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NATURAL URANIUM AS A TRACER

IN RADIONUCLIDE

GEOSPHERE TRANSPORT STUDIES

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Academic Dissertation

To be presented with the permission of the Faculty of Science
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ABSTRACT

Uranium (U) is a common element in the earth's crust. Because of its solubility characteristics it has been moved and will be moved by naturally occurring geochemical processes. Accordingly, study of the mobile fraction of U offers an opportunity to obtain information on geochemical evolution in general and on how the geochemical evolution controls U transport. This interrelation was utilised in the present study to gain an understanding of U transport in crystalline bedrock. Such information is important in assessing the fate of radionuclides possibly escaping from a nuclear waste repository excavated deep in the bedrock.

Uranium transport was studied in the network of water-conducting fractures in the vicinity of a small U-Th deposit. Investigations were focused on U fractions susceptible to groundwater, *i.e.* U on fracture surfaces and in rock pores close to fractures. Uranium-series disequilibria were examined to obtain spatial and temporal information on past transport. Reference U samples prepared in the laboratory and other U-bearing samples were examined to assist the interpretation.

Simultaneous carrying out of *in situ* studies and laboratory experiments assisted the development of experimental methods. Similar observations of U fixation *in situ* and in the laboratory provided a good insight into the mechanisms by which U is fixed. Information on reversible and irreversible U fixation was obtained. Attachment of U to ferric compounds appeared to take place through mechanisms that fix U more firmly than adsorption. Movement of U isotopes in the rock matrix close to fractures in centimetre scale was observed.

Because of the interest in future evolution of an underground waste repository environment, the observations on geologically recent U transport were scrutinised for information they might contain on events in past evolution. Uranium-series disequilibrium signatures that might reflect such events were identified. These signatures could not have been preserved so long unless they had been shielded from present groundwater leaching, and they could not have formed in the first place unless significant amounts of U had been subject to groundwater leaching. Additionally, in order for groundwater leaching to have generated such distinctive disequilibria it must have occurred not later than 300,000 years ago.

The findings of the study suggest that the loosely bound U (labile U) that was abundantly present in the samples is a sensitive indicator of the changes occurring in groundwater−rock conditions. Labile U can serve as a valuable tracer of radionuclide migration, and also as an indicator of the possible impacts of processes (*e.g.* glaciation−deglaciation processes) that might occur in the geochemical evolution under future climatic changes.

PREFACE

The studies making up this thesis were carried out in the Laboratory of Radiochemistry at the University of Helsinki. The Finnish Radiation and Nuclear Safety Authority and the Ministry of Trade and Industry were responsible for the research projects within which most of the work was carried out. Teollisuuden Voima OY Nuclear Waste Management (now Posiva OY) provided essential support in developing the experimental tools.

I wish to express my sincere thanks to Professor Timo Jaakkola, for his unfailing support and encouragement. I am further most grateful to my co-workers and co-authors Dr. Kari Rasilainen, Mr. Timo Ruskeeniemi, Prof. Runar Blomqvist, Mr. Antero Lindberg, Dr. John Smellie and Dr. Joél Casanova, all of whom made valued contributions to the research and writing of the articles. My special thanks to Dr. Kari Rasilainen for his invaluable input.

Warm thanks are due to my colleagues Mr Martti Hakanen, Doc. Risto Harjula, Doc. Jukka Lehto, Dr. Jussi Paatero, Mrs Marja Siitari-Kauppi and Pirkko Hölttä. This work is in many ways an outgrowth of working beside and discussing problems with them. I was most fortunate to have been helped in my experimental work by such congenial and talented colleagues and students as Fil. Lic. Heini Ervanne, Fil. Lic. Leena Brodkin (formerly Saarinen), Tiina Laurila, Anni Kukko, and Paula Juntunen.

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Finally, I wish to express my dearest thanks to my wife Seija and our son Jere for their understanding on the many occasions when I became inattentive to duties at home.

Helsinki, November 30, 2001   Juhani Suksi

LIST OF PUBLICATIONS

The thesis is based on the following publications:

I   Suksi, J., Ruskeeniemi, T., Lindberg, A., and Jaakkola, T., 1991. *The distribution of natural radionuclides on fracture surfaces in Palmottu analogue study site in SW Finland*. Radiochim. Acta **52/53**, 367-372.

II   Suksi, J., Ruskeeniemi, T., and Rasilainen, K., 1992. *Matrix diffusion - evidences from natural analogue studies at Palmottu in SW Finland,* Radiochim. Acta **58/59**, 385-393.

III   Suksi, J., Saarinen, L., Ruskeeniemi, T., Rasilainen, T., and Siitari-Kauppi, M., 1995. *U series concentration distributions around rock fractures - qualitative indication of matrix diffusion*. Mat. Res. Soc. Symp. Proc. **353**, 441-448.

IV   Suksi, J., Ruskeeniemi, T. and Saarinen, L., 1996. *Selective extractions in uranium migration studies - findings from a natural analogue study at Palmottu, southern Finland*. J. Contamin. Hydrol. **21**, 47-58.

V   Suksi, J. and Rasilainen, K., 1996. *On the role of α-recoil in uranium migration – some findings from the Palmottu natural analogue site, SW Finland*. Radiochim. Acta **74**, 297-302.

VI   Finch, R.J., Suksi, J., Rasilainen and Ewing, R.C., 1996. *Uranium-series ages of secondary uranium minerals with applications to the long-term evolution of spent nuclear fuel*. Mat. Res. Soc. Symp. Proc. **412**, 823-830.

VII   Suksi, J. and Rasilainen, K., 1997. *Reconciliation of experimental and modelling concepts in a natural analogue of radionuclide migration*. Mat. Res. Soc. Symp. Proc. **465**, 1169-1176.

VIII   Suksi, J., Rasilainen, K., Casanova, J., Ruskeeniemi, T., Blomqvist, R. and Smellie, J.A.T., 2001. *U-series disequilibria in a groundwater flow route as an indicator of uranium migration processes*. J. Contamin. Hydrol. **47**, 187-196.

IX   Suksi, J., and Rasilainen, K., 2001. *Isotopic fractionation of U reflecting redox conditions around a groundwater flow route*. Mat. Res. Soc. Symp. Proc. (in print).

All publications except publication VI deal with U migration studies at the Palmottu natural analogue study site and related laboratory experiments. Publication VI presents studies on samples from other sites. Geologically recent U transport and associated phenomena are considered in all publications, however. The advance in interpretation and related conclusions since the appearance of the publications has been taken into account in the present manuscript.

CONTENTS

1   INTRODUCTION

1.1   Background

Present plans call for the spent nuclear fuel from the Finnish nuclear power industry to be disposed of in a repository excavated at depths of about 500 metres in the granite bedrock (TVO 1992; Ruokola 2000). The aim of the disposal is to isolate the highly radioactive waste material from the biosphere until its radioactivity has decayed to a level where possible radionuclide releases will be harmless. Because of the very long half-lives of some of the radionuclides, the safety of the disposal must be assured for tens of thousands of years into the future. Safety assessments over such a long period of time necessarily involve uncertainties. One major uncertainty is related to the geochemical evolution of the repository environment. This has been approached by studying consequences for a set of alternative scenarios that are assumed to cover the probable evolutions (see Vieno and Nordman 1999).

An alternative way to deal with these uncertainties is a natural analogue approach, which seeks to obtain information directly from naturally occurring geochemical systems (Chapman and Smellie 1986; Côme and Chapman, 1987; Ewing and Jercinovic 1987; Petit 1992; Miller *et al.*, 1994 and 2000). A natural analogue can broadly be regarded as an uncontrolled long-term natural experiment, which terminates when the system is sampled by the researcher. Natural U deposits have been widely used as an analogue for assessing the fate of radionuclides escaping from a waste repository (Chapman *et al.* 1991; Duerden 1992; Chapuis and Blanc 1993; Cramer and Smellie 1994; Rivas *et al.* 1998). In Finland, such studies have been performed in the vicinity of a small U deposit at Palmottu, Nummi-Pusula (Blomqvist *et al.* 1998; 2000). The present study forms part of the Palmottu studies.

The principal interest in U deposits lies in the mechanisms that have been responsible for their low-temperature weathering and the subsequent remobilisation of U-series elements. This is because these mechanisms operate in conditions that are essentially similar to those under which the evolution of a nuclear waste repository will take place. Naturally occurring U and Th are of particular interest because they show different solubility characteristics (Langmuir 1978; Langmuir and Herman 1980) and their isotopes occur in the same radioactive decay series. They also

represent useful analogues of the future waste actinides in groundwater–rock conditions (*e.g.* Krauskopf 1986; Bruno *et al.* 1997; Choppin 1999).

1.2   Scope and objectives

Whatever processes affect a repository in the future the only natural mechanism able to return harmful radionuclides in a repository to the biosphere is groundwater flow in fractures cleaving the bedrock. Radionuclide transport during such flow will mainly be governed by advection, dispersion, and diffusion. An important additional control is provided by the chemical reactions occurring on mineral surfaces.

Realistic modelling of radionuclide transport through the low permeability crystalline basement is a challenging task. The transport route from repository to biosphere is difficult to characterise, and complex chemical interactions are involved. Our incomplete knowledge of future evolution further complicates the modelling. To cope with these difficulties, reality must be considerably simplified in modelling. Critical flow path is characterised as a smooth and straight fracture and complex chemical interactions are modelled with the help of a laboratory-based distribution coefficient [1]K_d, which is normally determined in one set of chemical conditions. Such overly simplified modelling is justified by the assumption of conservatism, *i.e.* the model assumes a pessimistic situation (Vieno and Nordman 1999 and references therein).

In the present study the problem of long-term radionuclide geosphere transport was approached experimentally by studying U behaviour historically. Information was sought by examining U dispersion and associated mechanisms around a natural U source situated in granite rock. For interpretation U decay series measurements were used. Because of several ice-ages at Finnish latitudes (see reviews of Eronen & Olander 1990 and Forsström 1999) groundwater–rock systems have undergone severe physical and chemical changes. Since U is a mobile element, if these changes affected natural U, this should also be evident in the U decay series, showing up as characteristic radioactive disequilibria between U and immobile Th. The detection of these disequilibria today is facilitated by the coincidence that the evolution of the latest glaciation overlaps the best application range of the U-series disequilibrium technique.

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[1] K_d is defined as the ratio of the quantity of the adsorbate (*i.e.* metal or radionuclide) adsorbed per unit mass of solid to the quantity of the adsorbate remaining in solution at equilibrium (ml/g or m^3/kg).

The U-series disequilibrium technique has become an important tool in developing concepts for purposes of repository safety assessment (Ivanovich *et al.* 1992; Ivanovich 1994). Owing to the diverse chemistry and a wide range of half-lives of the decay series nuclides the technique is particularly useful for studying processes that have dominated during the last 200,000 years.

The potential risk of future glaciations for the stability of an underground nuclear waste repository has received a fair amount of attention in the literature (*see* OECD/NEA 1993; Fontes 1993; King-Clayton *et al.* 1997). An interest in providing information to evaluate the consequences of future evolutions has been one of the driving forces of this study.

1.3 Organisation of the thesis

The thesis is divided into four parts. Background information relevant to study recent U transport in groundwater–rock systems is provided in Chapter 2. The experimental approaches are considered in Chapter 3, and the main findings are presented and discussed in Chapter 4. Chapter 5 presents conclusions, implications and proposals for the future.

2   OBSERVING RECENT U TRANSPORT

2.1   Natural uranium

Uranium is a common element in the earth's crust. Samples taken from our natural environment (water, rock, sediment, fossil and living plants) contain from a few ppb up to several per cent of uranium (Ivanovich and Harmon 1982). Natural U consists of three isotopes, of which two, ^{238}U and ^{235}U, are primordial and initiate two of the three naturally occurring radioactive decay series (Table 1). The third isotope ^{234}U, being a member of the ^{238}U decay series, is radiogenic (see Fig. 1). In terms of U transport studies, the ^{238}U decay series forms the most important decay chain.

The isotope ^{235}U occurs in constant amount (0.72 %) relative to the ^{238}U isotope except in samples from a fossil natural fission reactor site at Oklo, Gabon, where the proportion of ^{235}U is significantly lower (Lancelot *et al.* 1975). The amount of radiogenic ^{234}U is very low (some 10^{-4} % of ^{238}U), which means that the mass of U almost entirely consists of the isotope ^{238}U. The amount of ^{234}U expressed as radioactivity units may be many fold that of ^{238}U, however. ^{234}U/^{238}U activity ratios exceeding ten have been observed in groundwaters (Ivanovich and Harmon 1982).

Table 1. Natural radioactive decay series.

Name of series	Type	Primordial nucleus Nucleus	Half-life (y)	Longest-lived daughter Nucleus	Half-life (y)	Final nucleus (stable)
Thorium	4n*	^{232}Th	$1.39 \cdot 10^{10}$	^{228}Ra	5.7	^{208}Pb
Neptunium**	4n + 1	^{237}Np	$2.20 \cdot 10^{6}$	^{233}U	$1.59 \cdot 10^{5}$	^{209}Pb
Uranium	4n + 2	^{238}U	$4.49 \cdot 10^{9}$	^{234}U	$2.48 \cdot 10^{5}$	^{206}Pb
Actinium	4n + 3	^{235}U	$7.13 \cdot 10^{8}$	^{231}Pa	$3.3 \cdot 10^{4}$	^{207}Pb

* n is an integer
** the neptunium series, characterised by the geologically short half-life of ^{237}Np, does not occur in nature

Because of the importance of U in nuclear chemistry and technology a great deal is known about its aqueous chemistry (*e.g.* Wanner and Forest 1992). Uranium has two relatively stable oxidation states, 4+ and 6+, in essentially all geologic environments. The tetravalent state is the normal ionic condition within rocks while the hexavalent state is the normal form in oxidising conditions and in many secondary U minerals (Langmuir 1978; Smith Jr. 1984).
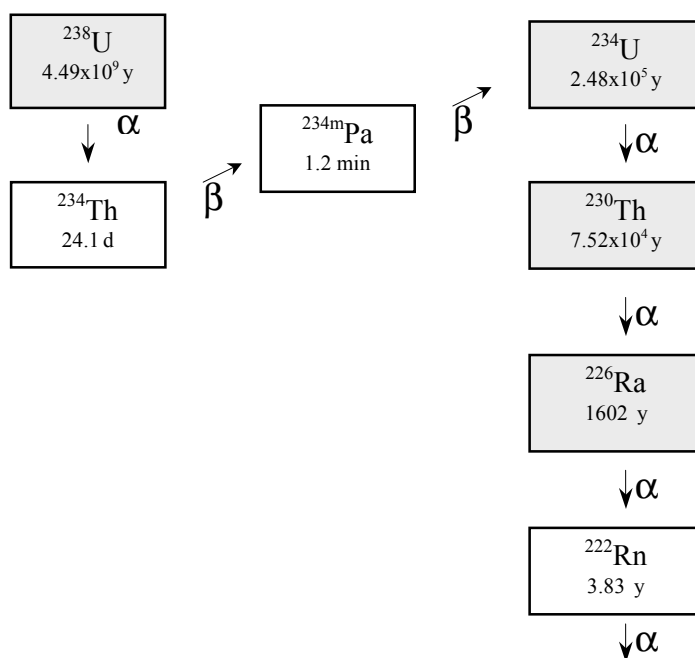
Fig. 2. Beginning of the uranium decay series with respective half-lives. Important nuclides in terms of long-term radionuclide transport studies are indicated.

