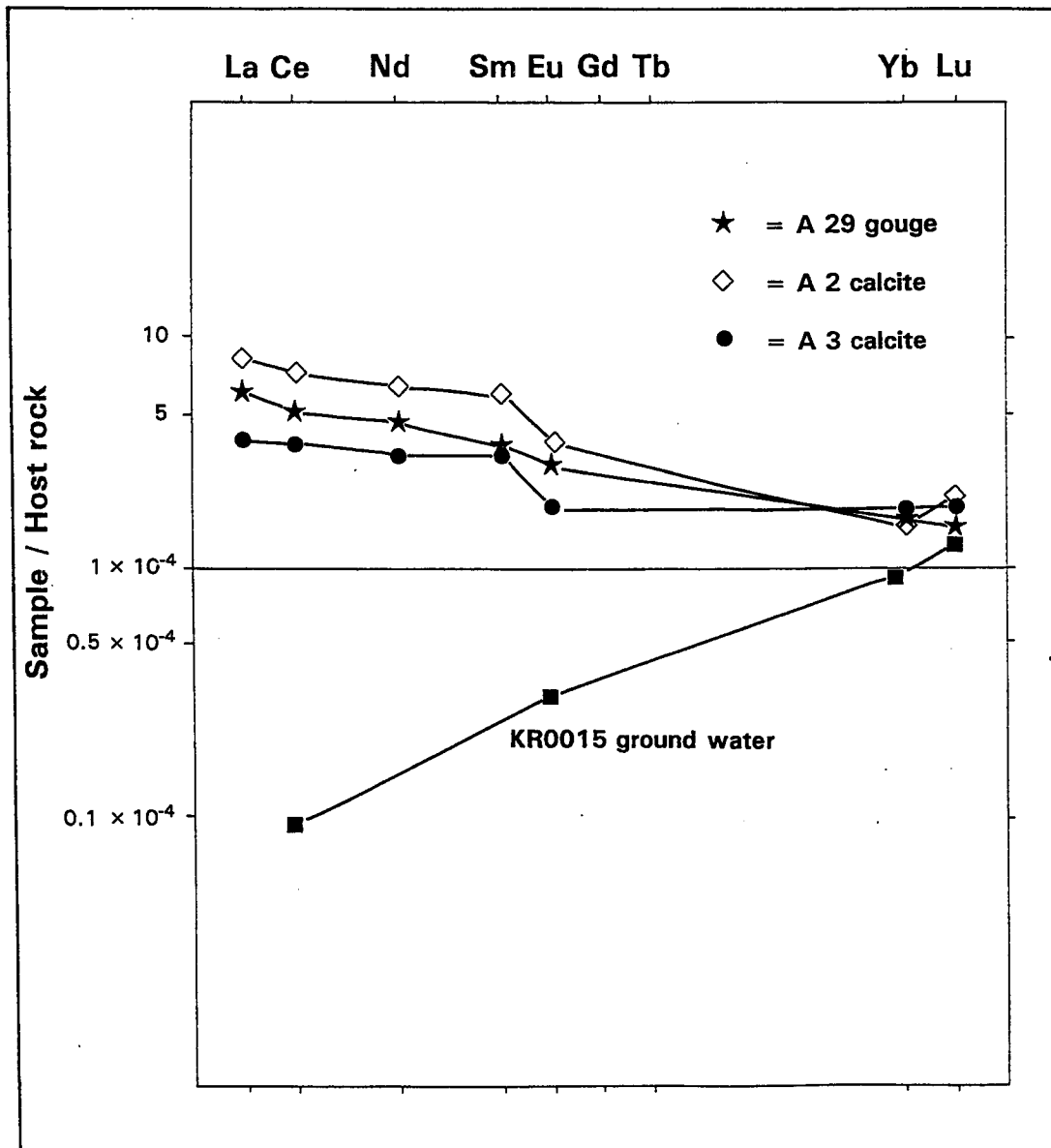


Figure 13. Trends of REE patterns of solid samples and groundwater (see text for discussion).

6. TRACE ELEMENT UPTAKE IN CALCITE

6.1 CONCEPT

The geochemical studies on fracture coatings from Äspö (results in this report, Landström & Tullborg, 1991 and Tullborg et al. in manuscript) include a number of calcite dominated samples. A common feature of these samples is enrichment of REEs, but also e.g. Ba, Sr, Sc, U and Th. This uptake involves co-precipitation but also includes surface adsorption with subsequent irreversible incorporation of trace elements in the surface layer of calcite (cf. Jensen, 1993; Bruno, 1989). Reversible sorption on calcite is small according to laboratory measurements (e.g. Byegård, 1994).

Available trace element analyses on calcites from fractures and fracture zones in the Äspö area are compiled in this section. It includes earlier published data, and new data from a fracture at 207 m depth in borehole KAS 02, from the Redox zone, and from fresh calcite precipitates on the tunnel walls (cf section 4.). The aim of the compilation is to identify trace element patterns typical of low temperature calcite.

Some important questions can be posed when interpreting the data; Are the trace elements transported by the groundwater to the calcite or is the enrichment a result of in situ weathering? Is it possible to find characteristic trace element patterns which distinguish for example hydrothermal calcites from low temperature precipitates? Are the trace element contents dependent on precipitation rate? Are there any variations with depth?

It is likely that the fracture calcites were precipitated during long periods of time and that the bulk analyses of calcite represent mean values which can not simply be related to the present groundwater chemistry. For this reason fresh calcite precipitates which are in equilibrium with the present low temperature groundwater are included (cf section 5).

