Matrix diffusion model

In situ tests using natural analogues

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ABSTRACT

Matrix diffusion is an important retarding and dispersing mechanism for substances carried by groundwater in fractured bedrock. Natural analogues provide, unlike laboratory or field experiments, a possibility to test the model of matrix diffusion in situ over long periods of time. This thesis documents quantitative model tests against in situ observations, done to support modelling of matrix diffusion in performance assessments of nuclear waste repositories, which must cover long, even geoletical time periods.

A model testing methodology was developed by combining measurements of long-lived natural decay chains yielding the experimental reference, rock matrix characterisations, and matrix diffusion simulations. Valuable support to matrix diffusion simulations was provided by independent uranium-series disequilibria simulations, done to date radiometrically the accumulated uranium.

Repeated model tests, applying the methodology, were carried out at two Finnish natural analogue study sites, the U-Th deposit at Palmottu, and a boulder sample near Hämeenlinna; both sites show elevated natural radioactivity. The deposit at Palmottu is extremely old, while the uranium accumulation in the boulder appears postglacial.

The most important lesson learned at Palmottu is that the experimental reference must be conceptually in line with the model being tested. In this view, reconciling the respective concepts of attachment of radionuclides on rock is absolutely essential, otherwise quantitative model testing is pointless. In situ simulations require a complete and consistent site-specific data base for the model, because in model testing even partly generic input data may lead to false conclusions. The boulder sample indicates that recent uranium accumulations are easier to interpret than old ones, because matrix diffusion response is easier to trace, and boundary conditions for the simulations are easier to quantify.

The iterative model validation process is a powerful method to refine both theoretical and experimental tools. The tests with the boulder sample support the classical matrix diffusion concept used in performance assessments. The tests at Palmottu indicate, however, a clear need to improve the technique used to obtain the experimental reference.

PREFACE

This work has been carried out at VTT Energy within the Nuclear Energy Research Field. I am grateful to Dr. Seppo Vuori for his encouragement and support during the whole project. I also want to thank Prof. Rainer Salomaa for his encouragement and valuable comments in the final stages of the work. I would further like to thank Prof. Timo Jaakkola and Prof. Jussi Timonen for their careful review of the manuscript, and for their valuable comments.

The substance of the work greatly benefited from the expertise of my colleagues within the Nuclear Waste Management Research Group, and from the open atmosphere within the group. I want to thank, besides Seppo Vuori, Dr. Timo Vieno, Dr. Aimo Hautojärvi, Mr. Henrik Nordman, Mr. Antti Poteri, and Mr. Lasse Koskinen for the many stimulating discussions. They helped me to stick to the point.

The studies reported here were started as part of the Finnish natural analogue project at Palmottu, and later the boulder sample, located near Hämeenlinna, was included in the work. Natural analogue studies are team work by definition, and model testing in particular requires intensive co-operation. I am, therefore, indebted to all colleagues who provided me with the necessary input data and the related experimental knowledge. This credit goes to Mr. Juhani Suksi, Mr. Martti Hakanen and Ms. Seija Kulmala at the University of Helsinki, Mr. Timo Ruskeeniemi and Mr. Antero Lindberg at the Geological Survey of Finland, Dr. Karl-Heinz Hellmuth at the Radiation and Nuclear Safety Authority, and Dr. Markus Olin at VTT Chemical Technology. The enthusiasm of Juhani Suksi, my co-author in all publications, deserves to be mentioned.

The studies were part of the Publicly Administrated Nuclear Waste Management Research Programme in Finland funded jointly by the Ministry of Trade and Industry, and the Radiation and Nuclear Safety Authority.

The facilities at VTT Energy, and especially the co-operative people running them, made it possible for me to concentrate on the issue, because I could always with confidence turn to an expert with my technical problems.

During the whole project, my wife Heidi and my son Kimmo never forgot my place and role in the family, neither did they let me forget.

LIST OF PUBLICATIONS

The thesis is based on the following publications (Appendices B - I):

1 Suksi, J., Ruskeeniemi, T. & Rasilainen, K. 1992. Matrix diffusion - Evidences from natural analogue studies at Palmottu in SW Finland. Radiochimica Acta, vol. 58/59, pp. 385 - 393. ISSN 0033-8230

2 Rasilainen, K. & Suksi, J. 1993. Modelling in-situ matrix diffusion at Palmottu natural analogue site in SW Finland. In: Interrante, C.G. & Pabalan, R.T. (eds.). Scientific Basis for Nuclear Waste Management XVI. Pittsburgh, PA: Materials Research Society. Pp. 489 - 495. (Mat. Res. Soc. Symp. Proc., vol. 294). ISBN 1-55899-189-1

3 Rasilainen, K. & Suksi, J. 1994. Modelling prospects for in situ matrix diffusion at Palmottu natural analogue site, SW Finland. In: Proceedings of the Fourth International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere, Charleston, SC 12 - 17 December 1993. Special Issue of Radiochimica Acta, pp. 581 - 587. ISBN 3-486-64247-2

4 Rasilainen, K., Suksi, J., Hakanen, M. & Olin, M. 1995. Sorption aspects for in situ matrix diffusion modelling at Palmottu natural analogue site, SW Finland. In: Murakami, T. & Ewing, R.C. (eds.). Scientific Basis for Nuclear Waste Management XVIII. Pittsburgh, PA: Materials Research Society. Pp. 1169 - 1177. (Mat. Res. Soc. Symp. Proc., vol. 353. Part 2). ISBN 1-55899-253-7

5 Suksi, J. & Rasilainen, K. 1996. On the role of α-recoil in uranium migration - Some findings from the Palmottu natural analogue site, SW Finland. Radiochimica Acta, vol. 74, pp. 297 - 302.
ISBN 3-486-64251-0

6 Suksi, J. & Rasilainen. K. 1997. Reconciliation of experimental and modelling concepts in a natural analogue of radionuclide migration. In: Gray, W.J. & Triay, I.R. (eds.). Scientific Basis for Nuclear Waste Management XX. Pittsburgh, PA: Materials Research Society. Pp. 1169 - 1176. (Mat. Res. Soc. Symp. Proc., vol. 465). ISBN 1-55899-369-X

7 Rasilainen, K., Suksi, J., Hellmuth, K.-H., Lindberg, A. & Kulmala, S. 1996. Postglacial matrix diffusion in a boulder sample. In: Murphy, W.M. & Knecht, D.A. (eds.). Scientific Basis for Nuclear Waste Management XIX. Pittsburgh, PA: Materials Research Society. Pp. 855 - 862. (Mat. Res. Soc. Symp. Proc., vol. 412). ISBN 1-55899-315-0

8   Rasilainen. K. & Suksi, J. 1997. On the accuracy of uranium-series dating: A comparison with a known matrix diffusion case. In: Gray, W.J. & Triay, I.R. (eds.). Scientific Basis for Nuclear Waste Management XX. Pittsburgh, PA: Materials Research Society. Pp. 1177 - 1184. (Mat. Res. Soc. Symp. Proc., vol. 465). ISBN 1-55899-369-X

The first six publications represent studies at Palmottu natural analogue site, and the last two studies with the boulder sample. The disputant is the principal author of publications 2, 3, 4, 7, 8, and participated actively in the writing of publications 1, 5, 6.

Publication 1 is, actually, an experimental paper. It is, however, included in this model testing work for two reasons. First, it is the beginning of an exceptionally fruitful co-operation between a modeller, the present author, and an experimenter, Juhani Suksi, who is mainly responsible for the paper. Second, it emphasises the fact that the model testing approach applied in this thesis stands or falls with the experimental reference.

All publications are based on interdisciplinary co-operation, and the present author, as the modeller in the group, has performed all matrix diffusion and/or uranium-series disequilibria simulations and the subsequent discussion of results. Furthermore, he has been responsible for emphasising the model validation aspects in all publications, as well as for developing the related conceptualisation.

CONTENTS

Appendices of this publications B - I are not included in the PDF version.
Please order the printed version to get the complete publication
(http://www.inf.vtt.fi/pdf/publications/1997/)

1 INTRODUCTION

Final disposal of highly radioactive nuclear wastes has attracted much attention in all countries producing nuclear energy. Geological disposal deep in the bedrock is the most extensively studied disposal option, and there is widespread consensus about its merits (CEC & NEA 1984, Chapman & McKinley 1987, IAEA 1993, NEA RWMC 1995, Savage 1995). The basic idea of geological disposal is to isolate the nuclear wastes in a deep stable geological formation. The geosphere has demonstrably protected man's environment from e.g. concentrated natural uranium deposits, and also from the huge amounts of dispersed natural radioactive and toxic minerals within the earth. In this sense the concept of geological disposal is active in nature everyday.

The specific geologic formation considered as host formation varies from country to country, depending on the geological setting. The Finnish disposal concept of spent nuclear fuel is based on a repository deep in the crystalline bedrock (TVO 1992, Vira 1994). As the repository is situated in saturated rock below groundwater surface, the groundwater will gradually cause the planned engineered multibarrier system to deteriorate, and after it has been eroded, the subsequent spreading of radionuclides will be controlled by natural migration processes with the groundwater acting as the carrier.