Chemically, uranium is a hard-donor cation with a strong tendency to complex with oxygen-containing ligands. The greater solubility of U^{6+} as the uranyl ion (UO_2^{2+}) is due to its ability to form stable soluble complexes with various organic and inorganic ligands. The occurrence and distribution of uranyl species in surface and subsurface environments is controlled by the redox conditions, pH and the CO_2 partial pressure (*e.g.* Giblin *et al.* 1981; Dongarra 1984; Gascoyne 1992). The behaviour of the ^{234}U isotope is further controlled by α-decay and related recoil "hot atom" chemistry (see section 2.3).

Uranium concentration in aqueous solutions is affected by dissolution, precipitation, coprecipitation and sorption, U(IV) being affected more strongly than U(VI). In low ionic strength solutions with low U(VI) concentrations dissolved uranyl concentrations will likely be controlled by cation exchange and adsorption processes (*e.g.* Ames *et al.* 1983; Hsi and Langmuir 1985; Payne *et al.* 1994). In oxidising conditions with high U concentrations uranyl concentrations are additionally controlled by the formation of U(VI) minerals (*e.g.* Langmuir 1978).

2.2 Importance of labile U

According to Neuerburg (1956) uranium has six modes of occurrence in igneous rocks: (1) in U minerals, (2) in crystallographic sites or structural defects of major

rock forming minerals and minor accessory minerals, (3) in cation exchange positions, (4) adsorbed and precipitated on mineral surfaces, (5) dissolved in fluid inclusions, and (6) dissolved in intergranular fluids. These modes may vary considerably depending on the geochemical history of a rock. Neuerburg called that part of uranium that is weakly bound (modes 3-6) labile U. Alpha particle and fission track radiography has been applied for the detailed mapping of U sites within rocks (*e.g.* Zielinski *et al.* 1981; Thiel *et al.* 1983; Guthrie 1989).

Labile U has been discussed at length by Stuckless and Ferreira (1976), who considered U sources in igneous rock. Occurrence and distribution of labile U is controlled by the alteration of rock forming minerals (*e.g.* Zielinski *et al.* 1981; Rosholt 1983; Michel 1984; Guthrie and Kleeman 1986). Because of its susceptibility to groundwater leaching, it is mainly labile U that is involved in U mobilisation from granitic rocks.

The susceptibility of U to dissolution in groundwater has been demonstrated in leaching tests (see the review in Rosholt 1982). The "age" of labile U varies from hydrothermal origin to very recent load. Exceptionally young U loaded in rock pores was recently observed in investigations on a muscovite granite boulder (Suksi *et al.* 1995,1996; Rasilainen *et al.* 1996). Most of this load was dated not older than 10,000 years. Irrespective of the age of labile U it appears to be a sensitive indicator of changes in water–rock interaction.

2.3   Origin of U-series disequilibria

Radioactive disequilibrium develops because the decay series elements have diverse chemical properties and half-lives. The radioactive decay chain is said to be in secular equilibrium if the activities of the member radionuclides are equal to the activity of their long-lived parent (activity ratio = 1). If any member radionuclide is departing from, or being added to, the decay series system by any process other than radioactive decay, a state of radioactive disequilibrium exists (activity ratio ≠ 1). The time needed to restore radioactive equilibrium after disruption of the initial state of equilibrium and the rate at which the restoration occurs are determined by the half-lives of the respective nuclides (cf. Table 1). This unique characteristic of the natural radioactive decay chains has long been utilised in the dating of geochemical processes (Ivanovich and Harmon 1982; 1992).

The following mechanisms have been recognised as responsible for disequilibration of natural radioactive decay chains: (1) dissolution/precipitation, (2) diffusion, (3) α-recoil and (4) recoil-induced vulnerability to leaching (see review in Osmond and Ivanovich 1992). Selective leaching by groundwater when it percolates past mineral grains is a common disequilibration mechanism in the bedrock environment. The susceptibility of U to groundwater leaching and, consequently, disequilibration of its decay chains depends on the location and binding of U in the rock matrix (cf. section 2.2).

A pronounced disequilibrium is easily produced between the U and Th isotopes because pH and Eh control U behaviour (Langmuir 1978) and Th is practically insoluble in a wide range of natural conditions (Langmuir and Herman 1980). Accordingly, any disequilibrium occurring between ^{234}U and ^{230}Th, for example, indicates past changes in the chemical environment, *i.e.* in pH and Eh. In groundwater–rock systems such changes are generally brought about through groundwater recharge and when oxic groundwaters are introduced in anoxic conditions. Taken together, as a result of disequilibration processes the liquid phase has an excess of soluble radionuclides, and surfaces of the solid phase have a deficiency of them.

Observation of U-series disequilibrium in crystalline basement rocks not only reveals that the responsible chemical change is geologically very recent (Table 2) but, importantly, the disequilibrium has been produced as a result of low-temperature water–rock interaction. The degree of disequilibrium defines the time elapsed since the disequilibrium formed.

The realisation of the linkage between geochemical processes and the disruption of radioactive decay chains has inspired a large number of applications. Cherdyntsev (1971), who can be regarded as the pioneer of U-series disequilibrium studies, wrote the first comprehensive review of U-series applications. Improved measurement techniques (α-spectrometry and mass spectrometry) enabled still other applications (Ivanovich and Harmon 1982). In his more recent reviews, Ivanovich has discussed the application of U-series disequilibrium concepts to the problem of deep underground radioactive waste disposal in the light of numerous examples (Ivanovich 1991; Ivanovich and Harmon 1992; Ivanovich *et al.* 1992; Ivanovich 1994).

Table 2. Equilibration times for the longest-lived parent/daughter pairs in the ^{238}U decay series. The minimum time between the adjacent disequilibration events needed for their reliable discrimination by α-spectrometry is also indicated. Mass spectrometry, because of its much smaller analytical errors, enables discrimination of much closer events.

Parent/daughter pair	Equilibration time[1] (y)	Difference between datable events[2] (y)
^{234}U/^{238}U	1 200 000	~ 200 000
^{230}Th/^{234}U	300 000	~ 25 000
^{226}Ra/^{230}Th	8000	~ 2000

[1] Here the equilibration time is defined as the time period for which a disequilibration event can be detected within the analytical error of α-spectrometry.

[2] Values are based on counting errors in routine α-spectrometry

2.4 Importance of α-recoil

Perhaps the most notable mechanism contributing to the disruption of radioactive decay chains is the recoil of daughter products as a result of α-decay. Natural decay series α-particles have energies from 3.9 to 8.8 MeV. Conservation of momentum necessitates that the decay product obtains energy commensurate with the energy of the α-particle, according to equation $E_d = E_{\alpha*}4/M_d$ (1), where E_d is energy of a decay product and E_α that of corresponding α-particle (Rössler 1983). The recoil energies thus obtained in the natural decay series vary between 70 and 140 keV. As these energies are considerably greater than those involved in chemical bonding, bond breaking easily occurs and mineral lattices are destroyed. In the case of ^{234}Th recoil (Fig. 4), the recoil energy is 72 keV which causes a displacement of some 20 nm from the original ^{238}U position.

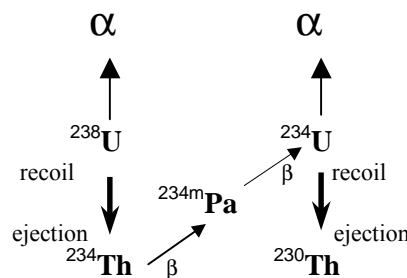**Fig. 4.** Beginning of the ^{238}U decay chain. Primordial ^{238}U decays to ^{234}U via one α-decay and two β-decays. In the ^{238}U decay, a 4.2 MeV α-particle is emitted, giving a recoil energy of 72 keV to ^{234}Th, which ejects the ^{234}Th atom several nanometres, to an environment that may be chemically different (in terms of U oxidation states) than the original crystal site of ^{238}U (see text).

A geochemically important consequence of α-recoil is fractionation of U isotopes. The fractionation is seen as ^{234}U excess in water and deficiency in rocks. Two basic models, physical and chemical, have been suggested as an explanation of fractionation. The physical model implies recoil across phase boundaries as the main mechanism, whereas the chemical model attributes the fractionation to recoil induced preferential ^{234}U dissolution.

Cherdyntsev (1971) was the first to discuss the radiological aspects of α-recoil in terms of geochemistry. In their review, Osmond and Cowart (1976) examine the issue in more detail, classifying the processes that might favour the preferential mobilisation of ^{234}U:

(1) Direct transfer of the recoil daughter by α-recoil across the phase boundary.

(2) Increased vulnerability to solution resulting from:
   (a) Recoil displacement causing

   - lattice destruction and bond breakage

   - unstable location, *e.g.* interstitial lattice resting sites
   (b) Oxidation from U^{4+} to U^{6+}

   - related to oxidation potential difference between displaced site and original site

   - related to the decay process itself

(3) Chemical fractionation of ^{234}Th

From the point of view of Th geochemistry the third mechanism seems unimportant (see Langmuir and Herman 1980). And since the general grain size of rocks is orders of magnitude larger than the recoil range (~20 nm), the first mechanism is scarcely important either. Evidently, then, the second mechanism dominates the fractionation of U isotopes. Four mechanistic models related to the second mechanism have been proposed to explain the fractionation. In a detailed consideration of the models Rössler (1983) and Petit *et al.* (1985) concluded that the oxidation of ^{234}U might be the main reason for the observed ^{234}U/^{238}U disequilibrium. Indeed, the oxidation-based fractionation was suggested by Petit *et al.* as the best model to quantitatively account for the disequilibrium between U isotopes observed in nature.

More recently, a model was derived to explain the preferential dissolution of ^{234}U (Ordonez-Regil *et al.* 1989; Adloff and Rössler 1991). The model predicts that ingrowing ^{234}U tends toward an easily leachable, oxidised $^{234}U(VI)$ form as a result of the oxidation potential developed between the original crystal site of ^{238}U and the new environment of ^{234}U after recoil displacement. In this model the recoiling large ^{234}Th atom, while being ejected several nanometres, "heaps" smaller oxygen atoms in front of it at the end of its trajectory where it decays to ^{234}U. The oxidising microenvironment that is produced contributes to the easy oxidation of ^{234}U (Fig. 4).

From the findings of "hot atom" chemistry in inorganic compounds (see the review in Rössler 1983), it seems that the recoil atom prefers the hexavalent state over the tetravalent one. In these systems the recoil creates oxygen defects or radicals, which may act as oxidants for uranium and at the same time provide the ligands necessary for the formation of UO_2^{2+} oxyanions.

2.5   U-series disequilibria as an interpretative tool

The linkage between geochemical processes and U-series disequilibria offers information about temporal and spatial U transport. The interpretation starts from the fact that Th and U^{4+} are essentially insoluble in groundwater while U^{6+} and Ra are soluble. Osmond and Cowart (1976;1983;1992) presented a systematic method for using U isotopic activity ratios in the study of groundwater circulation and mixing patterns.

The applicability of the U-series technique to underground radioactive waste disposal problems was first thoroughly discussed by Schwarcz *et al.* (1982) who presented simple principles for interpreting disequilibria in rocks. They described the different U sites in the rock matrix where disequilibrium could be generated. They also presented an experimental approach for disequilibrium analysis. In a review of a large amount of U-series data compiled from studies in crystalline bedrock Rosholt (1983) outlined five predominant geochemical processes that affect U mobilisation. As a follow-up to this review, basic principles were developed for interpreting disequilibria in crystalline bedrock (Table 3). Rosholt's review was later complemented by Gascoyne and Cramer's (1987) interpretation of $^{226}Ra/^{230}Th$ disequilibrium observations.

Table 3. Linkage between U-series disequilibrium and groundwater-rock interaction in fractured crystalline rocks (Rosholt 1983; Gascoyne & Cramer 1987 and Scott *et al.* 1992).

Process	Isotope effect	Typical activity ratios			Typical occurrence
		$\frac{^{234}U}{^{238}U}$	$\frac{^{230}Th}{^{234}U}$	$\frac{^{226}Ra}{^{230}Th}$	
U leaching (chemical)	No fractionation of U isotopes, excess ^{230}Th generated	~ 1.0	>> 1.0	≤ 1.0	Very recent near-surface leaching of a weathered rock; oxidising environment
U leaching (chemical and recoil-induced)	Some fractionation of U isotopes; preferential loss of ^{234}U, excess ^{230}Th generated if U releases within time comparable to the half-life of ^{230}Th	≤ 1.0	> 1.0	≤ 1.0	Recent near-surface leaching of relatively fresh rock; mildly oxidising environment
U leaching (recoil-induced vulnerability of ^{234}U)	Fractionation of U isotopes; significant preferential loss of ^{234}U (groundwater labelling); the greater the deviation from equilibrium, the slower has been the rate of bulk dissolution	< 1.0	≥ 1.0	< 1.0	Intermediate to deep location, little U leaching; Ra leaching in high salinities: reducing environment
U addition (sorption and precipitation)	Tends to attain ^{234}U/^{238}U ratio of groundwater	> 1.0	< 1.0	≤ 1.0	Moderate depth location; no leaching; at a redox front, recent addition

An approach increasingly used to interpret radioactive disequilibria is to plot the measured ^{234}U/^{238}U activity ratio against the ^{230}Th/^{238}U activity ratio (see Thiel *et al.* 1983). The resulting graph (see Fig. 19 later in the text) can be divided into areas corresponding to dissolution and deposition processes. Moreover, evolution curves can be constructed to describe the return of systems towards radioactive equilibrium after disruption of the initial state of secular equilibrium.

Although the mechanisms and conditions that can cause disequilibria are fairly well understood the quantitative interpretation is not straightforward because of the inherent complexity of natural systems (see *e.g.* Latham and Schwarcz 1989;

Scott *et al.* 1992; McKinley and Alexander 1996; Rasilainen 1997). U-series modelling offers a tool for simulating radioactive disequilibrium evolution. In suitable cases, constraints can be placed upon the rates and time-scales applicable to certain geochemical processes, and radionuclide release or deposition rates can be derived (Latham and Schwarcz 1987). Simulations are also useful for excluding non-physical scenarios from further consideration (Rasilainen and Suksi 1997). Supporting geochemical data will facilitate the exclusion of unlikely scenarios.