6.2 FRACTURE FILLING CALCITES AT ÄSPÖ – FREQUENCES AND ORIGIN

Calcite is together with chlorite the most frequent fracture coating mineral in single fractures as well as in fracture zones from the Äspö area. Different generations of calcite have texturally been identified in thin sections. Analyses of stable oxygen and carbon isotopes in calcite (Wallin 1990, Tullborg & Wallin

1991, Banwart et al., 1994a; Wallin & Peterman 1994) show that calcites of quite different origins and ages are present within the fractures. The extremely large variations in both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ (from -20 to 0 ‰ and -74 to -2 ‰, respectively) are the result of repeated hydrothermal activity and complex past and present hydrological situations. The latter are characterised by interaction with modified marine water, old saline water, glacial meltwater and fresh water. The very low $\delta^{13}\text{C}$ isotope ratios are most probable due to anaerobic degradation of organic matter under closed conditions, although interaction with methane is also possible.

Three major groups of calcite can be distinguished from stable isotope ratios;

- 1) Calcite which is generally in oxygen isotope equilibrium with present groundwater; these calcites can be found at all depths investigated (from 0–950 m) and they show large variations in $\delta^{13}\text{C}$ values. Most of the calcites have values within the interval -20 ‰ to -3 ‰ indicating various input of biogenic carbon dioxide. However, still lower values from -74 ‰ to -25 ‰ have been detected in a number of samples.
- 2) Calcite precipitated from marine water of oceanic character ($\delta^{18}\text{O}$ of approximately 0 ‰ SMOW); these calcites are found in a few fractures at depths down to 300 m. Since the Baltic Sea is not likely to have had water of oceanic signature during post glacial time, these calcites should be older. Their carbon isotope compositions varies between -5 to -25 ‰, indicating input of oxidised organic carbon.
- 3) Calcite with very low $\delta^{18}\text{O}$ -values (c. -10 ‰) and high $\delta^{13}\text{C}$ values are generally found at depths exceeding 400 m; these calcites are not in equilibrium with present groundwater. Two alternative explanations to their stable isotope signature are given; a) they are precipitated from a glacial melt water with extremely low $\delta^{18}\text{O}$ - values or b) they are precipitated during hydrothermal conditions. The latter hypothesis is favoured by the observation of hydrothermal mineral paragenesis in some of these fractures.

Surface related calcite dissolution is common as a result of acid precipitation recharge. However, in the Äspö bedrock only slightly lower calcite frequencies are observed in the upper tens of metres. This indicates that Äspö is not a pronounced recharge area, except for the Äspö shear zone, EW-1 (Smellie & Laaksoharju, 1995) or that the upper part of the bedrock has low conductivity. Furthermore, 14-C analyses of fracture coatings from the upper 150 m show a very low content of modern carbon (<4 pmC). This means that the formation of new calcite in the fractures is minor during undisturbed conditions. However, dramatic disturbances in the hydrological flow patterns caused by the tunnel increase the dynamics in the carbonate/ groundwater interaction. This is exemplified in the Redox zone where the recharge of surface water has caused dissolution of calcite in the near surface region. Changes in temperature will also affect the carbonate/groundwater equilibria. Heat produced from the radioactive waste will form an important temperature anomaly around a repository causing increased carbonate

precipitation. This means that knowledge about incorporation (and subsequent release) of radionuclides in carbonate minerals is important when modelling "near field" radionuclide migration.

6.3 CALCITE SAMPLES

Most of the calcites included in this compilation (Table 12) have stable isotope values that correspond to group 1 (above); for example the calcite samples from water conducting zones in boreholes KAS 02 and KAS 06 (earlier reported in Landström and Tullborg, 1991). Sample KAS 03:115 m represents the marine group (2) and sample KAS 02:843 m represents group 3. These two calcite coatings were very thin leading to mixing with some K-feldspar and quartz at sampling.

Calcites from a subvertical fracture (KAS 02:207 m) have been investigated in detail. The drillcore displays a 0.7 m long exposure of the fracture and this has facilitated sampling different parts of the coating. The wall rock (Småland granitoid) has been chemically and mineralogically analysed; in contrast to most wall rock samples from Äspö, this rock showed no mineralogical or chemical trends characteristic of alteration or oxidation. This in turn indicates that the trace elements found in the calcite are likely to be a result of uptake (sorption and/or coprecipitation) from the fluid phase. Fifteen calcite samples from the fracture coating were analysed for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ and the results showed extremely large variations in isotopic composition ($\delta^{18}\text{O}$ -7.2 to -15.9 and $\delta^{13}\text{C}$ -7.0 to -46.5 o/oo). However, most of the samples have $\delta^{18}\text{O}$ -values around -10 o/oo (PDB), indicating equilibrium with present groundwater. The large variations in $\delta^{13}\text{C}$ -values are interpreted as being due to oxidation of organic material under closed chemical conditions; for example anaerobic respiration caused by sulphate reducing bacteria. Pyrite is also present in the fracture coatings. Five calcite samples with different isotopic signatures were analysed for trace elements.

Two calcite samples (A2 and A3) from gouge material in the Redox zone are also included. They were sampled at the fracture exposure in the tunnel during 1992, i.e. about one year after the tunnel was built. The $\delta^{18}\text{O}$ -values of the two samples indicate different origins of these calcites; sample A2 shows equilibrium with the present groundwater whereas sample A3 shows equilibrium with the native groundwater. Fresh precipitates from the NE-1 zone and from the wall of the Redox side tunnel are also included in the compilation.

6.4 RESULTS OF ANALYSES

The chemistry of the fracture calcites and fresh precipitates are shown in Table 12.

Sr and Ba:

Strontium and barium, in common with calcium, form carbonates, and co-precipitation of these elements with calcium in calcite can be expected. Co-precipitation may also be the case for Ra which is regarded as largely analogous with barium. However, Sr is generally low (< 100 ppm to 500 ppm) in the fracture calcites but considerably higher (up to 1700 ppm) in fresh carbonate crystals and even higher (c. 9 000 ppm) in the cryptocrystalline calcite aggregates in the fresh precipitates on the tunnel walls. The Ca/Sr ratios of the latter (21–55) are more similar to that of the groundwater (70) whereas the Ca/Sr ratio of fresh hand-picked calcite crystals is 230 and of fracture calcites significantly higher (450 to 6700). Higher partition coefficients for Sr are recorded in laboratory experiments when increasing the precipitation rate (Morse & Bender, 1990) and this can be an explanation for the high Sr contents in the fresh precipitates.