Fractured crystalline rock can be visualised as a mosaic-like structure of bedrock blocks bounded by fracture zones of different sizes. The bedrock blocks in turn are intersected by individual fractures. In this medium, groundwater exists in two interacting continua (e.g. Niemi 1994). Water-conducting fractures contain a continuum of flowing water. The rock matrix bounded by the water-conducting fractures contains a continuum of non-flowing water which, however, is accessible via molecular diffusion. Interaction between these two continua takes place as mass exchange at the water-conducting fractures (Neretnieks 1980, Grisak & Pickens 1980).

A rough picture of the relative amounts of water in the two continua can be obtained by studying their respective volumetric fractions. Typically, the fraction of water-conducting fractures (flow porosity) in a bedrock block is $1 \cdot 10^{-4}$ (Gale et al. 1987, Vieno 1994, Löfman 1996), and the fraction of pore network in the rock matrix (matrix porosity) is above $1 \cdot 10^{-3}$ (Gale et al. 1987, Valkiainen 1992). It can be seen that most of the water in a bedrock block lies in the rock matrix, and is only accessible via molecular diffusion. This diffusion is called matrix diffusion.

Matrix diffusion retards the radionuclides migrating in the bedrock in two ways. First, it retards all nuclides by spreading them physically from the flowing groundwater into the diluting reservoir of stagnant pore water. Second, it provides a dramatic increase (several orders of magnitude) in mineral surface for geochemical

sorption reactions, as compared to migration in the fracture only, see Fig. 1. The increase in reacting surface increases, in turn, the amount of radionuclides that can be accommodated in the rock-groundwater system, and thereby the overall retardation of the migrating radionuclides. Currently matrix diffusion, together with sorption, is considered to be the most important retardation mechanism in fractured crystalline rock (SKBF 1983, SKI 1991, SKB 1992, Vieno 1994, see also the priorities in Wernicke 1995).
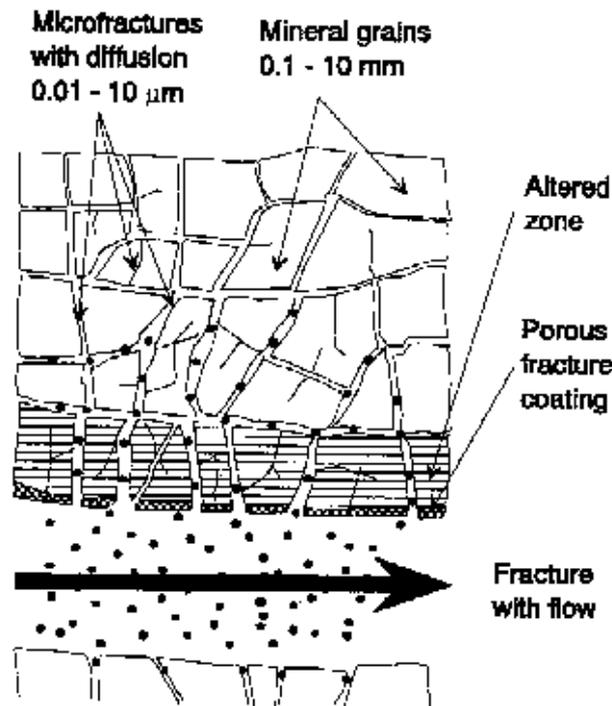
Fig. 1. Diffusion of water-carried substances into rock matrix. Some fractures are surrounded by porous coating material and/or altered minerals.

Performance assessment is a modelling methodology developed to analyse the safety of the proposed nuclear waste disposal concept in advance, prior to the actual disposal. Performance assessments cover very long time scales, as all major migration scenarios from repository to biosphere must be considered. It is therefore essential to their credibility that all submodels are validated against relevant evidence over comparable time scales.

Matrix diffusion has traditionally been studied in short-term laboratory or field experiments. Therefore, there are unavoidable uncertainties in extrapolating the results to long-term performance assessments. In addition, correspondence between the experimental set-up and the in situ conditions is not always self-evident.

Experimental artefacts, usually introduced in sampling and sample preparation, are a specific group of deviations from the in situ conditions, and represent, thus, a further problem from the extrapolation point of view.

The present study investigates matrix diffusion in situ, i.e. under natural site-specific conditions, and uses natural analogues as the source of information. A natural analogue can be broadly defined as a long-term natural experiment not controlled by man (IAEA 1989); the experiment actually continues in situ until the moment of sampling. With respect to the possible disturbance of sampling on the outcome of the experiment, this sequence is clearly different from laboratory experiments, in which sampling always precedes the actual experiment.

The aim of this work is to study critically whether the matrix diffusion model can be quantitatively validated (or invalidated) using measured in situ data from natural analogues. Technically speaking, model validation necessitates a reliable experimental reference for the simulations, and reliable input data for the simulation model. Because the model is universal as such, in situ features are transferred into simulations only via the measured input data. Therefore, quality assurance considerations in measurements form a built-in element throughout this work.

In Chapter 2 a short introduction to the theory of matrix diffusion will be given, reviewing the classical model and three variations on it. In Chapter 3 natural analogues will be discussed with emphasis on quantitative validation of the matrix diffusion concept. An introduction to the use of natural radioactive decay chains in natural analogue studies will also be given. Some reported natural analogue studies on matrix diffusion will be reviewed briefly. In Chapter 4 a systematic model testing methodology will be formulated for the present work. This methodology is the actual tool for studying critically whether matrix diffusion can be seen in the natural analogues. In Chapter 5 the methodology will be applied to two Finnish natural analogues: the Palmottu natural analogue site, and the boulder sample near Hämeenlinna. The study will be concluded with a discussion of the main results obtained, and the development needs observed.

2 MATRIX DIFFUSION THEORY

2.1 ON THE POTENTIAL OF MATRIX DIFFUSION

The retardation capability brought about by matrix diffusion can be quantified by studying the amount of pore water available for dilution, and mineral surface area available for sorption. By comparing these matrix-specific characteristics with those representing the fracture alone (i.e. assuming rock matrix absolutely impermeable), one obtains a quantitative measure of the potential of matrix diffusion. For this purpose, the fractured bedrock is described by the dual-porosity concept (e.g. Narasimhan 1982, Niemi 1994), and for the calculations below, a simplified cubic block structure is assumed, see Fig. 2.
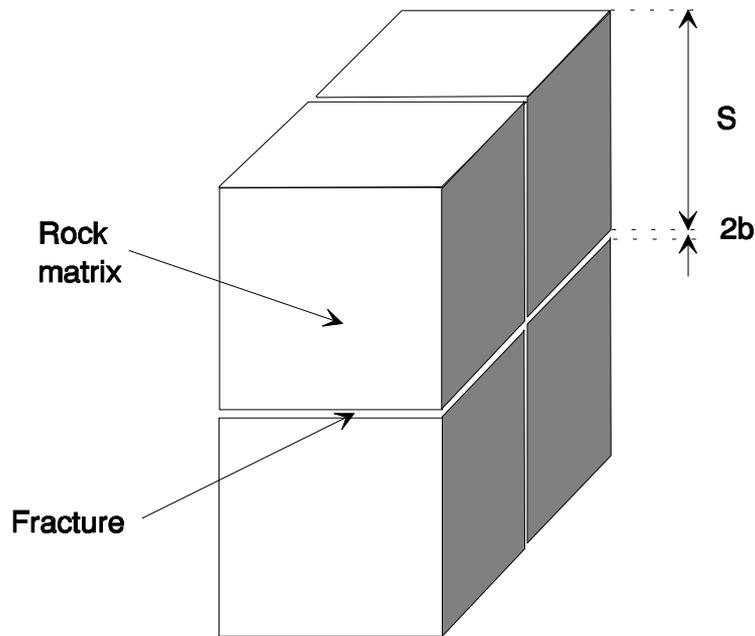
Fig. 2. Simplified cubic block structure of bedrock.

In this system the 3-dimensional flow porosity can be expressed as

$$\varepsilon_f \;\approx\; 3 \cdot \frac{2b}{s}\,, \quad 2b \;<<\; s \tag{1}$$

where ε_f is the flow porosity, 2b is the aperture of the water-conducting fracture (m), and s is the fracture spacing (m). In the following examples we assume $\varepsilon_f = 1 \cdot 10^{-4}$ (Gale et al. 1987, Löfman 1996) and s = 1 m.

For unaltered granite, matrix porosity $\varepsilon_p \geq 1\cdot10^{-3}$ is typical (Valkiainen 1992). Comparing this with the flow porosity, it can be seen immediately that within a bedrock block, the rock matrix contains typically an order of magnitude more groundwater than the water-conducting fractures.

From the migration point of view, the surface area within the rock matrix is more important than the amount of water, however, because it provides reaction surface for sorption, see Fig. 1. Assuming again the cubic block geometry from above, one obtains the fracture aperture $2b = 3\cdot10^{-5}$ m from Eq. (1). For a parallel plane fracture, the specific surface area is (e.g. SKBF 1983)

$$a_f \approx \frac{2}{2b} \tag{2}$$

where a_f is the volume-specific surface area in the fracture (m^2/m^3 water). With the input from above, one obtains $a_f = 6\cdot10^4$ m^2/m^3.