3 EXPERIMENTAL APPROACHES

3.1 Samples and sampling

Most samples were taken from nearby bedrock fractures and fissures. The sample material consisted of fracture coating material (mainly calcite with kaolinite) and the bulk rock beneath. In addition, museum specimens of altered secondary U(VI) minerals from Zaire (**publication VI**) and laboratory-prepared Fe(III) minerals were used. Sampling and subsampling procedures are presented in Figs. 5 and 6.
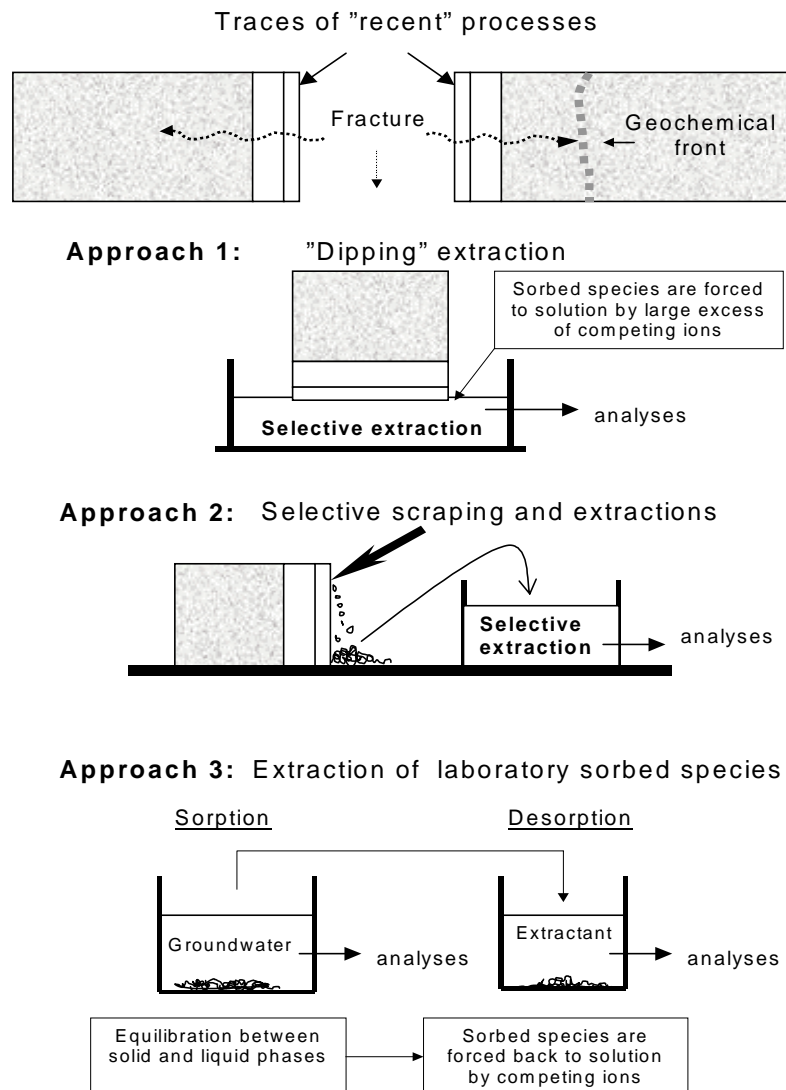

Fig. 5. Illustration of experimental approaches for the study of recent U transport.

Sampling was concentrated on U phases susceptible to groundwater leaching (labile U). Labile U was either totally separated or selective extraction of its possible components was attempted. The basic idea of applying selective extraction is to disassemble *in situ* formed phases in a controlled manner. In practice, selective desorption is used to loosen adsorbed species and selective dissolution to loosen species incorporated into geochemical phases.
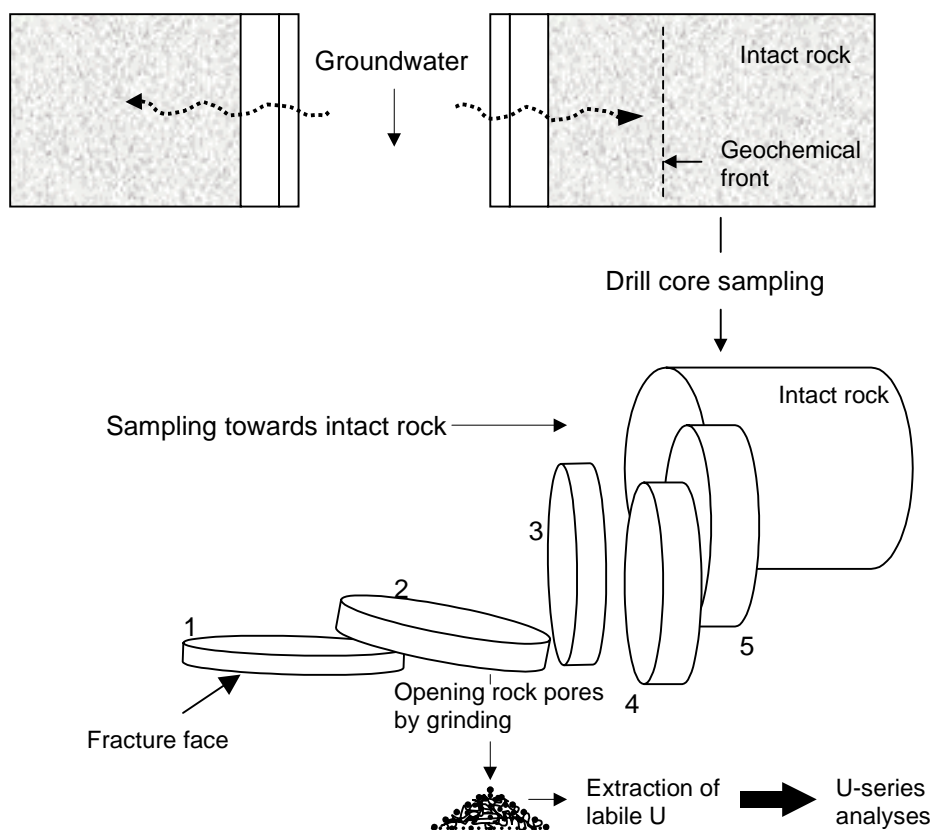

Fig. 6. Sampling procedures to study changes in long-term groundwater–rock interactions.

3.2   Occurrence and separation of U

Autoradiography and SEM studies showed that a significant fraction of U is distributed in rock pores (**publications II and III**). These studies, while producing information on the accessibility of U to groundwater, also gave information on its binding to the rock matrix and suggested how it could be chemically separated.

Sequential extractions have been widely used to study the geochemical association of various trace elements (*e.g.* Chao 1984; Pickering 1986; Rauret and Quevauviller 1992). One commonly applied approach is to operationally divide the

sample material into target phases (*e.g.* adsorbent, coprecipitate and mineral component), which are then attacked. An ideal chemical reagent should thus include (1) sufficient reactivity to dissolve the target phase and associated radionuclides, (2) adequate complexation capability to keep dissolved radionuclides in solution and maintain their original proportions and (3) good phase specificity so that impact on radionuclides in other phases can be kept as low as possible. Several alternative extraction procedures, depending on sample material, have been applied for U (*e.g.* Michel 1984; Lowson *et al.* 1986; Bolle *et al.* 1988; Yanase *et al.* 1991; MacKenzie *et al.* 1991; Suksi *et al.*1991 and Edis *et al.* 1992).

The present study made use of an extraction sequence capable of differentiating phases relevant to recent water–rock interaction (datable by U-series disequilibrium technique). It should be noted that the choice of an extraction procedure is always sample dependent and the knowledge of the sample material and its geochemical background is crucial for the best possible result.

Selective separation of U from different sites has received a fair amount of attention in the literature (Schwarcz *et al.* 1982; Latham and Schwarcz 1989; Alexander *et al.* 1990; Edis *et al.* 1992; Heath 1995). The use of the extraction results in radionuclide migration models has aroused discussion concerning the use and misuse of this technique (*e.g.* McKinley and Alexander 1993; 1996). The discussion is important because the selective chemical extraction technique is one of a very limited number of ways to obtain quantitative information on *in situ* association of trace elements to minerals (see also Pickering 1986; Martin *et al.* 1987). In fact, chemical extractions may be the only way to quantify various *in situ* phases. Though various surface spectroscopic techniques are available, their greatest use is to study the bonding of chemical species on mineral surfaces (see the review in Davis and Hayes 1986).

Table 4. Extraction sequence used in this study. The procedures are based on studies cited in the text and on the reviews presented in Chao (1984) and Pickering (1986).

Target phase	Reagent	Extraction conditions
adsorbed	strong electrolyte solutions ($CaCl_2$); no pH adjustment, generally around 6	argon atmosphere, carbonate-free reagents, short equilibration time (minutes), pH adjustment
	synthetic groundwater labelled with tracer U	argon atmosphere, equilibrium pH of the extraction
specifically sorbed	ammonium acetate (mixed with 0.02 M EDTA) buffered with acetic acid to pH 4.8 (hereafter NH_4OAc)	determined by the reagent; with calcites pH exceeds 5.0 when more than 100 mg/10 mL of calcite is used; slow dissolution rate; can be accelerated in ultrasonic bath
associated with fracture calcite ($CaCO_3$)		
coprecipitated with hydrous Fe-oxides	Tamm´s oxalate: sodium oxalate-oxalic acid solution, pH 3.5	determined by the reagent; extraction for 2 h in dark
labile U (sum of previous phases)	*aqua regia* (HNO_3+HCl)	slow boiling
incorporated in silicate residue	$HF+HNO_3+HCl$	slow boiling

3.3   Determination of radioactive disequilibrium state

The following procedure was applied for the determination of radioactive disequilibrium state: The sample solutions obtained after the extractions were evaporated to dryness. Organic matter of the reagents was wet-oxidised in hot concentrated nitric acid and the residue, after dissolving in 9 M HCl, was loaded into an ion chromatographic column for the separation and purification of the radionuclide fractions (Fig. 7).

Fracture coating samples (mainly $CaCO_3$) were dissolved in cooled 1 M HCl (~ 7 ^{o}C) in an injection tube to obtain the fastest possible dissolution and minimum possible interference from mineral impurities in the calcite. Dissolution of calcite was followed by the developing CO_2 bubbles. The resulting sample solution was pressed through the 0.45 μm membrane filter and the filtrate was evaporated and dissolved in

9 M HCl. The quality control of the analytical procedure was carried out by regular analyses of certified reference rock samples (see Appendix).

3.4   Determination of U oxidation states

U oxidation states in solid phases were determined by using a method described in Ervanne and Suksi (1996). In this method sample material is leached with a mixture of 4.5 M HCl and 0.03 M HF under anaerobic conditions in an inert gas flow. The solution obtained is passed through an ion-exchange column regenerated with the leaching mixture. The U(VI) fraction is sorbed while U(IV) is eluted through the column. The sorbed U(VI) is eluted with 0.1 M HCl. The concentrations were determined by α-spectrometry. Information on U oxidation states was needed in studying the penetration of oxic conditions into the rock (see section 4.3).

3.5   Dating of U migration events

Successive U accumulation and removal events govern U transport in groundwater–rock systems. Information on their time-scales is derived by measuring the ^{230}Th/^{234}U activity ratio (*see* Thiel *et al.* 1983). The basic assumption is that U accumulation is rapid (*i.e.* within a time period much shorter than the half-life of ^{230}Th) and the system is closed and no U mass exchange occurs after the accumulation. During the accumulation ^{230}Th grows in as a function of time. Thus the only mechanism that changes the relative activities of U and its daughter ^{230}Th is radioactive decay. The age calculation is based on the measured ^{230}Th/^{234}U and ^{234}U/^{238}U activity ratios according to the following equation:

$$^{234}Th/^{234}U = \frac{1-e^{-\lambda_{230}t}}{^{234}U/^{238}U} + \left[1 - \frac{1}{^{234}U/^{238}U}\right] \times \frac{\lambda_{230}}{\lambda_{230}-\lambda_{234}} \times \left[1-e^{-(\lambda_{230}-\lambda_{234})t}\right] \qquad (2)$$

The derivation of equation (2) and the computer program for the age determination are given in Ivanovich and Harmon (1982a;b). The computer program was slightly modified for the needs of the present study.
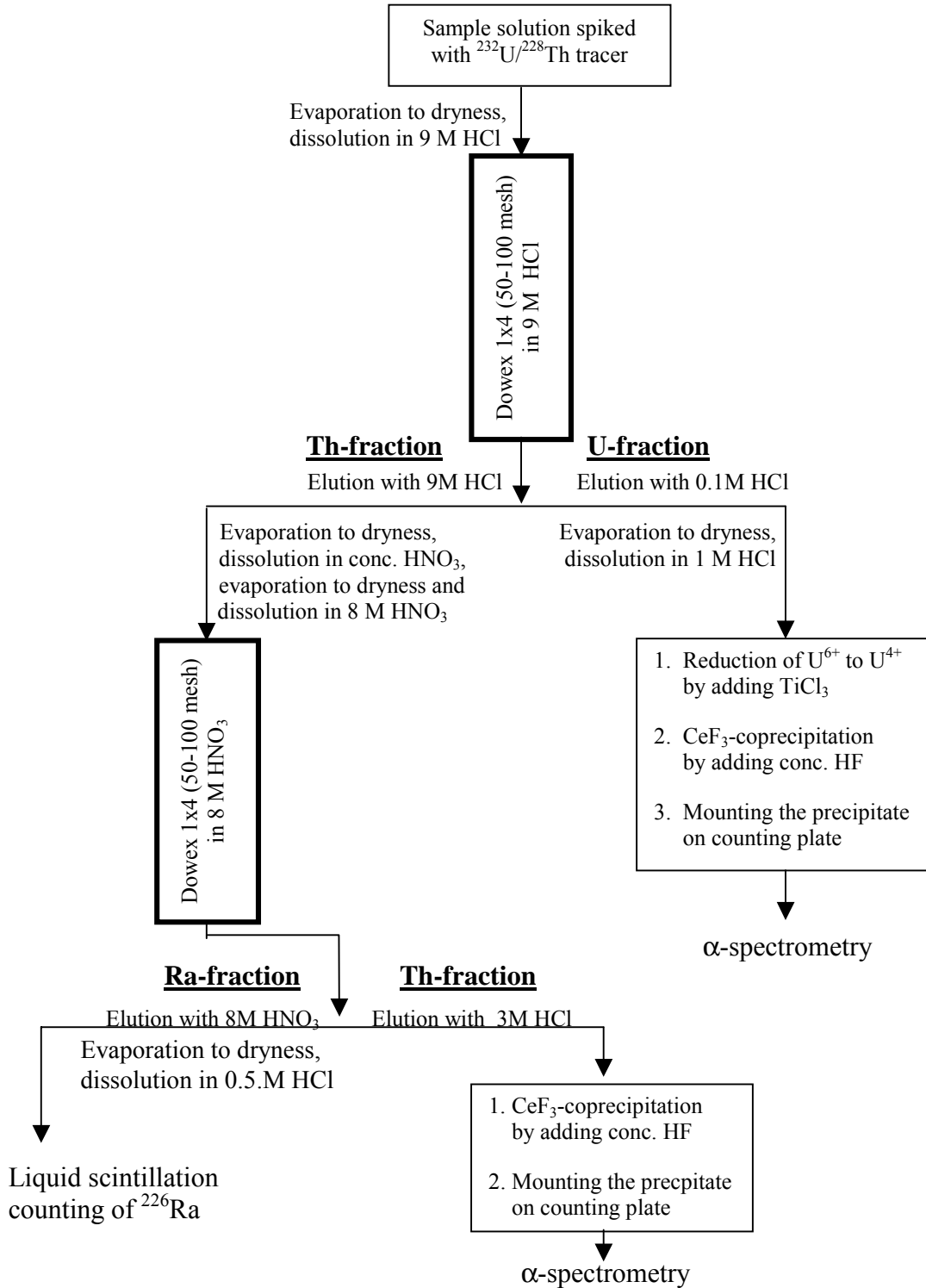
Sample solution spiked
with ^{232}U/^{228}Th tracer

Evaporation to dryness,
dissolution in 9 M HCl

Dowex 1x4 (50-100 mesh)
in 9 M HCl

Th-fraction

Elution with 9M HCl

U-fraction

Elution with 0.1M HCl

Evaporation to dryness,
dissolution in conc. HNO$_3$,
evaporation to dryness and
dissolution in 8 M HNO$_3$

Evaporation to dryness,
dissolution in 1 M HCl

Dowex 1x4 (50-100 mesh)
in 8 M HNO$_3$

1. Reduction of U^{6+} to U^{4+}
   by adding TiCl$_3$

2. CeF$_3$-coprecipitation
   by adding conc. HF

3. Mounting the precipitate
   on counting plate

α-spectrometry

Ra-fraction

Elution with 8M HNO$_3$

Th-fraction

Elution with 3M HCl

Evaporation to dryness,
dissolution in 0.5.M HCl

1. CeF$_3$-coprecipitation
   by adding conc. HF

2. Mounting the precpitate
   on counting plate

Liquid scintillation
counting of ^{226}Ra

α-spectrometry

Fig. 7. Sequential analysis of U-series nuclides. A ^{232}U/^{228}Th spike in transient equilibrium is used as yield tracer.