A Sr content of 460 ppm has been measured for a hydrothermal calcite at 843 m (KAS 02) which is in accordance with the Sr contents in calcites from depths exceeding 800 m reported by Wallin & Peterman (1994). These calcites are not interpreted to be in equilibrium with present groundwater. In contrast to Sr, barium seems to be significantly enriched both in the fracture calcites and in the fresh carbonate precipitates (cf. section 4). The Sr/Ba ratios of the fracture calcites are 0.05–2 whereas in the groundwater the ratio varies from 5 to > 1000. The differences in the behaviour of Sr and Ba is also clear from their K_d -values for calcites (much lower for Sr) measured in batch experiments (Byegård et al., 1994).

Rb and Cs:

The rubidium and cesium concentrations are low in most of the calcites. From the present data it is usually difficult to determine whether the Rb and Cs concentrations are an effect of contamination of clay minerals and feldspar, or caused by a real uptake from the water phase. The indicated low affinity for calcite is supported by the sequential extractions of a gouge sample from the Redox zone, and a sample of Fe-oxyhydroxide/calcite precipitates from the NE-1 zone which both showed insignificant amounts of Cs and Rb in the carbonate fraction (cf. chapter 4 and 5).

Table 12. Trace element composition of fracture calcites and fresh precipitates

	KAS 02' 209.9m	315.6	315.7	KAS 06' 398.7	557.3	KAS 02'' 843.7	KAS 09''' 132.2	Kas 03'''' 115.8 m
Ca %	35	45	44	37	42	31	40	32.8
Na	0.18	0.14	0.07	0.17	0.30	0.19	0.02	0.61
K	-	-	-	-	-	0.72	-	0.52
Fe	0.70	1.1	0.73	5.0	1.1	0.45	0.045	0.15
Cr ppm	-	57	27	28	19	105	5.5	66
Co	2.4	4.6	3.9	22	4.1	2.5	2.8	1.0
Zn	-	47	54	-	59	155	<10	-
Sb	<0.5	0.28	-	<0.2	0.2	1.8	-	0.39
Rb	13	40	39	44	12	30	<20	9.9
Cs	0.15	0.79	1.4	5.3	<0.5	0.4	<0.5	1.1
Sr	72	85	127	183	209	460	33	-
Ba	240	320	290	208	125	250	150	82
Hf	0.27	0.87	2.0	1.0	1.3	0.16	<0.2	-
Th	3.4	2.7	2.1	1.7	1.3	<0.2	<0.2	1.3
U	3.2	2.0	1.0	0.7	1.7	<0.2	0.27	<0.3
Sc	1.5	3.0	2.5	4.5	2.8	0.43	9.7	0.73
La	542	127	110	105	75	3.3	57	295
Ce	506	146	130	128	97	4.7	94	510
Nd	128	67	49	45	43	<	32	152
Sm	14	6.7	7.0	8.7	6.5	0.20	6.7	16
Eu	2.9	1.0	0.8	1.8	1.2	0.09	1.0	1.6
Tb	1.9	0.66	0.6	1.7	0.86	<	1.6	-
Yb	4.2	0.68	0.51	5.0	2.1	<	7.6	2.1
Lu	0.62	0.065	0.057	0.74	0.30	<	1.3	0.30
$\delta^{18}\text{O}$ (PDB)	-9.8	-	-8.8	-12.9	-11.8	-20.1	-9.2	1.2
$\delta^{13}\text{C}$ (PDB)	-6.1	-	-6.7	-12.6	-7.9	-3.8	-7.3	-9.5

¹ Samples from water conducting zones in boreholes KAS 02 and KAS 06 (Tullborg et al., 1991,

² Hydrothermal calcite according to stable isotope values (Tullborg et al., 1991).

³ Calcite sample from a sealed fracture filled with fluorite and calcite (Tullborg et al., 1991)

⁴ Calcite with marine origin according to oxygen isotope signature (Tullborg et al., 1991)

Table 12. cont

	KAS 02:207m *		(7)	(11)	(12)	The Redox Zone**		YR 0010A	NE-1**
	(2)	(4)				A2	A3		Y
Ca %	43	39.8	38.4	39.4	39.0	29.5	30.5	39	35.4
Na	0.041	0.038	0.032	0.049	0.12	0.15	0.11	0.73	0.50
K	-	-	-	-	-	-	-	-	-
Fe	0.82	0.092	0.15	0.084	0.91	0.63	0.43	1.4	2.4
Cr ppm	34	9.5	14	18	180	67	7.2	25	7.6
Co	2.4	0.60	2.0	0.64	7.6	1.9	0.74	5.0	0.72
Zn	25	-	-	-	-	150	-	-	7.7
Sb	0.38	0.18	<0.2	0.22	0.20	<0.1	<0.25	1.3	0.32
Rb	5.2	-	-	-	6.4	89	59	<50	-
Cs	<0.25	-	-	-	0.15	9.7	7.5	<2	-
Sr	110	76	-	-	66	650	45	1660	1570
Ba	850	1070	460	580	1320	550	240	710	440
Hf	<0.1	-	<0.1	<0.1	0.30	0.69	0.20	<0.3	-
Th	0.72	0.18	0.90	0.44	0.63	3.9	2.0	<0.3	-
U	1.5	1.7	3.5	2.3	1.5	3.5	1.6	1.5	3.8
Sc	0.56	3.5	2.7	5.2	3.3	1.1	1.5	0.98	0.22
La	77	136	95	204	132	230	110	78	0.94
Ce	110	275	153	390	209	410	210	95	1.0
Nd	33	85	48	117	63	130	70	30	-
Sm	5.6	13.5	7.2	15.9	9.4	17	9.9	4.0	0.4
Eu	0.94	2.1	1.4	2.3	1.6	2.0	1.2	-	-
Gd	-	12	-	-	-	-	-	0.88	-
Tb	1.2	2.1	1.6	2.1	1.6	1.1	0.91	-	-
Yb	3.1	10.4	5.7	6.8	4.7	1.7	1.9	0.91	0.77
Lu	0.47	1.8	0.91	1.1	0.70	0.29	0.28	0.14	-
$\delta^{18}\text{O}$ (PDB)	-9.9	-11.4	-9.6	-8.1	-9.8	-8.9	-11.0	-	-
$\delta^{13}\text{C}$ (PDB)	-35.9	-10.4	-24.3	-46.5	-16.4	-7.8	-9.0	-	-

* Samples 2,4,7,11 and 12 are calcite samples from the same fracture coating.