Assuming that a mass-specific surface area a_m (m^2/kg) has been measured for the rock matrix, a comparable volume-specific surface area (i.e. relative to pore water volume) is

$$a_s = \frac{a_m \rho_s (1-\varepsilon_p)}{\varepsilon_p} \tag{3}$$

where a_s is the volume-specific surface area (m^2/m^3 pore water), ρ_s is the density of the solid (kg/m^3), and ε_p is the matrix porosity. Assuming $\rho_s = 2\,700$ kg/m^3, $\varepsilon_p = 0.1$ %, and a typical value $a_m = 100$ m^2/kg (Eriksen & Locklund 1989, Valkiainen et al. 1995), one obtains $a_s = 2.7\cdot10^8$ m^2/m^3. It can be seen that typically the rock matrix provides an increase of nearly four orders of magnitude in specific surface area as compared to that in the water-carrying fractures.

2.2 BASIC ROCK MATRIX CONCEPTS

Matrix geometry

A rock matrix consists of mineral grains of varying composition and size. Between, within and even across the mineral grains, there is a continuous and complex network of microfractures, a pore network, see Fig. 1. This connected pore network

is a necessary prerequisite for matrix diffusion. The geometrical structure of the pore network can in principle be characterised by porosity, tortuosity and constrictivity.

In saturated rock, porosity ε is generally defined by (e.g. de Marsily 1986):

$$\varepsilon = \frac{\textit{water volume of rock}}{\textit{total volume of rock}} \tag{4}$$

For diffusion considerations it is important, however, to make a distinction between the total matrix porosity, including the isolated residual porosity (e.g. fluid inclusions), and the connecting effective porosity that can be reached by diffusion (e.g. Pirhonen 1990, Valkiainen 1992). In this work, matrix porosity refers to effective porosity accessible by diffusion, and is denoted by ε_p.

Tortuosity τ ($\tau \geq 1$) describes the meandering pathways along the pores, i.e. deviation of the length of the pathway from the linear distance between its start and end points. Constrictivity δ_D ($\delta_D < 1$) accounts for the changes in the cross section of individual pores, i.e. pore constrictions and widenings along the pathway. There are numerous definitions of tortuosity and constrictivity (e.g. van Brakel & Heertjes 1974, Katsube et al. 1986). Tortuosity and constrictivity are, however, quite difficult to distinguish experimentally from each other. Therefore, they have been integrated into one practical parameter, the geometric factor (δ_D/τ^2) that relates pore geometry and diffusivity (Neretnieks 1980, Skagius 1986):

$$D_p = \frac{\delta_D}{\tau^2} D_w \tag{5}$$

where D_p is the diffusion coefficient of the tracer in the pore water (m^2/s), and D_w is the molecular diffusion coefficient of the tracer within free water (m^2/s). It can be seen that the geometric factor is, essentially, a measure of the decrease in diffusivity due to a complex pore geometry ($\delta_D/\tau^2 < 1$) as compared to unconfined water.

Sorption

Sorption reactions bind radionuclides onto mineral surfaces within the rock matrix by different physical and chemical phenomena (NEA 1983); in this work the term sorption is, however, restricted to mean solely adsorption. The magnitude of sorption varies considerably from one species to another; it also depends strongly on the mineral in question and on groundwater chemistry (ionic strength, Eh, pH, etc.). The most common way to characterise a solid with respect to sorption, is to use

experimental surface area or mass based distribution coefficients. Normally sorption equilibrium is assumed to prevail in the experiments.

Distribution coefficients are usually interpreted to represent fast, reversible, and concentration-independent direct uptake of radionuclides on the mineral surfaces by e.g. ion exchange and physical adsorption. Partially or entirely irreversible mechanisms, like precipitation or mineralisation, are not covered by distribution coefficients. A more detailed discussion of the features and limitations of distribution coefficients can be found in literature; see e.g. McKinley & Hadermann (1985), McKinley & Alexander (1992). The latter reference discusses in particular distribution coefficients in relation to natural analogues.

The area based distribution coefficient K_a (m) for a tracer is defined as (e.g. Vandergraaf et al. 1992)

$$K_a = \frac{C_{surface}}{C_{solution}} \tag{6}$$

where $C_{surface}$ is the adsorbed amount of tracer atoms per surface area (at./m^2), and $C_{solution}$ is the concentration of tracer in the water (at./m^3).

The mass based distribution coefficient K_d (m^3/kg) for a tracer is defined as (e.g. Vandergraaf et al. 1992)

$$K_d = \frac{C_{solid}}{C_{solution}} \tag{7}$$

where C_{solid} is the adsorbed amount of tracer per solid mass (at./kg). The two distribution constants are related to each other:

$$K_d = K_a a_m \tag{8}$$

where a_m is the mass-specific surface area of the rock sample (m^2/kg).

K_d is the most commonly used way to express sorption, and in this case, applying the porous medium concept, a retardation factor within the rock matrix is easily derived (e.g. Vandergraaf et al. 1992):

$$R_p = 1 + K_d \rho_s \frac{(1 - \varepsilon_p)}{\varepsilon_p} \tag{9}$$

The retardation factor expresses the ratio between groundwater velocity and tracer velocity. Depending on the scale of observation, the retarded transport of the tracer can be visualised either as slow monotonous movement, or as rapidly alternating consecutive intervals of fast movement and immobility. The inverse of the retardation factor $(1/R_p)$ expresses the fraction of the total inventory that is in the water phase and migrates with water velocity. The adsorbed fraction $(1 - 1/R_p)$ is assumed to be immobile. Actually, the term $(1/R_p)$ also expresses the time share which the tracer spends in the water phase (Rasilainen 1983). Assuming $\varepsilon_p = 0.1$ % and $\rho_s = 2\,700$ kg/m^3, and applying the performance assessment data base of K_d (Vieno 1994), one can obtain a range for R_p from 28 - 2 700 000, where the lower value represents weakly sorbing chloride ($K_d = 1 \cdot 10^{-5}$ m^3/kg) and the higher value strongly sorbing zirconium ($K_d = 1$ m^3/kg).

K_d's are usually measured in batch experiments that are carried out using crushed rock samples (Kulmala & Hakanen 1995). Assuming sorption as a surface reaction, and K_a as the basic measure of sorption, batch results can be used for intact rock matrix after correcting for the different specific surface area in the rock matrix, see Eq. (8): K_d(matrix) = K_d(crushed)·a_m(matrix)/ a_m(crushed).

K_d expresses the partition of tracer between mineral and water phases. The limited number of sorption sites in mineral phases may in some instances control sorption, and therefore sorption isotherms have been proposed (e.g. McKinley & Hadermann 1985); despite the name, isotherms essentially express concentration dependence of sorption [$K_d(C)$]. Saturation of sorption sites depends on solid/water (kg/m^3) ratio in the system, and in this respect there is a clear difference between the conditions in a batch experiment and in an intact rock matrix. In batch experiments the solid/water ratios are usually around 100 kg/m^3 (Kulmala & Hakanen 1995), while in intact rock matrix [cf. Eq. (3)] it is $\rho_s(1-\varepsilon_p)/\varepsilon_p \approx 2.7 \cdot 10^6$ kg/m^3, assuming $\varepsilon_p = 0.1$ % and $\rho_s = 2\,700$ kg/m^3. Dissolved nuclides see over four orders of magnitude more sorption sites in the intact rock matrix than in a batch experiment per unit volume of water, and, therefore, the saturation of sorption sites is much less probable in rock matrix.

Neither K_d nor sorption isotherm gives any direct information of sorption mechanisms, and for this purpose, mechanistic sorption models, e.g. surface complexation models have been developed (e.g. Davis & Kent 1990, Bradbury & Baeyens 1992). One important role of these detailed models is to support the more pragmatic "lumped parameter" concepts, e.g. K_d. In practice, K_d is in fact a well established modelling concept in performance assessments currently, and it is also incorporated in the classical matrix diffusion model.

Heterogeneity

Natural systems are generally highly heterogeneous, and in rock matrices also, alterations and other heterogeneities often occur. Altered layers or spots within the matrix are typically characterised by locally increased porosity, diffusivity, and sorption, cf. Fig. 1. The increase in sorption (i.e. K_d) is at least partly due to increased specific surface area, see Eq. (8). From the matrix diffusion point of view, the altered spots or minerals can simply be seen as sorbing sinks along the pore network, through which the diffusion takes place. In terms of overall rock characterisation, the heterogeneous structure of the rock matrix can be quantified by varying the parameter values within the matrix.

The extent to which the heterogeneous rock matrix properties can be utilised in simulations, depends on the type of the mathematical technique used in solving the diffusion equation. Numerical solutions (e.g. finite element or finite difference methods) can readily incorporate heterogeneous matrix properties, while analytical solutions usually assume homogeneous properties; for this reason, analytical models are also based on simplified versions of the diffusion equation. In this thesis, the geosphere migration code FTRANS, based on the finite element method (FEM), is used to simulate matrix diffusion.