An example of age determination in a closed system is given in Fig. 8. The example demonstrates the evolution of the ^{234}U/^{238}U and ^{230}Th/^{234}U activity ratios. This approach was applied to secondary U minerals (section 4.4) and accumulations found on fracture surfaces (section 4.6).

In the case of U removal, time information was derived using the ^{230}Th/^{234}U activity ratio as such (sections 4.3, 4.6 and 5.2). As a rule of thumb the higher the measured ^{230}Th/^{234}U activity ratio the more recent has been the U removal. For a more precise dating of U removal, the U removal rate needs to be known.

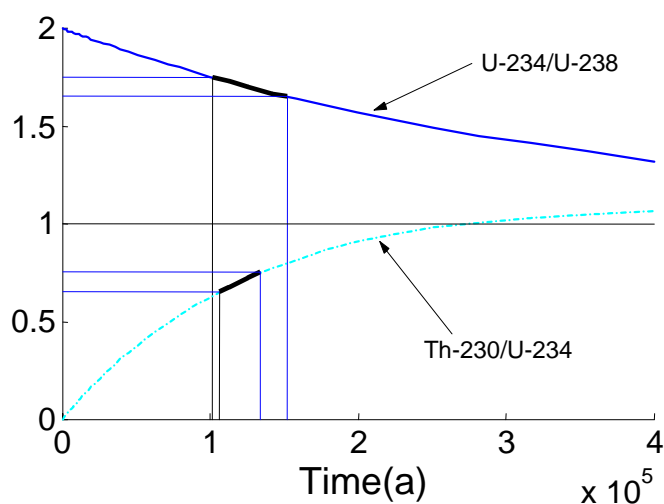**Fig. 8.** A hypothetical example of ^{234}U/^{238}U and ^{230}Th/^{234}U activity ratio evolutions in a closed system. The measured activity ratios ^{234}U/^{238}U and ^{230}Th/^{234}U with error envelopes are marked on the vertical axis, from which their projections are drawn in the time axis via simulated activity ratio evolution curves. The smaller the analytical error of the measured activity ratio the more accurate the dating and, consequently, the more accurately can adjacent events be identified (cf. Table 2). With use of α-spectrometry the counting error of the ^{230}Th/^{234}U activity ratio is normally about 5% (4−10% in this study), which gives a good enough accuracy for dating purposes in the age range between 10,000 and 200,000 years. (Note: This time range covers the most significant climatic changes that occurred at Finnish latitudes in the Quaternary period; see *e.g.* Eronen and Olander 1990).

4 DISCUSSION OF RESULTS

To obtain a good grasp of the meaning of this study it is advantageous to examine the results as a demonstration of deriving information from processes occurring in complex natural systems. This demonstration is made by first considering experiences with selective extraction studies and the important findings obtained from them. Evidence for processes and mechanisms considered important to recent U transport is then presented and discussed. Linkage between U behaviour and geochemical processes is discussed in terms of U-series disequilibria, which are used to determine the evolution of the geochemical conditions. Because the interpretations are mainly based on the U-series disequilibrium data, a detailed examination is made of this data.

4.1 Sampling and selective extractions

Sampling, and particularly subsampling formed an important part of the study. Subsampling was carried out by both mechanical and chemical means (see Fig. 5). The chemical subsampling was guided by the pre-extractions, though this was not always possible because of the small amount of sample (*e.g.* thin fracture surface coatings). Table 8 summarises the results and experiences obtained in applying selective extractions (**publications I, II, IV and V)** and shows the potential of the selective extraction approach for U transport studies. For more comprehensive conclusions, however, more versatile and systematic investigations than could be carried out during this study are needed.

4.2 Sorption of U

The behaviour of U under oxidising conditions is dominated by the sorption of uranyl species on minerals. Adsorption on the surface of oxyhydroxides and clays, coprecipitation with iron oxyhydroxides and surface precipitation have been identified as retardation processes for U(VI) (*see the review in* Del Nero *et al.* 1999). In this study, information on the *in situ* sorption of U(VI) was sought by using selective extractions and laboratory simulation studies.

Evidence of geologically recent U mobilisation/immobilisation (in the U-series disequilibrium time scales) was found on fracture surfaces. This provided an opportunity to study U fixation under conditions that may appear in the next 200,000 years. **Publication I** reports a study of U fixation where the binding strength of U was examined by sequentially extracting U from fracture coating material. Conclusions about the U fixation were drawn from the obtained distribution patterns (Fig. 9).
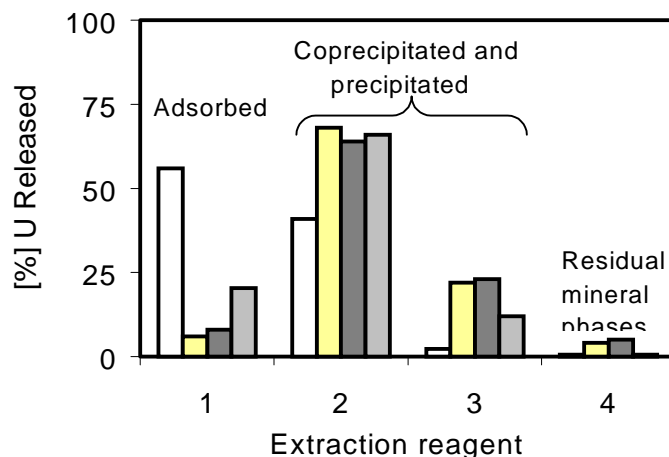

Fig. 9. Distribution of U in four (bars) fracture coatings (modified from **publication I**). Information on adsorbed U is based on the 0.5 M CsCl extraction (1). Information on more tightly fixed mobile U (coprecipitation/precipitation) is obtained by extraction with NH_4OAc (2) and Tamm's oxalate (3). Information of U incorporated in rock forming minerals (and in accessory minerals) and additional information of overlying U-rich phases can be obtained by dissolving residual minerals (4) (cf. Tables 4 and 8).

Strong electrolyte solution desorbed U to a significant extent, suggesting the presence of adsorbed U. In the following extraction with the ammonium acetate buffer solution, bulk U was released, indicating incorporation in phases (co)precipitated. The U-series disequilibrium information implicit in the separated phases supported the view that there was more than one discrete U phase. Similar distribution patterns were obtained in other studies by Crespo *et al.* (1996) in their study of granitic fracture infillings in the El Berrocal natural analogue study site in Spain.

Table 8. Summary of the results in selective extraction studies collected from **publications I, II, IV and V**.

Target U in rock samples	Chemical reagent	Extraction conditions	Effects of extraction	Comments and suggestions
adsorbed	synthetic or real groundwater labelled with a tracer	defined by the reagent	sorption equilibrium of desorbed natural U and added tracer is established	potential in "monitoring" uranium migration routes with the help of $^{234}U/^{238}U$; an *in situ* K_d approach [*)]; quantification of adsorbed U with the help of laboratory simulations
	I M $CaCl_2$ prepared in synthetic or real groundwater; no pH adjustment	defined by the reagent	replaces U species fixed by electrostatic forces	
specifically sorbed	1 M ammonium acetate buffered with acetic acid to pH 4.8; 0.02 M EDTA	defined by the reagent; short extraction time (~ 30 seconds)	completes $CaCl_2$ extraction result	"cleans" sorption sites
associated with fracture calcite ($CaCO_3$)		pH exceeds 5.0 when more than 100 mg/10 mL of calcite is used; slow dissolution rate; can be accelerated with ultrasonic bath	releases U-series nuclides without fractionation; stable complexes with U and Th; dissolves U(VI) minerals	can be replaced by careful extraction with mild mineral acids; calcite dating; also applicable to Ra and Pa
coprecipitated with hydrous iron oxides	oxalate–oxalic acid solution, pH 3.5 (Tamm´s oxalate)	determined by the reagent; extraction for 2 h in dark	dissolves selectively hydrous Fe-oxides; stable complexes with U and Th	also applicable to Ra and Pa
all previous target phases; labile U	*aqua regia* (HNO_3+HCl)	slow boiling	dissolves loosely bound mineral phases	information on annealing of recoil tracks (see below)
incorporated in silicate residue	HF+HNO_3+HCl	slow boiling	dissolves most mineral phases	"recoil detector": information on deposition time of overlying U phases (for details see ch. 4.6)

[*)]*In situ* K_d of U is defined as the ratio of U extracted with $CaCl_2$ and U in the corresponding groundwater. Technically the definition is similar to the standard K_d (see page 8).

4.2.1 Reversibility of U sorption

Reversible uptake of dissolved species on mineral surfaces may take place through ion exchange, physical adsorption and specific adsorption. The U distribution pattern in Fig. 9 shows a fraction of U compatible with adsorption. A similar fraction of U was obtained from a rock material sampled from a U-rich (~ 600 ppm) alteration zone close to a water-conducting fracture (**publication IV**): extraction with 1 M $CaCl_2$ removed over half (56%) of the total U from this sample material, indicating substantial adsorption of U (in the sense of the extraction concept). This fraction was further studied by desorbing it as a function of time. The results showed that the U release was quick: the releasing U reached a steady state within one minute, suggesting a surface reaction (see Fig. 1 in **publication IV**). The substantial adsorption deduced for this material may partly be due to the clay in the sample (kaolinite and illite).

Adsorbed U was also studied in a more systematic manner by a uranium isotope exchange technique (**publication VII**). A tracer (^{236}U) was used as a reference for fast fixation, which defines adsorption. The experimental approach used essentially puts together three partly different but interlinked elements: the *in situ* accumulation, the selective extraction, and the batch experiment routinely used for laboratory K_d. Because the dissolved natural U and the added tracer behaved similarly in the batch experiment, the proportion of natural U taking part in the adsorption/desorption process could be estimated.

After equilibration the adsorbed U was extracted as a function of time. No marked difference in the release rates was observed at the beginning of the extraction, indicating identical desorption for U isotopes. With time, however, the relative release of natural U increased, suggesting a different release mechanism for natural U, possibly its dissolution from a U sink. Noteworthy in this experiment was the abrupt change in redox conditions, during the equilibration (from + 140 mV to -100 mV) and related marked increase of the $^{234}U/^{238}U$ activity ratio in the equilibration solution (see Fig. 5 in **publication VII**). This may be explained by the change from oxic to anoxic conditions where the preferential ^{234}U release continued owing to its more soluble 6+ valence state (see sections 2.4 and 4.5). Noteworthy, too, is that the ^{236}U tracer could not be desorbed in this experiment: the amount desorbed varied from 25% to 60%, indicating much stronger fixation than adsorption (Suksi and Rasilainen 1997).

Information about the *in situ* adsorption of U was also sought by directly studying fracture surfaces (Blomqvist *et al.* 2000). The reasoning here is that if U sorbed from groundwater was present, then the ^{234}U/^{238}U activity ratio of the fraction should match that of the groundwater. Fracture surfaces were extracted by dipping them into the 1 M CaCl$_2$ extraction solution (*see* Fig. 5). The amount of extracted U was normalised to the fracture surface dipped (Table 5).

Table 5. Adsorbed U and the ^{234}U/^{238}U activity ratios on fracture surfaces and in corresponding groundwater. A possible match was obtained in sample R384.

Drill hole	Depth (m)	U$_{(min)}$ adsorbed (μg/ m^2)	U-234/U-238	U-234/U-238 in groundwater
R384	34.28	920	1.15 ± 0.10	1.12 – 1.36
R302	91.95	210	3.4 ± 0.3	1.93 – 2.18
R373	48.28	47	1.36 ± 0.22	-

4.2.2 Behaviour of U with ferric minerals

Ferric compounds are known to be effective geochemical sinks for U (see *e.g.* Hsi and Langmuir 1985; Payne and Waite 1991; Payne *et al.* 1994; Bruno *et al.* 1995). In the near-surface environment they are commonly found as thin precipitations on fracture surfaces. The behaviour of U with ferric compounds was investigated in two ways: by examining naturally occurring U-bearing iron phases (in **publication II**) and carrying out laboratory experiments where Fe-U systems were simulated with synthetic ferric minerals (Table 6) (Paananen *et al.* 1997). U-bearing rock was studied as a function of distance from the fracture. The loosely bound fractions varied from 1000 ppm to 2000 ppm for Fe and from 70 ppm to 300 ppm for U.

The geochemical association was studied by sequential extraction with 1 M NH$_4$OAc and Tamm's oxalate. The extraction with NH$_4$OAc released 61−76% of U and only 25−45% of Fe, indicating that U can be released without dissolving of Fe. The U/Fe ratio vs. distance from the fracture was closely similar in the two extracted phases, allowing the conclusion that the extractants dissolved the same iron phase that sorbed U (Fig. 10).
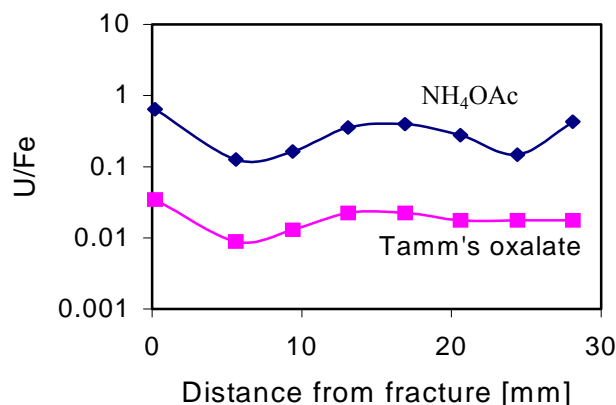
Fig. 10. Distribution of loosely bound U and Fe as a function of distance from a fracture (redrawn from Suksi *et al.* 1992). The major part of U was released in the NH$_4$OAc extraction (cf. Tables 4 and 8).

U was introduced onto ferrihydrite and lepidocrocite during their synthesis mimicking natural mineral formation, and ^{236}U tracer, after the synthesis in the K$_d$ batch experiment equilibrating minerals with synthetic granite groundwater. After U was introduced it was extracted as presented in Figs. 11 and 12.