** Samples A2 and A3 are calcite coatings from rock fragments in the Redox zone (cf. sample A29 in section 4), Sample YR 0010A is calcite crystals from the Fe/calcite-precipitate sampled in the Redox niche (cf. section 5).

*** Samples NE-1 Y is calcite crystals from the Fe/calcite-precipitate sampled in the NE-1 zone.

Co, Zn and Sb:

The Co content ranges from 0.6 to 7.6 ppm with one exception of 22 ppm in sample 398.7, where Co probably is associated with minor parts of Fe(III) oxyhydroxide or chlorite. Zn which is only analysed in some of the samples varies from <10 to 155 ppm; Zn is known to form carbonate minerals and can relatively easily be incorporated in calcite. The hydrothermal calcite (KAS 02, 843 m) shows the highest Zn and Sb values (155 and 9.8 ppm, respectively). Zn is also high in sample A2 (150 ppm). However, this sample is obviously contaminated by some clay as shown by the high Cs value and Zn cannot for certain be assigned to the calcite.

U and Th:

Both uranium and thorium are present in small amounts in the calcites (from <0.2 to 3.9 ppm Th and <0.2 to 3.5 ppm U). U is known to form carbonate complexes and is expected to occur in calcite (co-precipitation). This is also supported by the sequential extraction of the Fe-oxyhydroxide and calcite precipitate (cf section 5) where the U concentrations in the carbonate phase is a factor of 6 greater than in the Fe phases (cf. discussion in 5.3.1.)

Th is, in contrast to uranium, expected to have low mobility in groundwater. In sample KAS 02:207 m the host rock shows no alteration trend indicating that the elements found in the calcite originate from the fluid phase. Moreover, high Th/Hf ratios indicate that Th is not entirely due to contamination from accessory minerals contained in the host rock. The findings of "excess" Th in calcites thus suggests a higher mobility of Th in the groundwater than usually expected in this environment. Correlation of Th with the La/Yb ratio (Fig 13) indicates a similar behaviour for Th and light REEs (cf. also Fig 12). The U and Th contents in the analysed fracture calcites are usually not correlated indicating different behaviour of these two elements.

REEs:

The calcites show large variations in the REEs values from 14 to 542 ppm La and from 0.5 to 12.1 ppm Yb. It is reasonable to assume that the high content of REEs observed in most fracture calcites have been contributed from the fluid phase.

Heavy REEs form stronger carbonate complexes than light REEs and calcites with low La/Yb ratio are usual, especially in hydrothermal precipitates (cf. Möller 1979; Eliasson et al., 1990). In the Äspö samples large variations in La/Yb ratios are recorded (1 to 215); the lowest ratios obtained for the fresh calcite precipitate in the NE-1 zone and a probably hydrothermal calcite from a sealed fracture in KAS 09:132 m (1.1 and 7.5, respectively). About 50% of the other samples show significantly higher La/Yb ratios. The rest have ratios similar to the host rocks (15–30). High La/Yb ratios may indicate incorporation of light REEs, controlled by similar ionic radii for La and Ca. They also support the hypothesis of a general fractionation trend with preferential uptake in the solid phase of light REEs (section 5.4.3).

All samples show more or less well defined negative Eu-anomalies, except for the sample of hydrothermal calcite at 843 m depth (KAS 02); in this sample a positive Eu-anomaly is indicated. Positive Eu-anomalies are usually recorded in acidic hydrothermal waters (Michard, 1989). This is also in agreement with hydrothermal $\delta^{18}\text{O}$ signatures and low $\delta^{87}\text{Sr}$ values in calcites from the same depth (Wallin & Peterman, 1994). Together these results suggest that this calcite is formed in association with the hydrothermal alteration of plagioclase.

The small calcite crystals, handpicked from sample YR0010A-1 from the Redox zone are strongly enriched in light REEs (Fig. 13 c). This preferential uptake of light REEs may be controlled by the similarity in ionic radius for light REEs and Ca (such substitution processes are indicated in other fracture calcites as well). An alternative interpretation is, however, proposed: Ongoing anaerobic respiration through Fe reduction has been documented (Banwart et al., 1994c) and is in fact manifested as magnetite formation in the YR0010A-1 sample. When the organic material is oxidised bicarbonate/calcite is formed. REEs, bound in organic complexes and possibly dominated by light REE (see above) are released and may be incorporated in calcite. Similar processes are suggested as potential causes of light REE enrichments in, for instance, calcite from the Redox zone and other water conductive zones at Äspö; for example indicated in five samples from KAS 02:207 where an increase in La/Yb ratio corresponds to a decrease in $\delta^{13}\text{C}$ (-10 to -46 o/oo).

For many of the fracture mineral samples a correlation between La and Th is indicated which can reflect similarities in the transport of these elements (eg. in complexation). For the calcite samples from water-conducting fractures at Äspö a positive correlation between Th and the La/Yb ratio is observed (Fig. 14) supporting the hypothesis that Th and light REEs behave similarly.