2.3 MATRIX DIFFUSION MODEL

2.3.1 Classical theory

The classical diffusion theory is described by Fick's first law (Fick 1855, Crank 1956), which can be illustrated by considering the control volume in Fig. 3. For a 1-dimensional case in free water, Fick's first law can be expressed as

$$J = -D_w \frac{\partial C_p}{\partial z} \qquad (10)$$

where J is the mass flux of tracer (at./m^2/s), C_p is the concentration of the tracer in water (at./m^3), and D_w is the molecular diffusion coefficient of the tracer in free water (m^2/s). It can be seen that Fick's first law describes stationary mass flow under a time-independent concentration gradient.
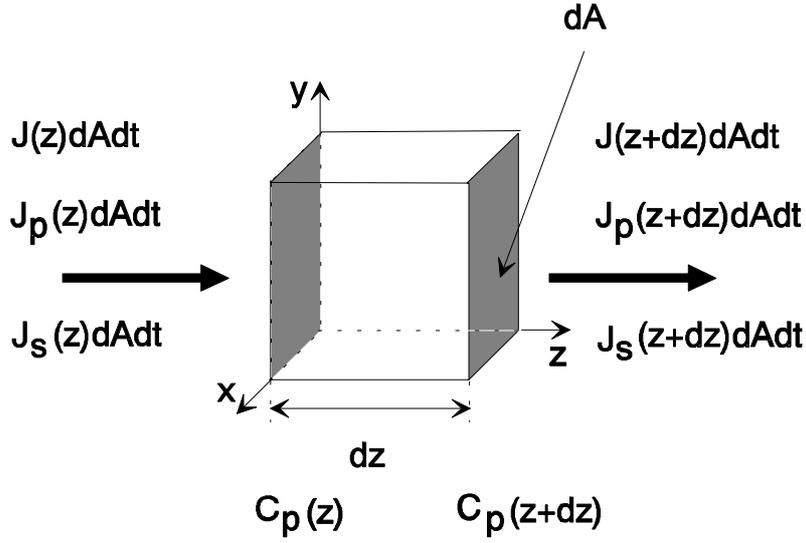
Fig. 3. Control volume for 1-dimensional mass flux considerations. J is the mass flux of the tracer in free water, J_p in the porous matrix, and J_s within the solid.

Assume a matrix of porous material (defined by ε_p, δ_D, τ) to be imposed in the control volume. The mass flux of tracer is now

$$J_p = -\varepsilon_p D_p \frac{\partial C_p}{\partial z} \tag{11}$$

where J_p is the flux of tracer in the porous material. The porosity ε_p is needed on the right hand side, because mass flux can only take place within the pore system; ε_p is also assumed to express the fraction of open pores in the surface over which mass flux is considered, see Fig. 3.

D_p is the diffusion coefficient within the pores [cf. Eq. (5)], and the term $\varepsilon_p D_p$ in Eq. (11) is called the effective diffusion coefficient D_e needed in mass flux considerations ($D_e = \varepsilon_p D_p$). D_e takes inherently into account the point that only the available fraction ε_p of the surface is being considered in mass flux equations, see Fig. 3.

Assume further that distribution coefficient K_d is added to the set of porous matrix characteristics. Applying the principle of conservation of mass, the following mass balance can be established (see Fig. 3):

$$\frac{\partial}{\partial t}\{[\varepsilon_p + (1-\varepsilon_p)K_d\rho_s]C_p\}dzdA = -\frac{\partial J_p}{\partial z}dzdA \tag{12}$$

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where dz is the length of the control volume (m), and dA the surface area through which mass flux is being considered (m^2). The term within the braces on the left hand side is the total concentration, consisting of a dissolved component in the pore water and of an adsorbed component in the solid. Substituting Eq. (11), the previous equation can easily be seen to reduce to

$$\frac{\partial}{\partial t}\{[\varepsilon_p + (1-\varepsilon_p)K_d\rho_s]C_p\} = \frac{\partial}{\partial z}(\varepsilon_p D_p \frac{\partial C_p}{\partial z}) \qquad (13)$$

In this general equation, no assumptions were made concerning the matrix properties. Assuming them to be constant over time and space, one obtains the standard formulation in matrix diffusion studies (Fick's second law):

$$\frac{\partial C_p}{\partial t} = \frac{\varepsilon_p D_p}{\varepsilon_p + (1-\varepsilon_p)K_d\rho_s}\frac{\partial^2 C_p}{\partial z^2} = \frac{D_p}{R_p}\frac{\partial^2 C_p}{\partial z^2} \qquad (14)$$

It can be seen that Fick's second law describes transient mass flow under a time-dependent concentration gradient. The term D_p/R_p on the right hand side is the apparent diffusion coefficient D_a, because it takes into account the physical (geometrical) as well as geochemical (sorption) effects. D_a can be expressed as

$$D_a = \frac{D_p}{R_p} = \frac{D_p}{1 + K_d\rho_s\frac{(1-\varepsilon_p)}{\varepsilon_p}} \qquad (15)$$

Equation (15) shows clearly the role of sorption in matrix diffusion: the more sorption there is, the slower the diffusion. Sorption also clearly increases the amount of tracer that can be accommodated within the rock matrix; the denominator of Eq. (15) shows that for even a weakly sorbing tracer, the sorbed inventory dominates in the rock matrix (the right term dominates for all $K_d > 3.7 \cdot 10^{-7}$ m^3/kg assuming typical values $\rho_s = 2\ 700$ kg/m^3, and $\varepsilon_p = 0.1$ %).

Equation (13) constitutes the classical matrix diffusion theory, and it will be solved under the following initial condition (IC):

$$C_p(z, t = 0) = C_0^{IC} \qquad (16)$$

The initial condition is most often $C_0^{IC} = 0$, indicating that there is no tracer within the rock matrix before diffusion.

Equation (13) will be solved under the following <u>boundary conditions (BC)</u>:

$$C_p(z=0,t) \;=\; C_0^{BC} \tag{17}$$

$$\frac{\partial C_p(z=s/2,t)}{\partial z} \;=\; 0 \tag{18}$$

The upstream boundary condition in Eq. (17) is a Dirichlet-type condition expressing the external source term, and basically it establishes the driving force for matrix diffusion ($C_0^{BC} - C_0^{IC}$). If $C_0^{BC} > C_0^{IC}$ the mass flow is directed from the fracture to the matrix. When $C_0^{BC} < C_0^{IC}$ the direction is reversed. The downstream boundary condition in Eq. (18) is a Neumann-type condition, and it states the reflecting boundary principle, in which the mass fluxes originating from neighbouring fractures meet and cancel each other at the midpoint between the fractures (cf. Fig. 2). Considering one fracture, this is equal to setting a reflecting boundary at a distance of s/2.

Concerning numerical and analytical solutions of the diffusion problem, the difference in their ability to handle heterogeneities can be illustrated with the previous equations. The general model in Eq. (13) can easily be solved numerically, but most analytical solutions are based on Eq. (14). In addition, analytical solutions must usually assume uniform initial and time-independent boundary conditions.

In this work diffusion model is referred to as the "trinity" of process [Eq. (13)], initial, and boundary conditions [Eqs. (16) - (18)]. By this means the uniqueness of the model can be preserved, as e.g. non-uniform initial conditions can induce mass fluxes within the rock matrix even without any external source term.

2.3.2 Variations to the classical theory

The above matrix diffusion model has in some experiments been interpreted as insufficient compared with the experimental observations. Therefore, some variations have been proposed in literature.

Surface diffusion

Surface diffusion assumes, unlike the classical theory above, that the adsorbed inventory is also mobile, and that it can diffuse within the solid at a rate controlled

by a specific surface diffusion coefficient D_s (m^2/s) (Rasmuson & Neretnieks 1983, Skagius 1986, Muurinen 1994, Olin 1994, Ohlsson & Neretnieks 1995). In this case, the surface diffusion induced mass flux of the tracer is, analogously to Eq. (11),

$$J_s = -(1-\varepsilon_p)D_s\frac{\partial C_s}{\partial z} \tag{19}$$

where J_s is the mass flux of the tracer due to diffusion within the solid (at./m^2/s), and C_s is the concentration of the tracer within the solid (at./m^3). The term $(1 - \varepsilon_p)$ is needed on the right hand side, because diffusion can take place only within the solid (i.e. in the "complement" of the pore system).

Assuming sorption equilibrium, C_s can be expressed as

$$C_s = K_d \rho_s C_p \tag{20}$$

Applying again the principle of conservation of mass, the following mass balance can be established for the diffusion within the solid (see Fig. 3):

$$\frac{\partial}{\partial t}\{[\varepsilon_p + (1-\varepsilon_p)K_d\rho_s]C_p\}dzdA = -\frac{\partial J_s}{\partial z}dzdA \tag{21}$$

Substituting Eq. (19), this can easily be reduced to

$$\frac{\partial}{\partial t}\{[\varepsilon_p + (1-\varepsilon_p)K_d\rho_s]C_p\} = \frac{\partial}{\partial z}[(1-\varepsilon_p)D_s\frac{\partial C_s}{\partial z}] \tag{22}$$

In this general equation, no assumptions were made concerning the matrix properties. Assuming them to be constant over time and space, and substituting Eq. (20), one obtains the standard formulation

$$\frac{\partial C_p}{\partial t} = \frac{(1-\varepsilon_p)K_d\rho_s D_s}{\varepsilon_p + (1-\varepsilon_p)K_d\rho_s}\frac{\partial^2 C_p}{\partial z^2} \tag{23}$$

Now the total pore and surface diffusion induced change in the concentration of the tracer per unit time can be expressed as

$$\left(\frac{\partial C_p}{\partial t}\right)_{total} = \left(\frac{\partial C_p}{\partial t}\right)_{pore\ diffusion} + \left(\frac{\partial C_p}{\partial t}\right)_{surface\ diffusion} \qquad (24)$$

which is easily [cf. Eqs. (14) and (23)] led to

$$\left(\frac{\partial C_p}{\partial t}\right)_{total} = \frac{\varepsilon_p D_p + (1 - \varepsilon_p) K_d \rho_s D_s}{\varepsilon_p + (1 - \varepsilon_p) K_d \rho_s} \frac{\partial^2 C_p}{\partial z^2} \qquad (25)$$

which is of the same form as Eq. (14) describing the classical matrix diffusion, only the coefficient term on the right hand side is different. This means in practice that e.g. the same code can be used for both cases. The numerator of the coefficient in Eq. (25) shows clearly the difference between the two components: classical matrix diffusion takes place only along the pores, and surface diffusion only within the solid.