Ferrihydrite is the poorly ordered Fe(III)oxide in young precipitates formed upon rapid oxidation of Fe(II)-bearing groundwaters (Carlson and Schwertmann 1981; Schwertmann *et al.* 1984). Lepidocrocite is precipitated under the same conditions but in lower Si concentration. The more crystalline lepidocrocite was used as reference for ferrihydrite.

Table 6. Synthesis of U-bearing ferric minerals lepidocrocite and ferrihydrite. Uranium (^{238}U) was added as U(VI) form.

	Precipitation I		Precipitation II	
	C (initial)	C (final)	C (initial)	C (final)
Ca	30 mg/l	31 mg/l	41 mg/l	43 mg/l
Fe	~ 27 mg/l[1]	0.003 mg/l	~ 27 mg/l[1]	bdl[2]
Si	0.5 mg/l	~0.5 mg/l	4.9 mg/l	4 mg/l
U	~ 90 µg/l[1]	44 µg/l	~ 110 µg/l[1]	64 µg/l
pH	5.6[3]	7.72	5.2[3]	8.09
Product	Lepidocrocite (γ-form)[4]		Ferrihydrite[4]	
Mass	3.9 g of dried mineral		4.1 g of dried mineral	
Surface area[5]	84 m^2/g		170 m^2/g	
U[6]	1092 ppm		1450 ppm	
Partition of U	40 · 10^6 ml/g		44 · 10^6 ml/g	

[1] Estimated from the added amount, [2] Below the detection limit, [3] After addition of CO$_2$
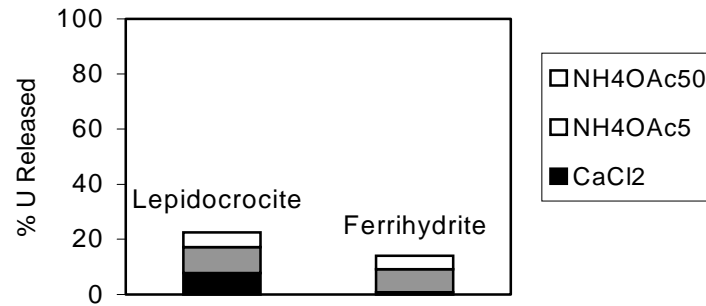[4] Determined by XRD, [5] Determined by BET, [6] Determined by α-spectrometry

Fig. 11. Extraction of U from lepidocrocite and ferrihydrite using $CaCl_2$ (20 min) and NH_4OAc (5 and 50 min). More U was released from crystalline lepidocrocite.
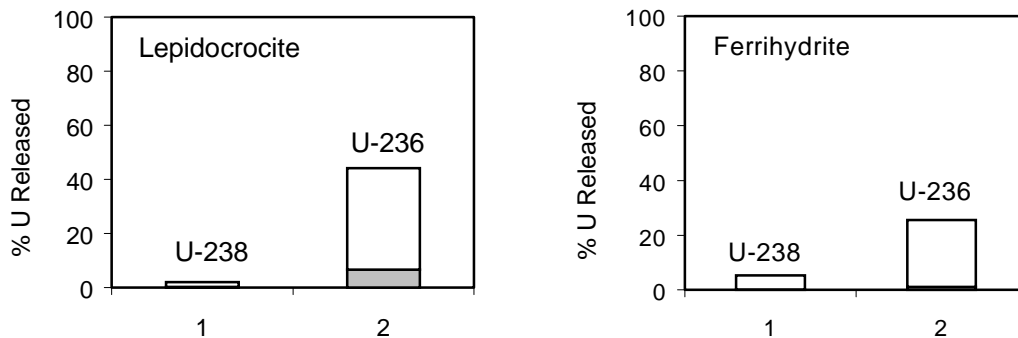

Fig. 12. Release of U (natural ^{238}U and tracer ^{236}U) from lepidocrocite and ferrihydrite under contact with synthetic groundwater for 4 days (dark bar) and by subsequent extraction with $CaCl_2$ for 20 minutes (white bar). More U was released from lepidocrocite.

An interesting result was that only a fraction of U was desorbed, indicating much stronger fixation mechanism than pure adsorption. Furthermore, the extractions showed that fixation in synthetic minerals appears stronger than in naturally occurring Fe phases.

4.3 Rock matrix diffusion

Rock matrix diffusion, occurring along the network of interconnected pores, is considered an important radionuclide retardation mechanism (Neretnieks 1980). The retardation occurs through physical dilution and through the increase in reactive surface area provided by the network of rock pores. The *in situ* conductive rock porosity has been demonstrated on numerous occasions with the help of U-series disequilibrium measurements (*e.g.* Smellie *et al.* 1986; Alexander *et al.* 1990; Heath 1995; Mazurek *et al.* 1996 and this study). Attempts have been also made to simulate measured U-series profiles mathematically, using the matrix diffusion theory, but success has been mixed (see Rasilainen 1997 and references therein).

The diffusion through water-filled rock pores can be exploited in the study of past groundwater flow. The changes occurred during the continuos long-term fracture flow, if they last long enough and are chemically active, may induce changes in the rock matrix further away from the fracture. Because matrix diffusion is a slow process, the responses may be preserved long after conditions have changed in the flowing groundwater. Several drill core samples were investigated for their U-series profiles to observe these responses (**publications II, III and VIII**).

Figure 13 shows two examples. One sample was taken from the oxidising near-surface conditions (R384) and the other from deeper in the bedrock (R357). In the near-surface sample (upper figure pair) the profiles indicates recent U leaching (Th-230/U-234>1). In the deeper sample more stable flow conditions may be inferred from the Th-230/U-234 ratio ($\approx$ 1) and from the U-234/U-238 ratios, indicating preferential ^{234}U release.

The considerable distance over which the radioactive disequilibria were measured clearly indicates the presence of a conductive pore network, which is one prerequisite for matrix diffusion. The observation of diffusion depth is limited to only a time period of one million years, which needed to equilibrate the ^{234}U/^{238}U activity ratio. Any diffusion of U that occurred earlier than one million years ago cannot be observed with the U-series technique.

The susceptibility of U to groundwater in drill core sample R384 was studied by equilibrating the ground rock with R384 groundwater. The equilibration released from 22% to over 60% of the total U, indicating the presence of labile U (Fig. 14). The smaller amount of labile U released close to the fracture is explained by the natural groundwater leaching.
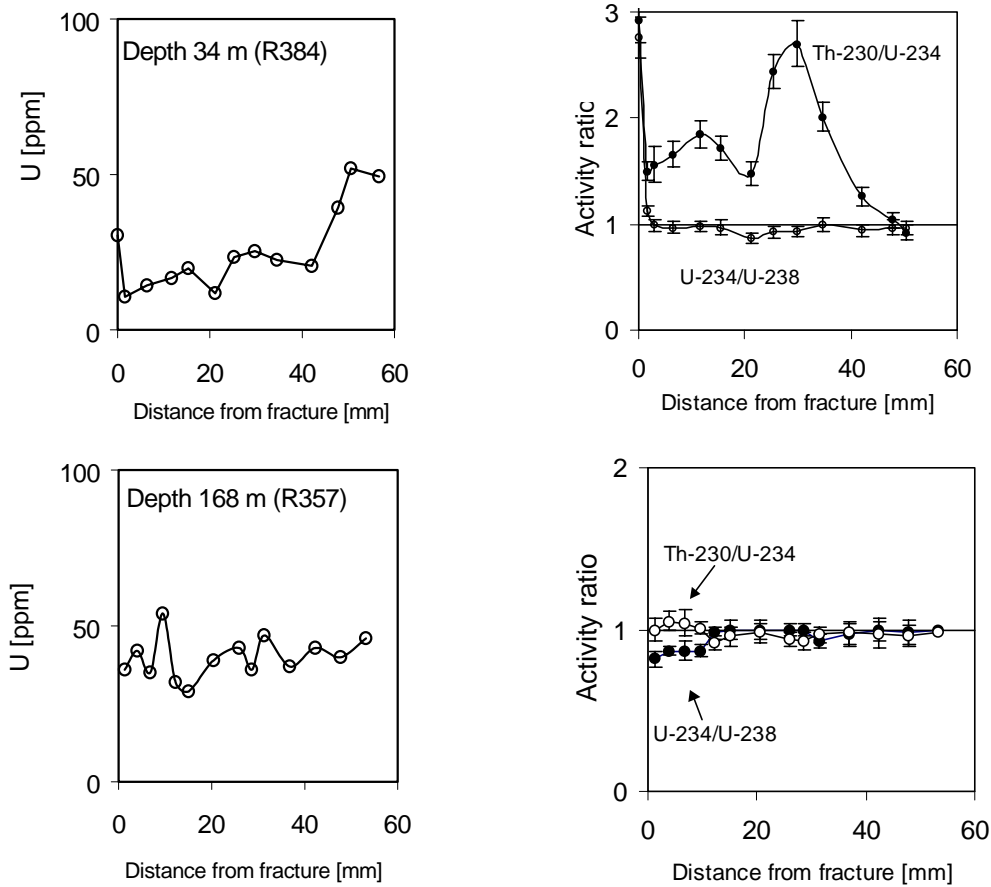
Fig. 13. U-series profiles in drill core samples measured as a function of distance from the water-conducting fracture. Past hydrological activity is reflected in sample R384 as large ^{230}Th/^{234}U disequilibria. Formation of such large disequilibria is facilitated by the geologically very recent perturbation and labile U in this sample (22–64%, see Fig. 14). In sample R357 collected from much deeper bedrock only a slight disequilibrium is observed, reflecting physically and chemically more steady conditions.
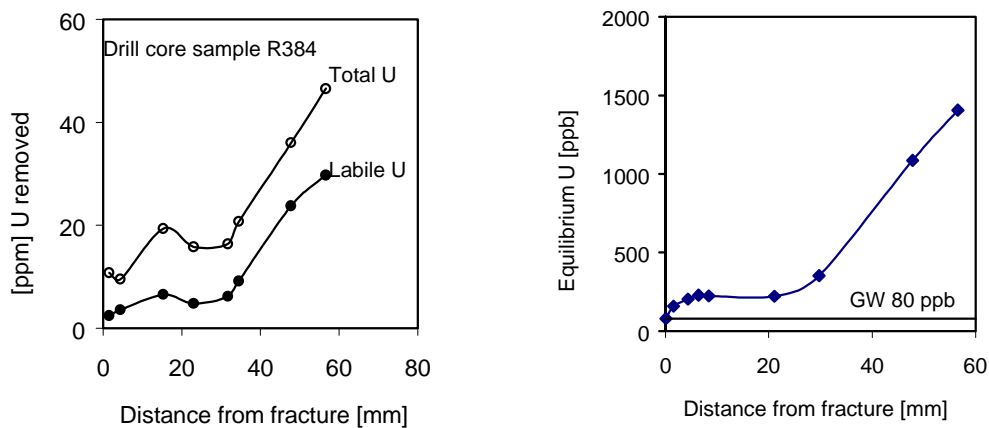

Fig. 14. Left: Labile U vs. total U as a function of distance from the fracture surface. The total U was obtained by dissolving the rock in a mixture of strong mineral acids (HF+HCl+HNO$_3$). Right: U concentration in the liquid phase after two hours equilibration. Original U concentration in the groundwater was 80 ppb.

4.4 Secondary U minerals as geochemical barriers

The assemblage of corrosion products that will form during the corrosion of spent UO_2 fuel is likely to be as complex as the mineral assemblages found in natural uranium deposit under similar conditions. **Publication VI** examined radioactive disequilibria in secondary U minerals to obtain information on their formation and alteration. U-series disequilibria were determined on hand-separated mineral crystals.

The $^{230}Th/^{234}U$ activity ratios of all samples were at or below unity, indicating U accumulation. The ages measured varied from 98 ky to beyond the limit of the method, indicating that the minerals were long-term sinks for uranium in solution and have not experienced significant U leaching since their formation (Finch *et al.* 1995).

Exceptionally young U formation was observed in a boulder sample found at the Hämeenlinna study site (**publications III and IV**). The U compound found (later identified as uranophane) was distributed in rock pores. According to the U-series data, most of this material has been added into the rock very recently, not earlier than some 10,000 years ago ($^{230}Th/^{234}U \sim 0.1$).

This and the above findings demonstrate that U transport in oxidising conditions is controlled by the formation of secondary U minerals. Similar findings have been reported at the Hyrkkölä study site near Palmottu (Marcos *et al.* 2000).

4.5 Role of α-recoil

Publication V examined the enrichment of ^{234}U and ^{230}Th in mineral fragments embedded as impurities in U-bearing calcites on fracture surfaces. The enrichment was interpreted as the result of α-recoil. Theoretically, the enrichment depends on the exposure time and effective recoil flux, thus offering an interesting possibility for dating applications. The U-bearing phase (recoil source) was separated from the sample material by selective dissolution. The remaining mineral material (target phase) consisting of fragments of major rock forming minerals and clay was totally dissolved.

The presence of ^{234}U and ^{230}Th in excess (*i.e.* $^{234}U/^{238}U$ and $^{230}Th/^{234}U \gg 1$) in this material, even after the dissolution of the U-bearing phase (*i.e.* dissolution did not seriously affect the enrichment), indicates annealing of the recoil tracks, which has blocked the nuclides.
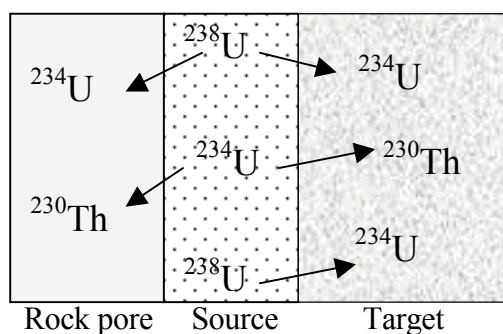
Fig. 15. Conceptual model for [234]U and [230]Th recoil enrichment (redrawn from Suksi and Rasilainen 1996). The arrows indicate net recoil fluxes across phase boundaries. The U-rich layer (recoil source) causes [234]U and [230]Th enrichment in the U-poor mineral phase (target).

The dating potential was considered by postulating a steady state and then it was asked whether the model fits the measured values (see Fig. 2 in **publication V**). An agreement with measurements was obtained with some samples, indicating that the postulated steady state is possible. The greatest uncertainty with respect to dating applications was associated with the effective recoil flux, which is determined by the thickness of the U source. Here, the thickness was assumed to be in the recoil range, *i.e.* ~ 20 nm.