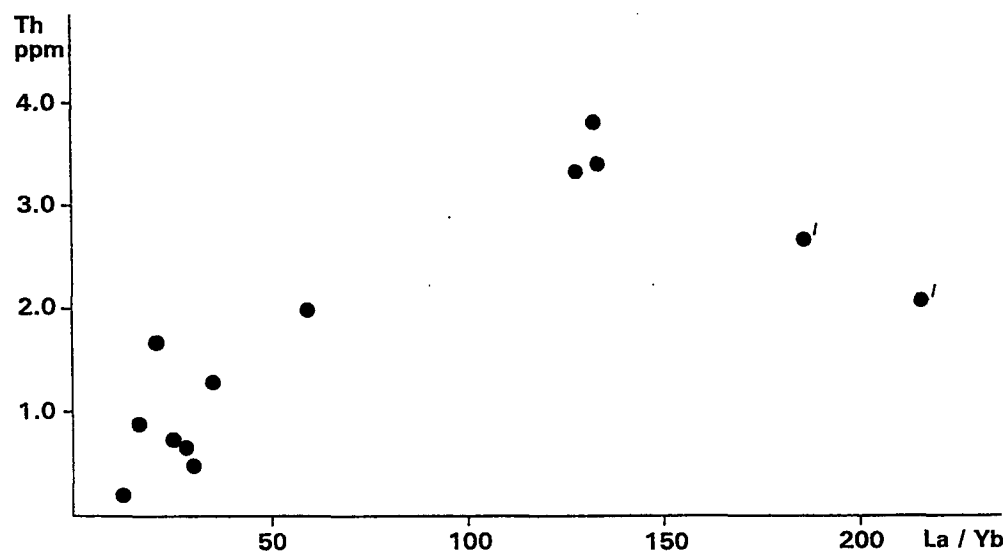


Figure 14. Th versus La/Yb in fracture calcites from water conducting fractures.
' = samples with high Hf content (possible contamination by host rock)

7. SUMMARIZING DISCUSSION

This study focuses on minerals and mineral/groundwater interactions that have key roles in the retardation of elements and natural radionuclides which are analogous to or identical with radionuclides occurring in a repository. The retardation is usually manifested as enrichments in fracture filling minerals which are in contact with the transporting groundwater.

A first step of the study comprised identification of fracture minerals with high retention capacity. The specific uptake of elements and radionuclides from the water phase ("net gain") was taken as a measure of this capacity. It was calculated by means of the immobile element method which allowed subtraction of components originating from the host rock (in situ alteration products and rock fragments). It turned out that large uptake from the fluid phase was associated with fracture fillings dominated by clay minerals, Fe-oxyhydroxides and calcite. These minerals are common in hydraulically conductive fractures and fracture zones, i.e. they offer a large active surface for groundwater/mineral interaction.

Three processes of interaction between trace elements and Fe-oxyhydroxide/calcite can be distinguished:

- 1) coprecipitation.
- 2) remobilisation in connection with dissolution and/or recrystallisation of the minerals.
- 3) sorption onto already formed minerals.

The significances of co-precipitation and remobilisation depend on the extent of formation and/or dissolution of these minerals within the time period covered by safety assessment. Since the formation of clay minerals is very slow compared to the time considered in predictive modelling, the retardation by clays will be mainly due to "sorption".

Only low temperature processes are expected to affect the migration of radionuclides within the next 100 000 years. However, high-temperature as well as low-temperature processes have been involved in the past redistribution of elements resulting in the enrichments observed. To elucidate the significance of the different low temperature retardation processes a second step of the work focused on studies of ongoing precipitations of Fe-oxyhydroxide and calcite and application of sequential extractions on fracture fillings containing clay minerals. A summary of the results is given below, focusing on the behaviour of the studied elements and radionuclides, the significance of clay, Fe-oxyhydroxide and calcite in retardation of radionuclides and implications to predictive modelling and fracture characterization.

7.1 BEHAVIOUR OF DIFFERENT ELEMENTS

7.1.1 Rb AND Cs

Rb and Cs are preferentially sorbed onto clay minerals and show little affinity to Fe-oxyhydroxide and calcite. Two forms of sorption were distinguished in extraction experiments on gouge material from the Redox zone; These are suggested to be fast ion exchange ("reversible") and slow diffusion into interlayer positions. The "reversible" uptake is in agreement with predictions based on laboratory determined K_d -values and concentrations of Cs in the groundwater. The fraction in the interlayer positions of clay minerals is large (amounting to 130 ppm Cs). It has not been possible to determine when this sorption occurred and if it is reversible in a longer time scale. Similar uptake of Cs-137 occurred during relatively short periods (years) after the Chernobyl accident (Riise et al., 1990; Carbol, 1993).

The slow sorption on interlayer positions in clay minerals and its mechanisms need further studies and has to be considered in predictive modelling since it is usually not accounted for in short time K_d -measurements. Also in planning of field tracer experiments using Cs isotopes this process should be considered because of the indicated high retention capacity of illitic clay and a time scale of years. Since this sorption is related to specific sites in micas and illite, the importance of characterization and quantification of clay minerals present in the water conductive fracture zones is emphasized.

The Rb/Cs ratio of groundwater from the Redox zone correlates with the Na/Ca ratios (and Na/Sr). Since the Na/Ca ratio is controlled by ion exchange processes on clay minerals (Banwart et al., 1994c; Viani & Bruton, 1994) this is probably the case also for the Rb/Cs ratio. Furthermore, Ca and Sr in the groundwater are correlated. The Sr isotope data presented by Wallin and Peterman (1994) for Äspö groundwaters indicate interaction with minerals having high Rb/Sr ratios (like clay minerals). Including the Rb/Cs ratios in the ion exchange calculations may refine the predictions on type and amount of clay minerals.

7.1.2 Sr AND Ba

The different behaviour of Sr and Ba is demonstrated by much higher K_d -values for Ba than for Sr in samples of granite, chlorite and calcite (Byegård et al., 1994) and a factor of ten higher partition ratio of Ba compared to Sr in Fe-oxyhydroxide/calcite precipitates from the NE-1 zone (this study).