Anion exclusion

The classical matrix diffusion theory does not explicitly take into account the different electrical charges of the tracers: all water-rock interactions of the nuclides are incorporated in the distribution coefficient K_d. The anion exclusion concept states that anions will not see the same pore system as neutral species due to electrical forces caused by the usually negative charge of mineral surfaces (e.g. Valkiainen et al. 1995). Instead, the anions experience electrical repulsion close to the surfaces, while the cations are adsorbed on the mineral surfaces. In the present work anion exclusion is not considered, because only neutral species and cations are studied.

From the modelling point of view, anion exclusion would essentially bring about the concept of species-dependent porosity in the rock matrix, because, in principle, all tracers of different size (or radius of charge) scan the pore space partly differently, especially the most narrow pores. The species-dependent porosity is technically easy to integrate into a numerical migration model; in fact, it has already been programmed into the FTRANS code used in Finnish performance assessments (Vieno 1994, Vieno & Nordman 1996). From the model input point of view, the extended porosity concept would increase considerably the experimental work in deriving the migration data base.

Limited matrix diffusion

In numerous natural analogue studies the experimental observations have shown a clear enrichment of natural radionuclides around water-carrying fractures. The problems met in matching the classical theory with the observed concentration

distributions have led to the proposal of a limited matrix diffusion, a concept in which the whole pore network in the rock matrix is not available for diffusion, but only a small fraction closest to the fracture, cf. Fig. 1. The depth of rock matrix available for diffusion is deduced basically from the zone of enrichment (e.g. Côme & Chapman 1991, Montoto et al. 1992, Miller et al. 1994). Limited matrix diffusion has also been considered in performance assessments, together with traditional "unlimited" cases (Nagra 1994, Vieno & Nordman 1996). Besides conceptually limited matrix diffusion, it is also possible to apply a multilayer rock matrix where the porosity and diffusivities vary as a function of the distance from the fracture surface (Vieno 1994, Vieno & Nordman 1996).

Mathematically, limited matrix diffusion means a simple adjustment in the downstream boundary condition of the classical model, Eq. (18):

$$\frac{\partial C_p(z = d, t)}{\partial z} = 0 \qquad (26)$$

where d is the assumed penetration depth available for diffusion (m), i.e. the distance where the reflecting boundary condition is set (d << s/2), cf. Fig. 2.

In long-term simulations, provided that the penetration depth available for matrix diffusion is small enough, the kinetic matrix diffusion model can roughly be approximated by an instantaneous sorption equilibrium within the available rock matrix. In this case, an "extended" retardation factor can be derived for tracers migrating in the fracture (Hadermann & Rösel 1985, Rasilainen 1986, Rasilainen 1987). Interestingly, by this means matrix diffusion was first taken into account in the early Finnish performance assessments (Peltonen 1987), as the extended retardation factor could be directly applied in standard advection-dispersion models (see also Snellman et al. 1988).

2.3.3 Selection of the reference model

Three variations on the classical matrix diffusion theory were discussed briefly above: surface diffusion, anion exclusion, and limited matrix diffusion. As compared to the variations, the classical theory appears to be the simplest, and it has also the minimum input data need. All variations discussed need at least the same input data base as the classical matrix diffusion model, and, in addition, some variation-specific extra information.

The input data needs of the classical matrix diffusion model can currently be met using established experimental techniques. This is of utmost importance, because only a model with reliably measurable input data can in principle be validated (or

invalidated). Furthermore, the input data base must also be consistent and comprehensively sample-specific for any sample-specific (= non-generic) modelling.

Therefore, the classical matrix diffusion concept was selected as the reference model in the current work. The model development strategy adopted here, is to start with a simple modelling concept, and to refine it gradually according to the conclusions from individual model tests. Thus, the direction of model development is left open, and, for the time being, all variations described above are in principle possible.

The deterministic Fickian model discussed above is by no means the only possible approach to handling the diffusion problem. For instance, the Monte Carlo method provides a stochastic way to simulate the Brownian random walk of individual molecules, or groups of molecules. However, in the case of natural analogues with long time periods and decay chains involved, a stochastic approach would probably lead to very long computing times. The computing time would also depend on the number of particles (groups of molecules) which must be relatively high in order to obtain a statistically representative case.

Fickian diffusion is an averaging simplification of the complex Brownian movement of tracer molecules. Therefore, if the scale of observation approaches molecular dimensions, the prediction power of the model decreases. It must also be kept in mind that the general statement in Eq. (10) is valid only for an isotropic medium, anisotropic media require special treatment, see Crank (1956) for details.

3 NATURAL ANALOGUE OF MATRIX DIFFUSION

Reasoning by analogy is based on the idea that a certain resemblance between two systems makes resemblance in other respects also more probable (e.g. Ewing & Jercinovic 1987, Petit 1992, Ewing 1995). It is essentially an effort to understand the behaviour of a less-known system with the help of a better-known similar system. In scientific inference, the strength of an analogy argument in supporting a theory concerning the less-known system depends, of course, on the degree of similarity between the two systems (see Niiniluoto 1980 for details).

3.1 GENERAL FEATURES OF NATURAL ANALOGUES

A natural analogue can broadly be regarded as an uncontrolled long-term natural experiment leaving a track at the site (IAEA 1989). What makes a "blind" experiment in the geosphere a natural analogue, is its resemblance to the specific process that we are studying. In other words, the natural analogue is defined by the purpose for which the experimental data is studied: a set of data may represent different things to different viewers. Basically, a natural analogue demonstrates that the particular process, in this case matrix diffusion, actually takes place in nature. In other words, a natural analogue shows that the process is not only an abstraction in a mathematical model, or an artefact in a laboratory experiment.

Natural analogues can build confidence in our modelling concepts in various ways that range from qualitative (most frequent) to quantitative (most rare). On the most rigorous level, quantitative model validation, the analogue must, of course, meet quite strict requirements (IAEA 1989). First, the process (i.e. matrix diffusion) should be distinguishable from other processes. Second, the physicochemical parameters should be determinable. Third, the boundaries of the system should be identifiable, so that the mass flows involved can be quantified. Fourth, and most importantly, the process should be datable. In order to avoid circular reasoning, the parameters of the system must be measured by independent means.

The requirements above must, actually, be met by any experiment used for model validation. Considering the general incompleteness of the geological record, however, the requirements are especially demanding for natural analogues. The reasons for this can be illustrated by comparing a laboratory experiment with a natural analogue in a model validation context, see Fig. 4.
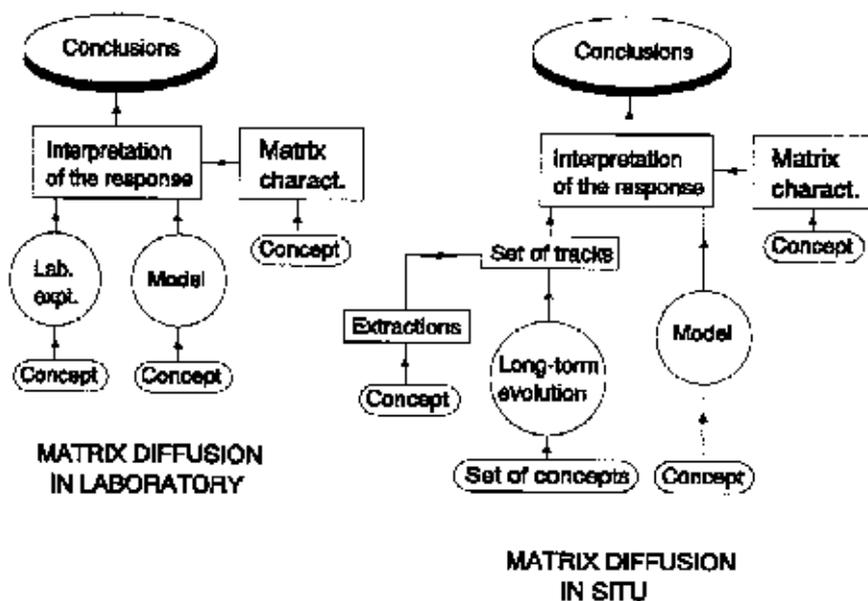
Fig. 4. Comparison of laboratory experiment and natural analogue in validating the matrix diffusion model.