4.5.1 Linkage between [234]U deficit and redox conditions

[234]U deficits within the rock matrix in most cases have been attributed to redox fronts (Osmond and Cowart 1983; MacKenzie *et al.* 1992; Mohamad *et al.* 1992; Mazurek *et al.* 1996). Another explanation is direct recoil across phase boundaries (see Griffault *et al.* 1993). **Publication IX** examined the dependence of [234]U deficit on redox conditions. The samples were systematically taken from oxic conditions close to the ground surface (R389 and R384) towards anoxic conditions (R302) (Fig. 16). Drill core samples were taken so as to extend across the redox front in the rock matrix in a direction perpendicular to the groundwater flow.
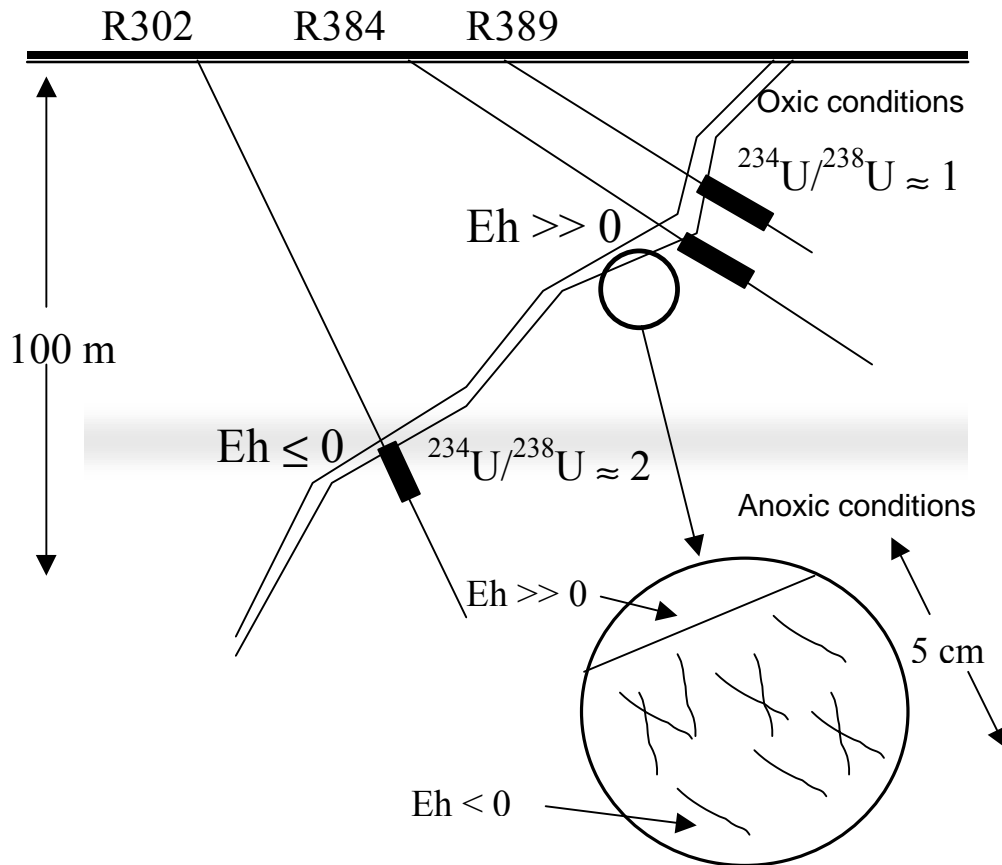
Fig. 16. Sampling of drill cores (black bars) across a redox front (see magnification) and fracture surfaces in anoxic conditions (lowest bar). The $^{234}U/^{238}U$ activity ratios in groundwater around sampling locations are indicated (modified from Blomqvist *et al.* 2000).

Several fracture coating samples from anoxic conditions were studied (Table 7). Exceptionally low $^{234}U/^{238}U$ activity ratios were observed, indicating considerable preferential ^{234}U release from these samples.

Table 7. Uranium data of fracture surface samples collected from anoxic conditions (R302). The first three samples represent tiny calcite crystals (0.5−24 mg) removed from the fracture surface with a steel needle and they were analysed by TIMS (Casanova 1999). The fourth sample is clayey material (33 mg) gently scraped from the uncovered section of the fracture surface and analysed by α-spectrometry.

Samples	U [ppm]	$^{234}U/^{238}U$
91-94E	44.0 ± 0.3	0.295 ± 0.014
91-94G	707 ± 3	0.256 ± 0.003
91-94P	139 ± 1	0.359 ± 0.003
MDS302	171 ± 10	0.25 ± 0.02

Penetration of oxic conditions into the rock was estimated with the help of studies on U oxidation states (Fig. 17). In samples R389 and R302 U(IV) approaches 100% at distances greater than 50 mm from the fracture. In sample R384 the U(IV) fraction remains practically constant and, lower than in the other samples, indicating deeper penetration of oxic conditions in this sample. Furthermore, the $^{234}U/^{238}U$ activity ratio remains about unity, indicating that the two isotopes were equally removed during U leaching and again the effects of oxic conditions.
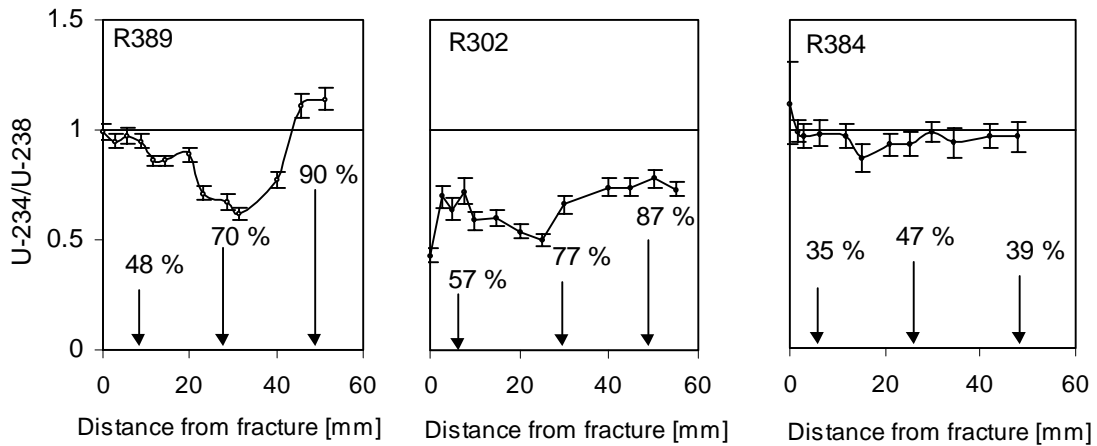

Fig. 17. Variation of the $^{234}U/^{238}U$ activity ratio and the percentage of U(IV) in the total U inventory as a function of distance from the fracture face. Percentages with the arrows below the curves indicate actual sampling points in the distance axis.

How the ^{234}U deficit can be shown to depend on the redox conditions? It appears that the creation of ^{234}U deficit within the rock matrix requires not only α-recoil but also a valence "contrast" between the U isotopes. It can easily be shown that the ^{234}U deficit induced by direct α-recoil is unlikely to be observed. It might be argued that even if direct α-recoil does not cause the deficit, recoil induced mineral lattice destruction and bond breakage could play a role (cf. section 2.4). However, since α-decays take place all over the rock matrix, if this process was dominating, one would expect to see the effect of the induced "looseness" uniformly in all places under the influence of water-rock interaction. Because such a uniform deficit is not seen, recoil displacement alone cannot be sufficient to cause the ^{234}U deficit. To obtain notable fractionation due to valence contrast requires that U first existed in the 4+ valence state and a time period long enough for the ingrowing ^{234}U inventory to replace the decayed original $^{234}U(IV)$ inventory. After an ingrowth period of about

one million years, the original $^{234}U(IV)$ atoms are replaced by ingrown $^{234}U(VI)$ atoms, while the original ^{238}U inventory remains in-the reduced U(IV) form.

On the basis of the drill core observations at Palmottu, the following conceptual model for the ^{234}U deficit was put forward (Fig. 18). After more than one million years since the formation of a U(IV) inventory, a substantial part of the ingrown ^{234}U is in valence state 6+ and is therefore preferentially released in anoxic conditions. The working hypothesis for ^{234}U release by groundwater assumes that when water diffuses from flowing water towards deeper rock matrix its U dissolution power decreases with the decreased dissolved oxygen fugacity. Preferential dissolution of ^{234}U takes place at the redox front, leading to marked fractionation of U isotopes.

Bedrock   Fracture   Bedrock

$^{234}U/^{238}U \approx 1$ $^{234}U/^{238}U < 1$ $^{234}U/^{238}U > 1$

Oxic groundwater

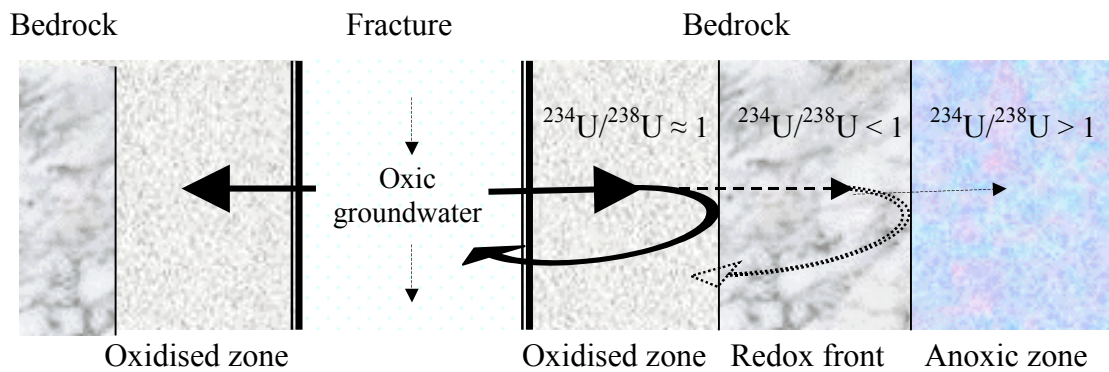Oxidised zone   Oxidised zone   Redox front   Anoxic zone

Fig. 18. A model for U isotope fractionation when oxic conditions penetrate the rock (redrawn from Suksi and Rasilainen 2001). The bold curved arrow indicates congruent U release (U isotopes are equally dissolved) and the dotted curved arrow preferential ^{234}U release. Oxic groundwater diffuses into the rock matrix and U(IV) close to the fracture is oxidised, leading to a congruent dissolution of U isotopes. Conditions at the redox front are no longer oxic enough to dissolve original U(IV), and ^{234}U because of its more soluble 6+ valence state is dissolved instead, establishing ^{234}U excess in pore water and deficiency in the rock. Deeper in the rock, dissolved oxygen has been exhausted and conditions that are more reducing prevail, possibly inducing precipitation of ^{234}U.

4.6   Uranium behaviour in past flow systems

A large number of fracture coatings, mainly calcites (and four uranophane samples), were studied for U-series disequilibria to see whether they might reflect changes in past flow systems (**publication VIII**). Uranium concentrations were much higher than in the rock matrix beneath, indicating that U had been transported by and accumulated from the groundwater. The general direction of the U mass transport in the accumulations was examined with a Thiel diagram (Thiel *et al.* 1983) (Fig. 19).
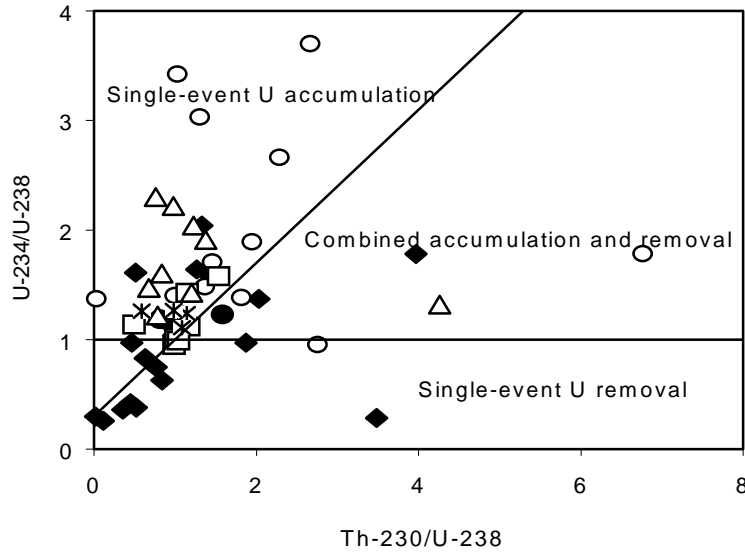
Fig. 19. U-series activity ratios of fracture coating samples taken from the Palmottu study site, plotted according to Thiel *et al.* (1983) (redrawn from Suksi *et al.* 2000). Analytical results have been presented in **publication VIII**. Samples plotted in the upper left sector were studied for the accumulation ages (Fig. 20).

Most samples displayed a net U accumulation. The fact that a clear accumulation signature was preserved most probably means that the respective fractures had sealed, or they otherwise had lower transmissivity, so that they were largely hydraulically isolated from the present groundwater flow. Only four of the samples displayed radioactive equilibrium, indicating that the fractures had been sealed or totally isolated for more than one million years. More complex behaviour (where, however, U removal appears to dominate) was seen in some fractures, indicating their higher transmissivity.

The ages of the U accumulations were calculated from the ^{230}Th/^{234}U activity ratio (see section 3.5) and compiled in a frequency plot (Fig. 20). Most accumulations were dated within a time period of 110 ka before present. Three young clusters were evident at around 110 ka (10 samples), 60 ka (5 samples) and 40 ka (3 samples). Because of the large error bars in the ^{230}Th/^{234}U activity ratios the older clusters are less well defined.

Interestingly, even though these ages may represent previous glaciation–deglaciation events, none seems to be related to the termination of the latest deglaciation, about 10,000 years ago (Eronen and Olander 1990). One explanation for this could be that the sampling represents more than one U accumulation event, providing a weighted average. Thus, the ages obtained provide

an upper limit for the accumulations. In spite of the uncertainties in absolute dating, a clear demonstration of periodic U accumulation was obtained, indicating fluctuations in the past groundwater flow.
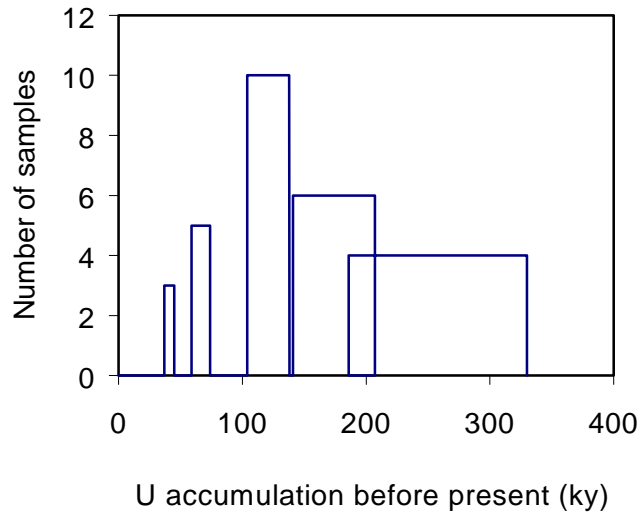

Fig. 20. Distribution of closed system model ages of U accumulations found on fracture surfaces (redrawn from Suksi *et al.* 2000). Accumulation of U in these samples is indicated in Fig. 19. The age bars between 100 ky and 220 ky include uranophane samples.

5   CONCLUSIONS

5.1   General remarks

Accepted knowledge of the immobility of Th and the mobility of U in groundwater conditions provided the necessary basis for coupling U-series disequilibria temporally and spatially with U transport. Important additional aid to the interpretation was provided by the redox sensitivity of U, which could be used to link the observed U isotopic fractionation with geochemical changes.