Sr concentrations in the Äspö groundwater seem to be controlled by ion exchange on clay minerals (Wallin & Peterman 1994). This is in agreement with studies by Eriksen & Cui (1994) which showed complete reversibility of Sr sorption on the surface of chlorite and muscovite minerals. Strong variations in Sr and Ca/Sr ratios in calcites (by a factor of ten higher Sr-values in fresh calcite precipitates compared with older fracture calcites) are attributed to high precipitation rates for the fresh carbonates and/or release of Sr during recrystallisation of the older fracture calcites.

An analogous behaviour of Ra and Ba in the uptake in Fe-oxyhydroxide/calcite precipitates is indicated. This is expected from the similarity in chemical properties of these ions. The relationship between Ra and Ba may be used to clarify the relative importance of Ra release through chemical dissolution and α -recoil, respectively.

7.1.3 Th

Th is usually considered as "immobile" in low temperature systems with reference to its low solubility, presence in resistant minerals and tendency to quickly sorb onto nearby solid phases. However, present as well as past mobility of Th isotopes in the Äspö environment has been demonstrated:

- ^{232}Th was measured in filtered (0.40 μ) samples from shallow fresh water (0.45 $\mu\text{g/l}$) and in groundwater from 70 metres depth (0.037–0.091 $\mu\text{g/l}$) from the Redox zone.
- $^{228}\text{Th}/^{228}\text{Ra}$ activity ratios significantly exceeding unity were measured in fresh Fe-oxyhydroxide/calcite precipitates implying present mobility of ^{228}Th .
- Uptake of ^{232}Th in fresh Fe-oxyhydroxide as well as in fracture calcites of low temperature origin was indicated.
- Increasing ^{232}Th concentrations with decreasing grain size of gouge material and findings of an "irreversibly" sorbed fraction of ^{232}Th in the same material suggest past mobilisation of ^{232}Th and subsequent deposition onto clay particle surfaces. Whether this redistribution is a result of hydrothermal and/or low temperature processes is unclear.

In general, sorption of Th isotopes on clay mineral surfaces will contribute to high Ra activity in groundwater due to release through α -recoil. The high $^{228}\text{Ra}/^{226}\text{Ra}$ ratios in precipitates and groundwater from the NE-1 zone support the hypothesis of a redistribution of Th isotopes (for example ^{232}Th and ^{230}Th) which occurred sufficiently long ago (>0.35 Ma) to allow decay of ^{230}Th (precursor of ^{226}Ra).

Correlations of Th with Sc, REEs and Fe in water from the Redox zone suggest similar behaviour of Th, Sc and REE and association of these elements with Fe (sorbed onto $\text{Fe}(\text{OH})_3$ colloids?). Correlation of Th with La/Yb ratios in fracture calcites indicates a similar behaviour of Th and light REEs.

7.1.4 REEs

This work has demonstrated uptake of REEs from groundwater in fresh precipitates of Fe-oxyhydroxide and calcite, in fracture calcites of varying age and origin and in gouge material (most probably in its clay fraction). These minerals are thus potential barriers to the migration of REEs (and analogue actinides).

The fresh precipitates of Fe-oxyhydroxide/calcite show characteristic REE compositions which vary significantly between different fractures, both in concentration levels and chondrite-normalised REE patterns. Fractionation of the REEs in the precipitates, relative to those in the contact groundwater, has not been determined. Sequential extractions of a precipitate from the NE-1 zone indicate enrichments of light REEs, relative to the "total" REEs, in the amorphous Fe-oxyhydroxide and organic phases and of heavy REEs in the carbonate and "crystalline" Fe-oxyhydroxide phases. These fractionation trends may be controlled by speciation of the REEs in the groundwater; for instance carbonate complexations of heavy REEs and a dominance of light REEs in organic complexes and iron colloids. Extraction of a gouge sample from the Redox zone showed similar fractionation of REEs for the different phases. A long term fractionation trend is indicated in the Redox zone; preferential sorption of light REEs on the solid phase and a corresponding depletion in the groundwater.

Based on the distribution of REEs on different grain sizes of gouge material and from the results of extractions on the same material it is suggested that a large portion of the deposited light REEs is bound in surface sites of clay particles (dominantly illite). This is in agreement with conclusions given by Griffault et al., (1991); U and light REEs are mainly sorbed on the clay particle surfaces and not incorporated in the clay structure. These authors also claimed that the migration and deposition of U and light REEs occurred during hydrothermal conditions. This may be the case also for the gouge material from the NE-1 and Redox zones.

The REE composition of fracture calcite samples show large variations (La 14–540 ppm and the La/Yb ratio 1–215). Rapid crystallisation of calcite seems to result in low La/Yb ratios which may be due to the fact that heavy REEs form stronger complexes with carbonate. On the other hand light REEs have similar ionic radii as Ca which can be one explanation for preferential uptake of light REEs observed in some calcites. An alternative explanation for the high La/Yb ratios is anaerobic respiration which causes oxidation of organic material and formation of bicarbonate/calcite. During this process REEs, bound in the organic material and possibly dominated by light REEs (see 6.4)) will be released and may be incorporated in calcite.

7.1.5 Ra

Ra isotopes are strongly retained in fresh precipitates of Fe–oxyhydroxide and calcite and show higher affinity for these precipitates than do U and Th. An analogous behaviour of Ra and Ba in the retention is indicated and Ra may, like Ba, partition between the carbonate and Fe–oxyhydroxide phases. Activities of ^{228}Ra and ^{226}Ra and the $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio in the precipitates vary largely between different fractures. The highest ^{228}Ra and $^{228}\text{Ra}/^{226}\text{Ra}$ values are found in samples from the highly conductive NE–1 zone.

High $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratios in precipitates from the highly conductive NE–1 zone can be due to short mineral/groundwater contact time which favours the relative release of ^{228}Ra to the groundwater. However, an additional explanation is proposed: Mobilisation of ^{232}Th and subsequent sorption onto the surfaces of particles (e.g. clay) in contact with the groundwater (e.g. clay). ^{228}Ra will then be easily released to the groundwater through α -recoil. The effect on the ^{226}Ra release of a corresponding redistribution of ^{230}Th is of less significance since unsupported ^{230}Th will decay relatively fast (compared to ^{232}Th) and completely within 0.35 Ma.