In the figure it can be seen that, in addition to the difference in time scale, the fundamental difference between a laboratory experiment and a natural analogue is that while the former is usually monomechanistic, the latter is strongly polymechanistic consisting of many overlapping tracks of simultaneous and/or successive mechanisms. This makes tracing of the right process in the rock sample (i.e. identifying the right response) quite demanding technically. All models and measurements are based on concepts, and therefore both in laboratory experiments as well as in natural analogues, the concepts must be internally consistent in order to arrive at internally consistent conclusions about the model. In addition, they must be mutually consistent for global validity of the model.

As compared to laboratory experiments, natural analogues can offer some valuable advantages. A natural analogue can provide an inherently consistent *site-specific* data base, which is indispensable in subsequent model validation. An analogue, unlike a laboratory (or field) experiment, can, at least in theory, give information on the relative magnitude and the importance of various simultaneous migration mechanisms, because there has been free competition in situ over long periods of time.

Unfortunately, a natural analogue is often difficult to define in modelling terms. The free competition between mechanisms leads to tracing problems, as mentioned above; furthermore, nature is generally highly heterogeneous and hard to quantify;

time scales involved are usually long making initial and boundary conditions especially difficult to determine.

As compared to natural analogues, laboratory experiments are short-term studies on well-defined, controlled, simplified systems; they are ideal for systematic sensitivity studies. Laboratory experiments are indispensable in studying detailed questions, because the experiments can be tailored for the particular problem at hand. Because laboratory experiments and natural analogues cover different time scales, neither one can replace the other; they can, however, support each other if studied in parallel.

Because the process has already taken place before sampling in a natural analogue, some artefacts hampering laboratory experiments can be avoided, most notably those introduced in sampling and sample preparation. By definition, natural analogues can also avoid the problems caused by oversimplified experimental set-up. Concerning rock matrix characterisation in a model validation situation, natural analogue studies are like any laboratory experiments, see Fig. 4, and they do not suffer from any extra uncertainties.

From the model validation point of view, natural analogues are equally valuable as laboratory (or field) experiments as such; the quality of data is more important than the source. The fundamental advantage of natural analogues is that, despite the problems, they enable the study of long-term processes that cover time periods comparable to those handled in performance assessments (Ewing & Jercinovic 1987, Petit 1992).

3.2 NATURAL RADIOACTIVE DECAY CHAINS

In principle, any natural tracer leaving an observable track will do in a natural analogue, because matrix diffusion, being a physical phenomenon, acts on all substances in the groundwater. Long-lived natural radioactive decay chains provide, however, good tracers for in situ matrix diffusion studies for many reasons.

Uranium is present everywhere in nature, making it, in principle, simple to take samples; the concentrations vary considerably, of course, between e.g. uranium deposits and ordinary uranium-poor surroundings. Due to the radioactivity of the chain members, they are technically easy to observe. High concentrations are, however, easier to measure reliably. All important chain-members are sorbing elements, thus staying in the rock matrix even under disturbances, e.g. due to accidental leaching by drilling fluids during sampling.

In terms of time scale, a decay chain provides a better possibility for a unique solution of the diffusion equation than a single nuclide, because daughter nuclides are generated at a known constant rate. Considering, namely, a single nuclide, the

effective penetration depth of the diffusion front of e.g. long-lived uranium is approximately a function of $[D_a \cdot t]^{1/2}$ (e.g. Neretnieks 1980), and the same solution is obtained for all combinations of the parameters that keep the product in the brackets constant. The decay chain contribution to the uniqueness of time estimate is that e.g. thorium is considered practically immobile under natural conditions, meaning in practice that a low thorium concentration indicates directly a young system, because the thorium must originate from chain decay, see Fig. 5.

Uranium is the most abundant (95 % of the mass) element in spent nuclear fuel. This makes it the most relevant element from the performance assessment point of view, and, consequently, the migration behaviour of uranium has been extensively studied under assumed disposal conditions for performance assessment purposes. Also, for natural analogue studies there is, therefore, a lot of useful laboratory-derived information available.

There are two independent long-lived natural radioactive decay chains that are often used in natural analogue studies: 4n+2 (U-series), and 4n+3 (Ac-series). The simplified versions of these decay chains that include only the longest-lived radionuclides are shown in Fig. 5. More complete presentations of the decay chains can be found in e.g. Kocher (1981).
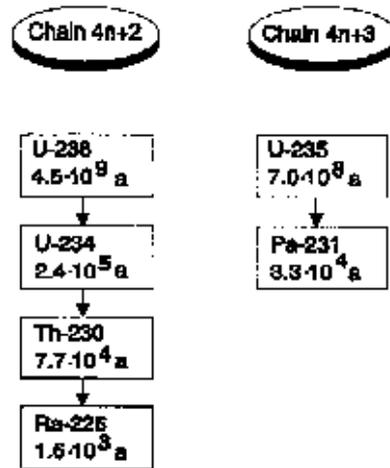
Fig. 5. Simplified presentations of decay chains 4n+2 and 4n+3. The radioactive half-life in years is given below the name of the isotope.

By using natural radioactive decay chains, it is, therefore, possible to work on good tracers as such, but also on the actual isotopes of spent nuclear fuel. In addition, uranium and thorium are good chemical analogues for actinides in general, because

different actinides with the same oxidation state, behave chemically in the same manner.

3.2.1 Radioactive disequilibria

The fundamental feature of a radioactive decay chain system is its continuous evolution towards radioactive equilibrium irrespective of its initial state. Therefore, if the system is isolated, or closed (i.e. there is no mass exchange between the system and its surroundings), it will eventually, depending on the radioactive half-lives of the chain-members, reach steady state, radioactive equilibrium. Strictly speaking, radioactive equilibrium is, actually, a quasi-steady state, because after the long-lived parent nuclide decays, the whole decay chain will vanish eventually. In radioactive equilibrium the activities of chain-members are equal, i.e. all daughter/parent activity ratios = 1. As a result, radioactive equilibrium is a direct indication of a closed system.

On the other hand, in an open system, external mass flows disturb the evolution of the decay chain and cause a radioactive disequilibrium (i.e. daughter/parent activity ratios ≠ 1). The continuous evolution towards steady state is still there[1], but in this case the steady state is deviated from radioactive equilibrium due to the external mass flows. Therefore, radioactive disequilibrium is a direct indication of mass flows into or out of the system, i.e. of an open system.

Radioactive disequilibria of individual daughter/parent pairs need different time periods to equilibrate in a closed system, depending on the respective radioactive half-lives. In other words, the various daughter/parent activity ratios give mass flow information of different time scales (e.g. Ivanovich & Harmon 1982, Rasilainen & Suksi 1992). Table 1 shows the radioactive equilibration times of the most important activity ratios for decay chains 4n+2 and 4n+3. As a rule-of-thumb, approximately five radioactive half-lives of the shorter-lived isotope is enough to equilibrate an activity ratio.

The radioactive equilibration times in Table 1 provide a more precise interpretation of radioactive disequilibria. If an activity ratio ≠ 1, it can be considered as an indication of mass flows of either of the isotopes within the respective radioactive equilibration time. On the other hand, if the activity ratio = 1, it can be considered as an indication of no mass flows within that time.

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[1] The time to reach steady state is slightly different for an open than for a closed system. For instance, a continuous accumulation of mass can be conceptually discretised into successively accumulating individual closed systems. A system accumulated later will, of course, also reach steady state later, and this causes a slightly later overall steady state for an open system.

Radioactive disequilibria are very useful in studying the direction of net mass flows in the system (see e.g. Thiel et al. 1983, and Alexander et al. 1990a for details). Normally U-234/U-238 > 1 in groundwater, and if U-234/U-238 > 1 in rock samples, it is interpreted to indicate accumulation of uranium. If U-234/ U-238 < 1 in rock samples, it is interpreted to indicate preferential release of U-234. Thorium is considered immobile, and therefore Th-230/U-234 is particularly useful. If Th-230/U-234 << 1 in the rock, this can be interpreted to indicate a young system, because Th-230 has not had time to be produced via chain decay. If Th-230/U-234 > 1, it is taken as an indication of recent uranium release from the system.

Table 1. Radioactive equilibration times for some activity ratios in decay chains 4n+2 and 4n+3, from Rasilainen & Suksi (1992).

Decay chain	Activity ratio	Radioactive equilibration time (a)
4n+2	Ra-226/Th-230	8 000
	Th-230/U-234	350 000
	U-234/U-238	1 200 000
4n+3	Pa-231/U-235	160 000

Radioactive disequilibria can also be used for dating quantitatively the beginning of a particular activity ratio evolution (Cherdyntsev 1971, Ivanovich & Harmon 1982). Ivanovich and Harmon (1982) use the term 'uranium-series disequilibria method' in this context (referring to decay chain 4n+2), and in order not to add terminological confusion, the same term is used systematically in this thesis, although here it is extended to cover also decay chain 4n+3.

The possibility to obtain independent time information of the decay chain -matrix diffusion system, or related systems (e.g. fracture coatings), is essential in interpreting natural analogues of matrix diffusion. Therefore, great pains have been taken in this thesis to develop a reliable modelling tool for the radiometric dating. This model development was further inspired by many recent natural analogue studies on matrix diffusion that utilised uranium-series disequilibria (USD) observations.