Geologically recent U transport could be clearly shown. The transport was indicated at mechanism level (sorption and α-recoil induced processes) as well as in a much larger scale as U accumulations in and removal from the fracture network. The fact that the recent U transport generally could be observed so clearly is mainly due to the substantial amount of labile U in the rock matrix. Labile U can serve as a valuable tracer of radionuclide migration, and also as an indicator of the possible impacts of processes (*e.g.* glaciation–deglaciation processes) that might occur in the geochemical evolution under future climatic changes.

Systematic and careful sampling, together with concurrent hydrogeological, hydrogeochemical, and other isotope geochemical studies, provided by the Palmottu project (see Blomqvist *et al.* 1998 and 2000), were indispensable to the overall interpretation of the U-series disequilibria.

5.2   The importance of U-series disequilibrium findings

Deviation of the decay chains from radioactive equilibrium occurs as a consequence of geochemical processes. For decades this linkage has been utilised in the solution of various geological dating problems, confirming that the assumptions, which are inevitable in radiometric dating, rest on a sound basis (Ivanovich 1994 and references therein). The numerous successful geological dating studies presented in the literature additionally indicate that U-series elements have behaved as they are expected to behave. In the present study this was established as a consistency of U-series disequilibrium data with other independent experimental data. The consistency of the U-series data was, in fact, the key factor in overall interpretation, and is critical

information in evaluating the long-term stability of deep underground nuclear waste repositories.

The different influence of the water–rock interaction on U behaviour under oxic and anoxic conditions was demonstrated. In oxic conditions, U removal from the rock matrix to fractures was seen as elevated ^{230}Th/^{234}U activity ratio without an accompanying decrease in the ^{234}U/^{238}U activity ratio, so indicating an equal release of U isotopes. Observations of the ^{234}U deficiency further from the fracture, on the other hand, indicate that ^{234}U was preferentially released deeper in the matrix. Thus, the absence of equal release of U isotopes behind the zone of equal isotope release is interpreted as a change from oxic to anoxic conditions. This is an important finding because it offers a tool to study low-temperature water-rock interaction derived redox fronts in rocks (Suksi *et al.* 2001).

Because the fracture coatings were sampled in bulk, the U accumulation ages that were determined could represent a mean. If so, episodes of U accumulation younger than indicated by the mean ages in Fig. 20 must have taken place. The observed periodic-like U removal and accumulation reflect perturbations that may have induced by glaciation-deglaciation periods.

The distinctive USD signatures could not have been preserved so long unless they had been shielded from present groundwater leaching, and they could not have formed in the first place unless significant amounts of U had been subject to groundwater leaching. Additionally, in order for groundwater leaching to have generated such distinctive disequilibria it must have occurred not later than 300,000 years ago.

5.3   Implications for radionuclide geosphere transport

The chemical extraction technique proved its potential in studying U fixation. The findings on U fixation in oxic conditions are important in suggesting that fixation mainly takes place through mechanisms stronger than adsorption. This finding is in agreement with observations made elsewhere (see the review in Del Nero *et al.* 1999). The formation of specific U compounds (*e.g.* secondary U minerals) may play a role in fixation, too. Importantly, these findings clearly show that the long-term partitioning of U is difficult to interpret using K_d because reversibly attached inventory is only a small part of the whole *in situ* inventory of U. By definition, K_d

applies only for the reversible subinventory. This important finding may be used to quantify the degree of conservatism in K_d selection for PA's.

The extensive fracture surface sampling performed during the study was useful in allowing fuller characterisation of the groundwater flow. Evidence for channelling during the fracture flow was obtained, and groundwater channelling means restricted interaction with the fracture surface minerals and the rock matrix accessible in the fracture system, *i.e.* decreased retardation for migrating radionuclides. Such decreased retardation is an important far-field parameter in repository performance assessments. The finding of U accumulation in some fractures and removal from some others within a relatively small bedrock volume suggests fluctuation in past flows.

5.4   Future studies

The U-series disequilibrium data describing the nature of the long-term water-rock interaction in the shallow bedrock at the Palmottu natural analogue study site will form valuable reference material when corresponding interaction is studied deeper in the bedrock.

The observation of the penetration of oxic conditions in the rock matrix centimetres from fractures is important and needs to be further studied with a larger number of samples. For more precise information on the processes affected, U-series modelling coupled with mass balance calculations and more detailed geochemical study should be undertaken.

REFERENCES

Abbey, S., 1979. Reference material–Rock samples SY-2, SY-3, MRG-1. Canmet Report 79-35 (Energy, Mines and Resources Canada, 1979), p. 66.

Adloff, J.P. and Rössler, K., 1991. Recoil and transmutation effects in the migration behaviour of actinides. Radiochim. Acta **52/53**, 269-274.

Alexander, W.R., MacKenzie, A.B., Scott, R.D. and McKinley, I.G., 1990. Natural analogue studies in crystalline rock: the influence of water-bearing fractures on radionuclide immobilisation in a granitic rock repository. Baden: National Cooperative for the Disposal of Radioactive Waste. 106 p. + app. 1 p. (Nagra Technical Report) 87-08.

Ames, L.L., McGarrah, J.E. and Walker, B.A., 1983. Sorption of trace constituents from aqueous solutions onto secondary minerals. Clays and Clay Minerals, Vol. 31, No. 5, 321-334.

Backman, C., 1990. Sampling and data evaluation of 13 rock samples for internal quality control (internal report). Geological Survey of Finland.

Blomqvist, R., Kaija, J., Lampinen, P., Paananen, M., Ruskeeniemi, T., Korkealaakso, J., Pitkänen, P., Ludvigson, J-E., Smellie, J. T. A., Koskinen, L., Floría, E., Turrero, M. J., Galarza, G., Jakobsson, K., Laaksoharju, M., Casanova, J., Grundfelt, B. and Hernan, P., 1998. The Palmottu natural Analogue Project − Phase 1: Hydrogeological evolution of the site. European Commission, Report EUR 18202, 95 p. + 1 Appendix.

Blomqvist, R., Ruskeeniemi, T., Kaija, J., Ahonen, L., Paananen, M., Smellie, J. T. A., Grundfelt, B., Pedersen, K., Bruno, J., Pérez del Villar, L., Cera, E., Rasilainen, K., Pitkänen, P., Suksi, J., Casanova, J., Read, D. and Frape, S., 2000. The Palmottu natural Analogue Project–Phase II: Transport of radionuclides in a natural flow system at Palmottu. European Commission, Report EUR 19611 EN, 192 p.

Bolle, J.N., Martin, H., Sondag, F. and Cardoso Fonseca, E., 1988. Selective chemical extraction of uranium from mineral, soil and stream sediment samples at Horta da Vilariça, Northeastern Portugal. Uranium **4**, 327-340.

Bruno, J., Cera, E., de Pablo, J., Duro, L., Jordana, S. and Savage, D., 1997. Determination of radionuclide solubility limits to be used in SR 97−uncertainties associated to calculated solubilities- SKB Technical Report 97-33, 184 p.

Bruno, J., de Pablo, J., Duro, L., Figuerola, E., 1995. Experimental study and modeling in the U(VI)-Fe(OH)$_3$ surface precipitation equilibria, Geochim. Cosmochim. Acta **59**, 4113-4123.

Carlson, L. and Schwrtmann, U., 1981. Natural ferrihydrites in surface deposits from Finland and their association with silica. Geochim. Cosmochim. Acta **45**, 421-429.

Casanova, J., 1999. Mass spectrometry uranium analyses of water/calcite pairs. The Palmottu Natural Analogue Project. Technical Note, June 1999, 9 p.

Chao, T.T., 1984. Use of partial dissolution techniques in geochemical exploration. J. Geochem. Explor. **20**, 101-135.

Chapman, N.A., McKinley, I.G., Shea, M.E., and Smellie, J.A.T., 1991. The Poços da Caldas Project: Summary and implications for radioactive waste management. NAGRA NTB 90-33 (SKB TR 90-24, UK DOE 90-055), 147 p.

Chapman, N.A. and Smellie, J.A.T., 1986. Natural analogues to the conditions around a final repository for high-level radioactive waste. Chem. Geol. **55**/3-4, 167-388.

Chapuis, A.M. and Blanc, P.L., 1993. Oklo: natural analogue for transfer processes in a geological repository–present status of the programme. *In:* H. von Maravic and J. Moreno (eds), Migration of radionuclides in the geosphere. Proceedings of a progress meeting. CEC Nuclear Science and Technology Report, EUR 14690.

Cherdyntsev, V.V., 1971. Uranium-234, Israel Program for Scientific Translations (Uran-234, Atomizdat, Moskva 1969), Jerusalem 1971, p. 234.

Choppin, G., 1999. Utility of oxidation state analogs in the study of plutonium behaviour. Radiochim. Acta **85**, 89-95.

Côme, B. and Chapman, N.A. (eds), 1987. Natural analogues in radioactive waste disposal. Commission of the European Communities (EUR 11037 EN), 492 p.

Cramer, J. and Smellie, J.A.T., 1994. Final report of the AECL/SKB Cigar Lake Analog Study, SKB TR 94-04, 393 p.

Crespo, M.T., Pérez del Villar, L., Jiménez, A., Pelayo, M., Quejido, A. and Sánchez, M., 1996. Uranium isotopic distribution in the mineral phases of granitic fracture fillings by a sequential extraction procedure. Appl. Radiat. Isot. **47**/9-10, pp. 927-931. applications. PSI Bericht Nr. 97-10, 107 p.

Davis, J. A. and Hayes, K. F., 1986. Geochemical processes at mineral surfaces: An Overview. *In:* Geochemical processes at mineral surfaces (eds. James A. Davis and Kim F. Hayes), ACS symposium series / American Chemical Society ; 323, 2-18.

Del Nero, M., Salah, S., Miura, T., Clément. A. and Gauthier-Lafaye, F., 1999. Sorption/desorption processes of uranium in clayey samples of the Bangombé natural reactor zone, Gabon. Radiochim. Acta **87**, 135-149.

Dongarra, C., 1984. Geochemical behaviour of uranium in the supergene environment. *In:* B. De Vivo, F. Ippolito, G., Capaldi and P. Simpson (eds.), Uranium geochemistry, mineralogy, geology, exploration and resources. The Institution of Mining and Metallurgy 1984 (ISBN 0 900488 70 0), 18-22.

Duerden, P., Lever, D.A., Sverjensky, D.A., and Townley, L.R., 1992. Alligator Rivers Analogue Project, Final Report Volume 1, Summary and findings. DOE/HMIP/RR/92/071 (SKI TR 92:20-1), 138 p.

Edis, R., Cao, L., Cashion, J., Klessa, D., Koppi, A.J., Murakami, T., Nightingale, T, Payne, T., Snelling, A. and Yanase, N., 1992. Chemistry and mineralogy of rocks and soil. Alligator Rivers analogue project, Final Report, Volume 8 (DOE/HMIP/RR/92/078, SKI TR 92:20-8), 255 p.

Eronen, M. and Olander, H., 1990. On the world's ice ages and changing environments. Report YJT-90-13. Nuclear Waste Commission of Finnish Power Companies. Helsinki.

Ervanne, H. and Suksi, J., 1996. Comparison of Ion-Exchange and Coprecipitation Methods in Determining Uranium Oxidation States in Solid Phases. Radiochemistry **38**, 324-327.

Ewing, R.C. and Jercinovic, M.J., 1987. Natural analogues: their application to the prediction of the long-term behaviour of nuclear waste forms. Mat. Res. Soc. Symp. Proc. **84**, 67-83.

Finch, R.J., Suksi, J., Rasilainen, K. and Ewing, R.C., 1995. The long-term stability of becquerelite. Mat. Res. Soc. Symp. Proc. Vol. 353, 647-652.

Fontes, J-C., 1993. Isotope palaeohydrology and the prediction of long-term repository behaviour. Terra Nova **6**, 20-36.

Forsström, L., 1999. Future glaciation in Fennoscandia. Posiva Report 99-30. Posiva Oy, Helsinki, 31 p.

Gascoyne M., 1992. Geochemistry of the actinides and their daughters. *In:* Uranium Series Disequilibrium: Applications to Earth, Marine, and Environmental problems, (M. Ivanovich and R.S. Harmon, eds.). Clarendon Press, Oxford, 33-55.

Gascoyne, M. and Cramer, J.J., 1987. History of actinide and minor element mobility in an Archean granitic batholith in Manitoba, Canada. Appl. Geochem. **2**, 37-53.

Giblin, A.M., Batts, B.D. and Swaine, D.J., 1981. Laboratory simulation studies of uranium mobility in natural waters. Geochim. Cosmochim. Acta **45**, 699-709.

Griffault, L.Y., Gascoyne, M., Kamineni, C., Kerrich, R., and Vandergraaf, T. T., 1993. Actinide and rare earth element characteristics of deep fracture zones in the Lac du Bonnet granitic batholith, Manitoba, Canada. Geochim. Cosmochim. Acta **57**, 1181-1202.

Guthrie, V.A., 1989. Fission-track analysis of uranium distribution in granitic rocks. Chem. Geology **77**, 87-103.

Guthrie, V.A. and Kleeman, J.D., 1986. Changing uranium distributions during weathering of granite. Chem. Geology **54**, 113-126.

Heath, M.J. (ed.), 1995. Rock matrix diffusion as a mechanism for radionuclide retardation: Natural radioelement migration in relation to the microfractography and petrophysics of fractured crystalline rock. Luxembourg: Commission of the European Communities. 128 p. (Report EUR 15977 EN).

Hsi, C.-K.D., and Langmuir, D., 1985. Adsorption of uranyl onto ferric oxyhydroxides: Application of the surface complexation site-binding model. Geochim. Cosmochim. Acta **49**, 1931–1941.

Ivanovich, M., 1991. Aspects of Uranium/Thorium Series Disequilibrium Applications to Radionuclide Migration Studies. Radiochim. Acta **52/53**, 257-268.

Ivanovich, M., 1994. Uranium series disequilibrium: concepts and applications. Radiochim. Acta **64**, 81-94.

Ivanovich, M. and Harmon, R.S., 1982. Uranium Series Disequilibrium, Applications to Environmental Problems. Clarendon Press, Oxford 1982, 571 p.

Ivanovich, M. and Harmon, R.S., 1982a. Appendix A: Derivation of the expressions for the $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ activity ratio age equations. *In:* Uranium series disequilibrium, applications to environmental problems. Clarendon Press, Oxford, 571 p.

Ivanovich, M. and Harmon, R.S., 1982b. Appendix C: UTAGE-3 computer program for the $^{230}Th/^{234}U$ age calculation. *In:* Uranium series disequilibrium, applications to environmental problems. Clarendon Press, Oxford, 571 p.

Ivanovich, M. and Harmon, R.S., 1992. Uranium-series disequilibrium, applications to earth, marine, and environmental sciences, Clarendon Press, Oxford (2nd ed.), 910 p.

Ivanovich, M., Latham, A.G., Longworth, G., and Gascoyne, M., 1992. Applications to radioactive waste disposal studies. *In:* Uranium-series disequilibrium, applications to earth, marine, and environmental sciences, Clarendon Press, Oxford (2nd ed.), 582-630.