In general, the migration (and migration ranges) of ^{226}Ra and ^{228}Ra are strongly dependent on the fate of their precursors ^{230}Th and ^{232}Th . The indicated and observed mobilities of Th isotopes (past as well as present) should therefore be paid attention to in modelling and predicting Ra migration. Primary migration of Th isotopes and subsequent sorption onto surface sites determine not only starting points for Ra migration but also provide efficient release of the Ra isotopes to the groundwater phase.

Accumulation of Ra isotopes in calcite/Fe–oxyhydroxide precipitates on the walls and floors of the underground laboratory in fact implies that sources of radon (^{222}Rn) and thoron (^{220}Rn) are localised within the tunnel. The relative release of radon from such sources is very efficient; up to 80% of the radon formed can escape to the air (Landström, 1978). However, compared to the amount of radon released from emerging groundwater these sources are probably of less significance.

7.1.6 U

U is generally low in fracture fillings from Äspö (<20 ppm) and also in the fresh Fe–oxyhydroxide/calcite precipitates; the highest value (4.5 ppm) is obtained for precipitates from the NE–1 zone. Comparison with groundwater data indicates a preferential uptake of Ra relative U in these precipitates. The oxidizing conditions in the tunnel may be one explanation for the very low U content in the fresh

precipitates.

Results from sequential extractions of a precipitate sample from NE-1 zone suggest an association of U with the carbonate phase. This is supported by analyses of U in hand-picked calcite crystals from the same sample. However, the possible release of some U from the Fe-oxyhydroxide phase in the carbonate leaching step is discussed in 5.3.1 and needs to be considered. According to Hsi & Langmuir (1985) the sorption of U on Fe-oxyhydroxide is very low in solutions with high carbonate contents and this may be the case in the NE-1 zone with a HCO_3^- content of 350 ppm.

7.2 RETENTION CAPACITY OF DIFFERENT MINERALS

7.2.1 CLAY MINERALS

Due to loss of clayish material during the drilling operation and difficulties in the identification of clay minerals in fracture surfaces exposed in drillcores, core mapping probably results in underestimation of the clay mineral content in the fractures. However, in fractures and fracture zones intercepted by the Äspö access tunnel it has been possible to sample and indentify undisturbed samples (Landström & Tullborg 1993; Maddock et al., 1993; Banwart et al., 1995). These investigations show that illite and mixed-layer clay with c. 90% illite are the dominating clay minerals although small amounts of smectite and kaolinite occur. The illite-rich mixed-layer clay has been formed at temperature $>100^\circ\text{C}$ and depths > 1 km according to Velde (1983, 1985) and has been dated to be 300–400 Ma (Maddock et al., 1993). Based on groundwater chemistry and temperature it is concluded that at present the formation of clay minerals at Äspö is very slow.

Clay minerals generally have high sorption capacity due to their large contact surface to the groundwater and their high cation exchange capacities (CEC). This ion exchange capacity can be very element specific (cf. Cs on illite). The Na/Ca ratio of groundwater in the Redox zone is suggested to be controlled by ion exchange on clay minerals (Viani & Bruton 1994; Banwart et al., 1995) and also the Sr content is controlled by ion exchange on clay minerals, as shown by the Sr isotope values of groundwater from the Redox zone (Peterman, 1995 written communication). This emphasizes the importance of ion exchange reactions with clays in the retention of these ions.

Laboratory studies of Sr sorption on chlorite and muscovite show complete reversibility (Eriksen and Cui, 1994). In contrast, significant portions of Cs and Rb were not desorbed in laboratory sorption/desorption experiments (e.g. Comans et

al., 1991; Byegård et al., 1994). This was explained by distribution of Cs on different sites; a rapid surface adsorption (ion exchange) and a much slower migration into interlayer sites. Although Cs in the interlayer sites appears to be "irreversible" it may be reversible in a long time perspective. For practical reasons, this is however not possible to study in laboratory experiments. The amount of mobile ("reversible") Cs (as determined in the "exchangeable" fraction of the sequential extraction scheme) is in agreement with that calculated from the Cs concentrations in groundwater from the Redox Zone and distribution coefficients determined in batch experiments (Andersson 1983; Comans et al., 1991). However, the slower interlayer sorption will probably contribute to the retention of Cs in time scales considered by radionuclide migration models. This is supported by studies of Cs-137 fall-out from Chernobyl which show that Cs-137 migration into interlayer sites starts immediately and probably continues for a long time (Riise et al., 1990; Carbol, 1993).

It is likely that clay minerals in fracture zones are significant in retaining REEs, Th, U and Ra. This is supported by sequential extractions of gouge material which indicate REEs and Th to be irreversibly sorbed onto the clay mineral surfaces. Th in such positions will effectively release radium to the groundwater through α -recoil.

The results discussed above emphasize the importance of clay minerals in radionuclide retention; also small amounts present within the fractures and fracture zones can significantly influence the radionuclide migration. Accurate determination of quantities and types of clay minerals is therefore important for modelling radionuclide transport. $^{228}\text{Ra}/^{226}\text{Ra}$, Na/Ca and Rb/Cs ratios in the groundwater seem to depend on reactions with clay minerals (due to sorption of ^{232}Th and ion exchange reactions) and may be used in such fracture mineral characterisation.

7.2.2 Fe-OXYHYDROXIDE

Fe-oxyhydroxide is common in fractures and fracture zones, especially in water-conducting ones. It can form as late stage precipitates during hydrothermal alterations, in low temperature environments e.g. as precipitates in oxygenated systems and through groundwater/mineral reactions in hematite bearing fractures. The origin of the Fe-oxyhydroxide occurring in fractures and fracture zones at Äspö is not always possible to determine. It is thus difficult to distinguish characteristic trace element patterns of Fe-oxyhydroxide formed at low temperature from those in Fe-oxyhydroxide formed at hydrothermal conditions.