3.3 SOME NATURAL ANALOGUE STUDIES ON MATRIX DIFFUSION

Currently, there are available in the literature numerous general surveys on natural analogues that include studies in granitic bedrock (e.g. Côme & Chapman 1987, KTM 1988, Alexander & McKinley 1991, Rasilainen et al. 1991, Ménager & Petit 1992, Brandberg et al. 1993, Cramer 1994, Miller et al. 1994, Smellie et al. 1995).

Well-defined natural analogue cases of matrix diffusion that would be suitable for quantitative model testing are, however, very rare. This was actually one of the reasons to start the present study, because matrix diffusion related conclusions often appeared to be drawn without much modelling consideration. In this section, some reported natural analogue studies on matrix diffusion in granite samples are discussed briefly with emphasis on model validation.

Shea (1984) studied the possibility of matrix diffusion as the explanation to the observed uranium concentration distributions within rock matrix around some hydrothermal veins in granitic rock near Marysvale, USA. The modelling consisted of bounding calculations, in which different scenarios for the product $(D_a \cdot t)$ were applied. This was the only possible modelling strategy, as no site-specific data were referred to; reasonable curve fits were obtained. This model calibration exercise indicated broadly that matrix diffusion can explain the observations.

Herzog (1987) developed an analytical diffusion model in an attempt to simulate natural radionuclide distributions in the pore water of drill core samples. The model was basically a 1-dimensional matrix diffusion model for the decay chain segment U-238→U-234→Th-230. It was noted that most experimental studies on rock-groundwater systems were incomplete for modelling purposes. Usually the studies were lacking detailed groundwater analyses (for boundary conditions), rock matrix characterisations, sorption experiments, and especially differentiation of different phases, e.g. pore water and the adsorbed phase.

Jefferies (1987) studied the possibility of matrix diffusion of Cl^-, Br^-, F^- and SO_4^{2-} ions in granite blocks (1.5 m x 1.0 m x 0.6 m) that had been in the sea as wavebreaks at Falmouth, Cornwall for 30 years. The measured concentrations in the pore water were presented as a function of distance across the block. The profiles for Br^- and Cl^- were flat indicating faster equilibration than that indicated by diffusivity measurements, while those of SO_4^{2-} and F^- had a bimodal shape. The conclusion was that the bimodal profiles close to the margins of the rock were due to weathering processes. The blocks had been drained before emplacement, and therefore non-diffusive phenomena, e.g. capillary forces dominated (see also Miller et al. 1994, p. 210).

Valkiainen (1992) studied the effect of changing groundwater regimes on the pore water composition in granitic bedrock, with matrix diffusion as the transmitting mechanism (see also Lehikoinen et al. 1992). The target area was at the island of Hästholmen on the southern coast of Finland. The basic idea was that due to land uplift (currently about 3 mm/a), the originally saline groundwater in the upper part of the island is gradually being replaced by fresh water, as rainwater infiltrates into the bedrock on top of the saline groundwater. Because matrix diffusion is a slow process, pore water acts as a "water archive" preserving its saline imprint long after the flowing groundwater has changed from saline to fresh. The sampled unfractured drill core section (32 - 39 m) was from an interphase zone between two water-bearing fractures. A matrix diffusion model was fitted to the measured chloride concentration profile; the fitted D_a value corresponds to a D_e value that is over an order of magnitude higher than the independently measured value. The conclusion was that an undetected nearby vertical water-conducting fracture could explain the discrepancy (Valkiainen 1992).

Jefferies and Valkiainen used non-sorbing tracers, which, due to their mobility, are sensitive to accidental leaching, e.g. due to drilling fluids during sampling. Fluid inclusions, comprising the isolated residual porosity (cf. Section 2.2) contain some of the measured ions, and may, therefore, be a further problem, because they can be released in the crushing of rock samples, a procedure which belonged to the experimental protocol in both studies. The following studies to be presented use uranium-series nuclides as tracers, which are less sensitive in this respect, because the radionuclides are sorbed on the pore surfaces. All the following studies are based on parallel measurements of many variables as a function of distance from the fracture face. USD measurements are supplemented and supported by e.g. rare earth elements (REE), Fe^{2+}/Fe^{3+} analyses, α-track autoradiography, fission-track analysis, and detailed mineralogy.

Smellie et al. (1986a, 1986b) studied migration of uranium-series nuclides in three 40 - 55 cm drill core sections of granitic rock, each containing a fracture. The drill cores originated from Kråkemåla in Sweden, and from Böttstein and Grimsel in Switzerland. The results for Kråkemåla were also presented in detail in Smellie et al. (1984). The Kråkemåla and Böttstein samples showed radioactive disequilibria indicating uranium migration over the whole core section within one million years; thorium was concluded to have been immobile. Uranium migration was classified into movement from granite to fracture and vice versa, although they were not considered mutually exclusive. For the movement from fracture into rock matrix, a limit of about 3 cm was suggested. It was stated that previous hydrothermal processes could be an important prerequisite for this movement due to the enhanced porosity around the fracture. The Grimsel sample was concluded to be intersected by a young fracture, and therefore no uranium mobility could be seen. No migration

modelling was referred to, the analysis was based on qualitative interpretation of the concentration and activity ratio profiles of uranium-series nuclides along the drill cores.

Alexander et al. (1990a) made a more detailed study of the same drill core sections as above, and added an extra granodioritic drill core section from Grimsel. This core, like the others, was intersected by a water-bearing fracture. A quantitative model was developed for the evolution of uranium-series disequilibria. This model was the main tool in interpreting the concentration and activity ratio profiles of uranium-series nuclides. Clear radioactive disequilibria were found in all drill core sections studied, and the conclusion was that at least some of the decay chain-members had migrated in all of them. Besides matrix diffusion, advection was also suggested as a possible migration mechanism in the rock matrix. This conclusion was based on scoping calculations of the penetration depth of diffusion into the matrix. Because the penetration depth calculated using some of the literature-derived diffusivities was clearly shorter than the observed depth of migration, advection could not be ruled out. The observations were seen in the context of the limited matrix diffusion concept used in Swiss performance assessments.

Alexander et al. (1990b) made a separate study on the granodioritic drill core section from Grimsel to clarify specifically the transport of Ra-226 in the drill core. They found, using again scoping calculations for the penetration depth of Ra-226, that matrix diffusion could explain the observed concentration profiles.

Montoto et al. (1992) made an extensive experimental effort to observe diffusion-related phenomena in granitic rock samples adjacent to water-conducting fractures. The numerous rock samples studied originated from el Berrocal in Spain, Stripa in Sweden, Whiteshell in Canada, and Grimsel in Switzerland. Additional samples were taken from three sites in Spain. The results were presented as a function of distance from the fracture. In all samples, a zone of uranium enrichment was associated with microstructural alteration adjacent to fractures. It was concluded that diffusion appears to have taken place where physical properties have changed most, i.e. close to the fracture. The radioactive disequilibria were analysed qualitatively.

Heath (1995) continued the previous study and concentrated on three drill cores from el Berrocal. Uranium microcartography using fission-track analysis and α-autoradiography indicated three modes for uranium occurrence in granite: 1) dispersed sources within primary phases, 2) point sources within accessory minerals, and 3) linear distributions within microfractures. It was noted that this distribution must be understood in order to interpret the isotopic data correctly. The radioactive disequilibria were interpreted qualitatively. A generic matrix diffusion modelling effort was included in the study, and the overall conclusion was that simple matrix

diffusion has not taken place, but the observed uranium-series profiles result from complex diffusion and chemical interactions within a zone of structural change adjacent to fractures.

Summary of the uranium-series studies

In the uranium-series studies above, radioactive disequilibrium was observed along the drill cores, which directly indicates mobility of the respective nuclides. In most drill cores there was a radioactive enrichment zone and an altered zone co-located adjacent to the fracture, and these appear to have been the grounds for the limited matrix diffusion conclusion drawn in most studies. No diffusion modelling with site-specific input data was conducted, however. Some generic simulations were done, and the results of these actually contradicted the limited matrix diffusion statement (Herzog 1987, Alexander et al. 1990a, 1990b). Therefore, the presented conclusion about the limited validity of the matrix diffusion concept appears strong as compared to the reasoning given. In spite of this, the current study could use many observations and experiences of these earlier investigations as a starting point.

The uranium-series studies reviewed above were all quite extensive experimentally, and especially at el Berrocal it is unfortunate that there were no serious diffusion process related considerations that would have taken into account the kinetics of matrix diffusion, because the material was quite interesting. Instead, the efforts were focused on justifying the concept of limited matrix diffusion (Montoto et al. 1992, p. 96).

4 IN SITU TESTING METHODOLOGY

Natural analogues provide a way to test the matrix diffusion model against *in situ* observations over long periods of time. This kind of model testing includes, therefore, comparison of measured and simulated matrix diffusion in situ. Relevant experimental observations can be provided by measured concentration profiles of natural long-lived radioactive decay chains around water-carrying fractures. To obtain the corresponding simulated concentration profile, one needs site-specific input data, because the model is universal and all site-specific features are entered into the simulations via the input data. This necessitates careful characterisation of the site and the rock sample.