King-Clayton, L., Chapman, N., Ericsson, L.O. and Kautsky, F., (eds.) 1997. Glaciation and hydrogeology. Workshop on the impact of climate change and glaciations on rock stresses, groundwater flow and hydrochemistry – Past, Present and future. Stockholm, Swedish Nuclear Power Inspectorate, SKI Report 97:13.

Krauskopf, K.B., 1986. Thorium and rare-earth elements as analogs for actinide elements. Chem. Geol. **55**, 323-335.

Lancelot, J.R., Vitrec, A., and Allegre, C.J., 1975. The Oklo natural reactor: Age and evolution studies by U-Pb and Rb-Sr systematics. Earth Planet. Sci. Lett. **25**, 189-196.

Langmuir, D., 1978. Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposit. Geochim. Cosmochim. Acta **42**, 547-569.

Langmuir, D. and Herman, J.S., 1980. The mobility of thorium in natural waters at low temperatures. Geochim. Cosmochim. Acta **44**, 1753-1766.

Latham, A.G. and Schwarcz. H.P., 1987. On the possibility of determining rates of removal of uranium from crystalline igneous rocks using U-series disequilibria-1: a U leach model, and its applicability to whole-rock data. Appl. Geochem. **2**, 55-65.

Latham, A.G. and Schwarcz, H.P., 1989. Review of the modelling of radionuclide transport from U-series disequilibria and of its use in assessing the safe disposal of nuclear waste in crystalline rock. Appl. Geochem. **4**, 527-537.

Lowson, R.T., Short, S.A., Davey, B.G. and Gray, D.J., 1986. $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ activity ratios in mineral phases of lateric weathered zone. Geochim. Cosmochim. Acta **50**, 1697-1702.

MacKenzie, A. B., Scott, R.D., Linsalata, P., and Miekeley, N., 1992. Natural decay series studies of the redox front system in the Poços de Caldas uranium mineralisation. J. Geochem. Explor. 45, 289-322.

MacKenzie, A.B., Scott, R.D., Linsalata, P., Miekeley, N., Osmond, J.K., and Curtis, D.B., 1991. Natural radionuclide and stable element studies of rock samples from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Poços de Caldas, Brazil. Poços de Caldas Report No. 7. NAGRA NTB 90—25 (SKB TR 90-16 or UK DOE WR 90-047), 185 p.

Marcos, N., Suksi, J., Ervanne, H. and Rasilainen, K., 2000. Fracture smectite as a long-term sink for natural radionuclides–Indications from unusual U-series disequilibria. Radiochim. Acta **88**, 763-766.

Martin, J.M., Nirel, P. And Thomas, A.J., 1987. Sequential extraction techniques: Promises and problems, Marine Chem. **22**, 313-314.

Mazurek, M., Alexander, W. R., and MacKenzie, A. B., 1996. Contaminant retardation in fractured shales: matrix diffusion and redox front entrapment. J. Contam. Hydrol. **21**, 71-84.

McKinley, I.G. and Alexander, W.R., 1993. Assessment of radionuclide retardation: uses and abuses of natural analogue studies. J. Contaminant Hydrology **13**, 249-259.

McKinley, I.G. and Alexander, W.R., 1996. On the incorrect derivation and use of in-situ retardation factors from natural isotope profiles. Radiocim. Acta **74**, 263-267.

Michel, J., 1984. Redistribution of uranium and thorium series isotopes during isovolumetric weathering of granite. Geochim. Cosmochim. Acta **48,** 1249-1255.

Miller, W., Alexander, R., Chapman, N.A., McKinley, I., and Smellie, J., 1994. Natural analogue studies in the geological disposal of radioactive wastes, Studies in Environmental Science 57, (Elsevier Science B.V., Amsterdam, 1994), 395 p.

Miller, W., Alexander, R., Chapman, N.A., McKinley, I., and Smellie, J., 2000. Geological disposal of radioactive wastes & natural analogues, Waste Management series, Volume 2. 2000 Elsevier Science Ltd, Oxford, 316 p.

Mohamad, D. B., MacKenzie, A. B., Stephens, W. E., and Russel, M. J., 1992. Exploration methods for nuclear waste repositories or mineral deposits - from source to sink, where's the front? Trans. Inst. Min. Metall. (*Sect. B: Appl. earth sci.)* **101**, 139-146.

Neretnieks, I., 1980. Diffusion in the rock matrix: An important factor in radionuclide retardation ? J. Geophys. Res. **88**, 4379-4397.

Neuerburg, G., 1956. Uranium in igneous rocks of the United States. U.S. Geol. Surv. Prof. Pap. 300, 55-64.

OECD/NEA, 1993. Palaeohydrogeological methods and their applications. Disposal of radioactive waste. Proceedings of a NEA Workshop, Paris 9-10 November 1992. Organisation for Economic Cooperation and development (OECD/NEA), Paris, France.

Ordonez-Regil, E., Schleiffer, J.J., and Adloff, J. P., 1989. Chemical effects of α-decay in uranium minerals. Radiochim. Acta **47**, 177-185.

Osmond J.K. and Cowart J.B., 1976. The theory and uses of natural uranium isotopic variations in hydrology. Atomic Energy Rew. **14**, 621-679.

Osmond J.K. and Cowart J.B., 1983. Uranium isotopic disequilibrium in ground water as an indicator of anomalies. Int. J. Appl. Radiat. Isot. **34**, No. 1, 283-308.

Osmond J.K. and Cowart J.B., 1992. Ground water, *In:* Uranium-series Disequilibrium: Applications to Earth, Marine, and Environmental Sciences (M. Ivanovich and R.S. Harmon, eds.). Clarendon Press, Oxford, 290-330.

Osmond J.K. and Ivanovich, M., 1992. Uranium-series mobilization and surface hydrology. *In:* Uranium-series Disequilibrium: Applications to Earth, Marine, and Environmental Sciences (M. Ivanovich and R.S. Harmon, eds.), Clarendon Press, Oxford, 259-289.

Paananen, M., Paulamäki, S. and Blomqvist, R., 1997. The Palmottu Analogue Project, Progress Report 1997, Geological Survey of Finland, Espoo. Report YST-98, 45-55.

Payne, T.E., Davis, J.A. and Waite, T.D., 1994. Uranium retention by weathered schists – The role of iron minerals. Radiochim. Acta **66/67**, 297-303.

Payne, T.E. and Waite, T.D., 1991. Surface complexation modeling of uranium sorption data obtained by isotope exchange techniques. Radiochim. Acta **52/53**, 487-493.

Petit, J.-C., 1992. Reasoning by analogy: Rational foundation of natural analogue studies. Appl. Geochem. Suppl. Issue, No. 1, 9-11.

Petit, J.-C., Langevin, Y., and Dran, J.-C., 1985. U-234/U-238 disequilibrium in nature: theoretical reassessment of the various proposed models. Bull. Minéral **108**, 745-753.

Pickering, W.F., 1986. Metal ion speciation - soil and sediments (A review). Ore Geol. Rev. **1**, 83-146.

Rasilainen K., 1997. Matrix diffusion model–In situ tests using natural analogues. 81 p. + app. 67 p. VTT Publications 331.

Rasilainen, K. and Suksi, J., 1997. A multisystem modelling approach for uranium-series dating. Nuclear Technology **120**, 254-160.

Rasilainen K., Suksi, J., Hellmuth K-H., Lindberg A., Kulmala S., 1996. Postglacial matrix diffusion in a boulder sample. Mat. Res. Soc. Symp. Proc. **412**, 855-862.

Rauret, G. and Quevauviller, Ph., 1992. Proceedings of the Workshop on the sequential extraction of trace metals in soils and sediments. Intern. J. Environ. Anal. Chem. **51**, 235 p.

Rivas, P., Hernán, P., Astudillo, J., Bruno, J., Carrera, J., De la Cruz, B., Guimera, J., Gómez, P., Ivanovich, M., Marín, C., Miller, W., and Pérez del Villar, L., 1998. El Berrocal project, Summary report, Report EUR 17830 EN, 70 p.

Rosholt, J.N., 1982. Mobilization and weathering. *In:* Uranium Series Disequilibrium: Applications to environmental problems, (M. Ivanovich and R.S. Harmon, eds.). Clarendon Press, Oxford, 167-180.

Rosholt, J.N., 1983. Isotopic composition of uranium and thorium in crystalline rocks. J. Geophys. Res. **88**, 7315-7330.

Ruokola, E. (ed), 2000. Posiva's application for a decision in principle concerning a disposal facility for nuclear fuel – STUK's statement and preliminary safety appraisal. STUK-B-YTO 198, 37 pp. + appendix 17 pp.

Rössler, K., 1983. Uranium recoil reactions. *In:* Gmelin Handbook of Inorganic Chemistry, 8th Edition, Uranium (*Supplement Volume A6),* Springer Verlag, Berlin, 135-164.

Schwarcz, H.P., Gascoyne, M. and Ford, D.C., 1982. Uranium series disequilibrium studies of granitic rocks. Chem. Geol. **36**, 87-102.

Schwertmann, U., Carson, L. and Fechter, H., 1984. Iron oxide formation in artificial ground waters. Schweiz. Z. Hydrol. **46/2**, 185-191.

Scott, R.D., MacKenzie, A.B. and Alexander, W.R., 1992. The interpretation of ^{238}U-^{234}U-^{230}Th-^{226}Ra disequilibria produced by rock-water interactions. J. Geochem. Explor. **45**, 323-343.

Smellie, J.A.T., MacKenzie, A.B., and Scott, R.D., 1986. An analogue validation study of natural radionuclide migration in crystalline rocks using uranium-series disequilibrium studies. Chem. Geol. **55**, 233-254.

Smith Jr., D.K., 1984. Uranium mineralogy. *In:* B. De Vivo, F. Ippolito, G., Capaldi, and P. Simpson (eds.), Uranium geochemistry, mineralogy, geology, exploration and resources. The Institution of Mining and Metallurgy 1984, 43-71.

Steger, H.F. and Bowman, W.S., 1980. DL-1a: A certified uranium-thorium reference ore. Canmet Report 80-10E, (Energy, Mines and Resources Canada, 1980), p. 12.

Stuckless, J.S. and Pires Ferreira, C., 1976. Labile uranium in granitic rocks. Exploration for uranium ore deposits. Proceedings of a symposium on exploration of uranium ore deposit, 29 March - 2 April 1976, Vienna. IAEA-SM-208/17, 717-729.

Suksi, U.J., Juntunen, P., Pitkänen, P., Rasilainen, K., Ruskeeniemi, T., and Casanova, J., 2001. Application of uranium-series disequilibrium data to interpretation of oxygen intrusion in rocks. R. Cidu (ed.), Water-Rock Interact., Proc. Int. Symp., 10th, Balkema, Rotterdam, 1395-1398.

Suksi, J. and Rasilainen, K., 1996. On the Role of α-Recoil in Uranium Migration, Radiochim. Acta **74**, 297–302.

Suksi, J. and Rasilainen K., 1997. Reconciliation of experimental and modelling concepts in a natural analogue of radionuclide migration. Mat. Res. Soc. Symp. Proc. **465**, 1169-1176.

Suksi, J., and Rasilainen, K., 2001. Isotopic fractionation of U reflecting redox conditions around a groundwater flow route. Mat. Res. Soc. Symp. Proc. (in print).

Suksi, J., Rasilainen, K., Casanova, J., Ruskeeniemi, T., Blomqvist, R. and Smellie, J.A.T., 2000. U-series disequilibria in a groundwater flow route as an indicator of uranium migration processes. J. Contamin. Hydrol. **47**/2-4, 187-196.

Suksi, J., Ruskeeniemi, T., Lindberg, A., and Jaakkola, T., 1991. The Distribution of Natural Radionuclides on Fracture Surfaces in Palmottu Analogue Study Site in SW Finland. Radiochim. Acta **52/53**, 367-372.

Suksi, J., Ruskeeniemi, T., and Rasilainen, K., 1992. Matrix diffusion - Evidences from natural analogue studies at Palmottu in SW Finland. Radiochim. Acta **58/59**, 385-393.

Suksi, J., Ruskeeniemi, T. and Saarinen, L., 1996. Selective extractions in uranium migration studies - Findings from a natural analogue study at Palmottu. J. Contamin. Hydrol. **21**, 47-58.

Suksi, J., Saarinen, L., Ruskeeniemi, T., Rasilainen, K., and Siitari-Kauppi, M., 1995. U-series concentration distributions around rock fractures–Qualitative indication of matrix diffusion. Mat. Res. Soc. Symp. Proc. **353**, 441- 448.

Thiel, K., Vorwerk, R., Saager, R., and Stupp, H.D., 1983. ^{235}U fission tracks and ^{238}U-series disequilibria as a means to study recent mobilisation of uranium in Archaean pyritic conglomerates. Earth Planet Sci. Lett. **65**, 249-262.

TVO, 1992. Final disposal of spent nuclear fuel in the Finnish bedrock. Technical plans and safety assessment. Nuclear Waste Commission of Finnish Power Companies, Report YJT-92-31E, 136 p.

Wanner, H. and Forest, I., 1992. Chemical Thermodynamics, Vol.1: Chemical thermodynamics of uranium. North-Holland, Elsevier Science Publishing Company, Inc., New York, p. 715.

Vieno, T. and Nordman, H., 1999. Safety assessment of spent fuel disposal in Hästholmen, Kivetty, Olkiluoto and Romuvaara. TILA-99. POSIVA-99-07, Posiva Oy, Helsinki 1999.

Yanase, N., Nightingale, T., Payne, T. and Duerden, P., 1991. Uranium distribution in mineral phases of rock by sequential extraction procedure. Radiochim. Acta **52/53**, 387- 393.

Zielinski, R.A., Peterman, Z.E., Stuckless, J.S., Rosholt, J.N., and Nkomo, I.T., 1981. The chemical and isotopic record of rock-water interaction in the Sherman Granite, Wyoming and Colorado. Contrib. Mineral. Petrol. **78**, 209-219.

APPENDIX 1   Analyses of reference rock samples

Three reference rock samples were studied for quality assurance purposes. Two of the samples were internationally certified reference samples and the third sample was provided by the Geological Survey of Finland and represents its own reference material.

Sample code	Sample material	References
RS 111	Granite	Backman 1991
SY-2	Syenite	Abbey 1979
DL-1a	Uranium-thorium reference ore; U-series is in radioactive equilibrium	Steger and Bowman 1980

Samples (50-750 mg) were spiked with a ^{232}U–^{228}Th tracer in radioactive equilibrium and dissolved in HF+HCl+HNO$_3$ mixture. The analytical procedure of the solution is as presented in Fig. 7 (section 4.3).

Table 2. Analytical results of this study and recommended/informational values.

Analyses		RS 111	SY-2	DL-1a
U	This study	14.6 ± 1.6 (8)	276 ± 7 (3)	119 ± 8 (6)
	Recommended	14	290	116
Th	This study	48.2 ± 1.9 (8)	364 ± 9 (3)	76 ± 3 (6)
	Recommended	53.4	380	76
^{234}U/^{238}U	This study (8)	0.89 ± 0.02 (8)	0.99 ± 0.03 (3)	1.02 ± 0.03 (6)
	Recommended	-	-	1
^{230}Th/^{234}U	This study	1.08 ± 0.05 (8)	1.15 ± 0.03 (3)	0.98 ± 0.03 (6)
	Recommended	-		1