Fresh precipitates of Fe-oxyhydroxide (representing low temperature conditions) at Äspö are effective scavengers of REEs, Sc, Ra, Th, U and Ba. It is, however, not

clear which processes dominate the uptake; sorption or co-precipitation.

Examples on important sites where Fe-oxyhydroxide can form are in the repository and surrounding fractures during the construction phase and at the interface between the geosphere and biosphere; in both cases due to contact with molecular oxygen. In the last case radionuclides can be retarded by sorption and/or by co-precipitation. In the former case the Fe-oxyhydroxide may form part of the near-field barrier.

Amorphous Fe-oxyhydroxide has a large active surface but this will decrease with aging (crystallisation) resulting in lower sorption capacity. During these processes parts of the accumulated elements/radionuclides may be released. For safety assessment it is important to evaluate the significance of Fe-oxyhydroxide in retarding radionuclide migrations.

7.2.3 CALCITE

Calcite is one of the most common fracture minerals. It exhibits a large surface in contact with the groundwater and responds quickly to changes in groundwater chemistry and temperature. This can result in significant precipitation/dissolution in the vicinity of a radwaste disposal due to the temperature anomaly introduced by the disposal. As a consequence the hydraulic properties and the sorption capacity of the fractures in the near-field will change.

Laboratory determined K_d -values for radionuclide sorption on calcite are small for most elements (Andersson 1983 and Byegård et al., 1994). Calculations based on these values and corresponding groundwater data would give much lower concentrations in for example fresh calcites from the Redox zone and the fracture zone NE-1 than those measured. It is thus suggested that irreversible incorporation is an important mechanism for retention of radionuclides caused by calcite.

Fracture filling calcite has been demonstrated to be a significant sink for REE, Ba, Sr, U and to some extent also for Th. Rapid calcite precipitation is suggested to increase the trace element content (exemplified in laboratory experiments for Sr; Morse & Bender 1990) whereas later recrystallisation may cause a release of trace elements to the fluid phase.

In disturbed hydraulic systems like those surrounding the Äspö tunnel, large variations in groundwater chemistry over short distances can occur. Mixing of different waters can cause disequilibria resulting in dissolution/precipitation of calcite and associated release or incorporation of trace elements. This may have implications on migration experiments where tracers may be irreversibly incorporated not only in preexisting fracture calcites but also in fresh calcite precipitates.

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1977-78

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KBS Technical Reports 1 – 120

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1979

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The KBS Annual Report 1979

KBS Technical Reports 79-01 – 79-27

Summaries

Stockholm, March 1980

1980

TR 80-26

The KBS Annual Report 1980

KBS Technical Reports 80-01 – 80-25

Summaries

Stockholm, March 1981

1981

TR 81-17

The KBS Annual Report 1981

KBS Technical Reports 81-01 – 81-16

Summaries

Stockholm, April 1982

1982

TR 82-28

The KBS Annual Report 1982

KBS Technical Reports 82-01 – 82-27

Summaries

Stockholm, July 1983

1983

TR 83-77

The KBS Annual Report 1983

KBS Technical Reports 83-01 – 83-76

Summaries

Stockholm, June 1984

1984

TR 85-01

Annual Research and Development Report 1984

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Stockholm, June 1985

1985

TR 85-20

Annual Research and Development Report 1985

Including Summaries of Technical Reports Issued during 1985. (Technical Reports 85-01 – 85-19)

Stockholm, May 1986

1986

TR 86-31

SKB Annual Report 1986

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1987

TR 87-33

SKB Annual Report 1987

Including Summaries of Technical Reports Issued during 1987

Stockholm, May 1988

1988

TR 88-32

SKB Annual Report 1988

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Stockholm, May 1989

1989

TR 89-40

SKB Annual Report 1989

Including Summaries of Technical Reports Issued during 1989

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1990

TR 90-46

SKB Annual Report 1990

Including Summaries of Technical Reports Issued during 1990

Stockholm, May 1991

1991

TR 91-64

SKB Annual Report 1991

Including Summaries of Technical Reports Issued during 1991

Stockholm, April 1992

1992

TR 92-46

SKB Annual Report 1992

Including Summaries of Technical Reports Issued during 1992

Stockholm, May 1993

1993

TR 93-34

SKB Annual Report 1993

Including Summaries of Technical Reports Issued during 1993

Stockholm, May 1994

1994

TR 94-33

SKB Annual Report 1994

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Maria Malmström¹, Steven Banwart¹, Lara Duro², Paul Wersin³, Jordi Bruno³

¹ Royal Institute of Technology, Department of Inorganic Chemistry, Stockholm, Sweden

² Universidad Politécnica de Cataluña, Departamento de Ingeniería Química, Barcelona, Spain

³ MBT Tecnología Ambiental, Cerdanyola, Spain
January 1995

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Marie Wiborgh (ed.)
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R S Forsyth¹, U-B Eklund²
¹ Caledon-Consult AB, Nyköping, Sweden
² Studsvik Nuclear AB, Nyköping, Sweden
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Ignasi Puigdomènech¹, Jordi Bruno²
¹ Studsvik AB, Nyköping, Sweden
² Intera Information Technologies SL,
Cerdanyola, Spain
April 1995

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Karsten Pedersen¹, Fred Karlsson²
¹ Göteborg University, General and Marine Microbiology, The Lundberg Institute, Göteborg, Sweden
² Swedish Nuclear Fuel and Waste Management Co., Stockholm, Sweden
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Solute transport in fractured media – The important mechanisms for performance assessment

Luis Moreno, Björn Gylling, Ivars Neretnieks
Department of Chemical Engineering and Technology, Royal Institute of Technology, Stockholm, Sweden
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**Literature survey of matrix diffusion
theory and of experiments and data
including natural analogues**

Yvonne Ohlsson, Ivars Neretnieks

Department of Chemical Engineering and
Technology, Royal Institute of Technology, Stock-
holm, Sweden

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