To facilitate in situ testing of the matrix diffusion model, a procedure was developed that combines concentration profile measurements, rock matrix characterisations, and concentration profile simulations. In the following, this testing approach is referred to as the concentration profile method, as the model testing is essentially reduced to comparing measured and modelled concentration profiles.

4.1 CONCENTRATION PROFILE METHOD

The concentration profile method is based on systematic comparison of measured and simulated concentration profiles within the same rock sample. Concentrations of radionuclides belonging to the long-lived natural decay chains 4n+2 and 4n+3 are measured as functions of distance from the water-carrying fracture, and the profiles so obtained are used as experimental references for matrix diffusion simulations.

The rock samples available from site investigations are most often drill core sections. In order to measure a concentration profile as a function of distance from the water-carrying fracture, the drill core section is usually cut into slabs parallel to the fracture plane. The subsamples so obtained will also be used in subsequent experimental rock matrix characterisation to obtain corresponding distance-related input data for simulations.

The input data for the simulation model are obtained from independent experimental studies; this independence ultimately enables an "honest" comparison with the measured concentration profiles. In particular, because of the mutual independence, one can avoid circular reasoning in model testing (input data could of course technically be derived from model fits, but that would be a circular argument). The independence, actually, enables one to predict concentration distributions in the rock samples, because the measured concentration profiles are needed only after the simulations. In that sense, the concentration profile method resembles "blind" prediction.

The currently available experimental rock matrix characterisation techniques support 1-dimensional modelling. This is approximative, but, however, good enough, because the measured concentration profiles are also 1-dimensional.

4.1.1 Measured concentration profiles

Measured radionuclide concentrations within the rock matrix around a water-carrying fracture are obtained by sequential extractions of the rock subsamples using more and more aggressive reagents in a step-wise manner. In this way, radionuclide inventories in each subsample can be presented as fractions depending on how loosely bound in the rock material they are. Sequential extractions are one of the very few experimental methods available for this kind of selective work. Details of the extraction techniques used can be found in Publication 1 in this thesis, and Suksi et al. (1994). The extraction technique consists of successive phase-selective extractions, and the term 'phase-selective extractions' is also used in this work to emphasise the selective nature of an individual extraction step.

The most loosely bound inventory is assumed to be the adsorbed radionuclide inventory, and it is thus mobile in the sense of the matrix diffusion model. Because sorption does not separate different uranium isotopes, the U-234/U-238 activity ratio in the extracted phase should equal that in the water, if the extracted phase represents the adsorbed inventory. This fact offers a feasible means to check whether sorption was actually seen in the extracted phase.

The concentrations representing the most loosely bound radionuclide inventories in the rock matrix are presented as functions of distance from the water-carrying fracture. This profile of the mobile inventory is assumed to represent matrix diffusion in situ in the sense of the model, and is subsequently used as the experimental reference for simulated concentration profiles.

4.1.2 Simulated concentration profiles

Simulated concentration profiles within the rock matrix are obtained by applying the standard 1-dimensional matrix diffusion model on a drill core sample taken around a water-carrying fracture. The input data are site-specific, and matrix properties are, in fact, sample-specific. The 1-dimensional modelling brings about certain approximative features, as compared to the real 3-dimensional situation. The measured matrix properties, presented as functions of distance from the fracture, represent weighted averages over the whole cross section of the drill core sample. Also, in the direction of the diffusion, the matrix properties represent averages over the characterised length of the rock sample. This results in an averaged smooth

progress of the simulated diffusion profile over the whole sample, while in 3-dimensional reality, the progress of a diffusion profile can be uneven and highly channelled, due to the natural heterogeneity of the rock matrix even within the scale of the drill core sample. Fig. 6 shows the general procedure of simulating concentration profiles.
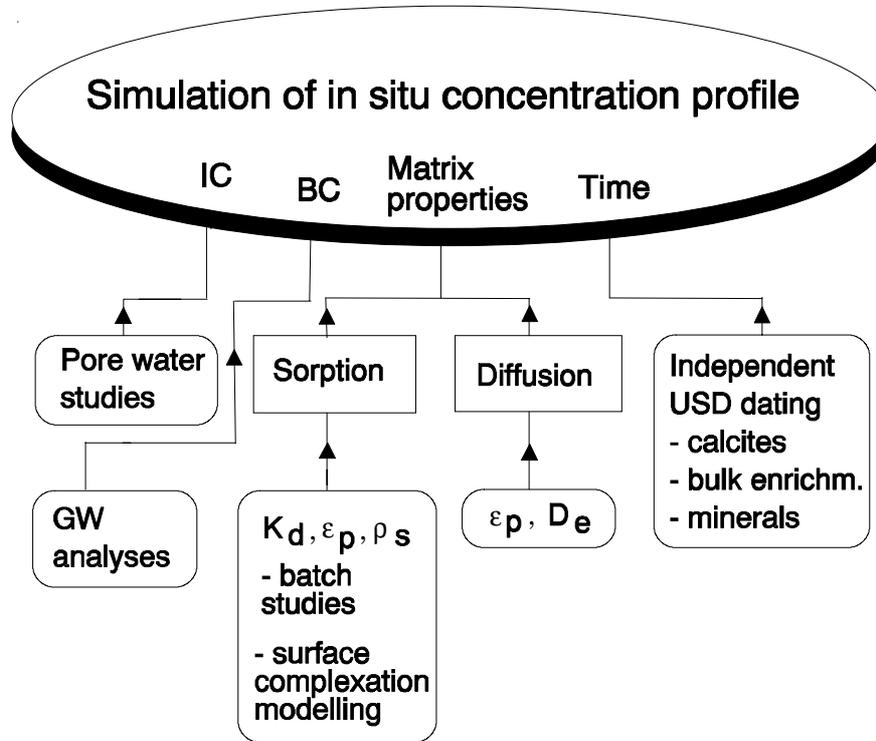
Fig. 6. Simulation of an in situ concentration profile. IC stands for initial condition, BC for boundary condition, and GW for groundwater.

Initial condition (IC) means the initial nuclide-specific concentrations in the pore water at the time matrix diffusion starts. So far, no direct pore water studies have been conducted, as the drill core samples had already dried before these matrix diffusion studies. Of course, current pore water data would only serve as a basis to estimate the initial condition: they do not necessarily as such represent past conditions. Indirect methods, e.g. in connection with sorption studies, can shed light on the possible pore water concentrations. Due to lack of data, 0-concentrations are normally assumed, that is, no nuclides are assumed to exist in the system before the diffusion starts. Sensitivity analyses, using different initial values, provide a method to quantify the effect of initial condition.

Boundary condition (BC) means the nuclide-specific concentrations in the groundwater flowing in the fracture. This information is obtained from detailed groundwater analyses at the natural analogue site. Considering the long time scales

involved, an inevitable question with the boundary condition, is its possible time dependence. Standard site investigations give at best the current situation, but we know that at Finnish latitudes fundamental changes have occurred in the form of repeated glaciations. Paleohydrogeological studies are one means to obtain insight into this problem.

Matrix properties are obtained by experimental studies independent of those yielding the measured concentration profiles, which, in fact, facilitates a genuine comparison between simulated and measured concentration profiles. The characterisation of the rock sample in terms of the matrix diffusion model includes first porosity and diffusivity measurements (ε_p, D_e). Sorption characterisation means in practice either K_d or isotherm [$K_d(C)$] determination via batch experiments and/or mechanistic sorption modelling, e.g. surface complexation modelling. The density of the solid ρ_s is also measured; in practice the values for granite have proved to be consistently very close to 2 700 kg/m^3.

The often occurring heterogeneity in rock matrix properties (ε_p, D_e, K_d) can be described as a function of distance from the fracture. The respective resolutions of rock matrix characterisation techniques (see e.g. International Society for Rock Mechanics 1979) determine in practice how accurately the heterogeneity can be described. The minimum physical sample size that can be characterised by all methods, is the largest of the respective minimum sample sizes for ε_p-, D_e-, and K_d-determinations. The method with the lowest spatial resolution thus determines the overall resolution in rock matrix characterisation, and, therefore, also the actual spatial resolution in the simulations. In numerical models the heterogeneous matrix properties are described in a discretised manner by elementary volumes that are internally homogeneous, but may differ from one another; the resolution of such a description depends directly on the overall resolution in the original rock matrix characterisations.

Time scale is usually difficult to quantify in natural analogues, because there is no direct information available. The indirect information can comprise independent uranium-series studies aiming to date radiometrically the evolution of the radioactive disequilibria observed. In addition to USD methods, there is a whole spectrum of traditional paleohydrogeological methods, that all give independent time information (NEA 1993). USD datings appear, however, the most natural choice here, because matrix diffusion observations are also based on uranium-series measurements. Independent dating considerations are emphasised in this thesis, due to the importance of time information in matrix diffusion modelling (IAEA 1989).

The simulated concentration profiles represent the solution of the diffusion model at the end of the simulation time. From the modelling point of view, D_a (i.e. ε_p, D_e, and K_d) and simulation time together adjust the depth of the simulated diffusion profile

in the rock matrix. Element-specific K_d values, on the other hand, scale alone the respective heights of the simulated diffusion profiles: the absolute concentration in the rock matrix (at./kg) is derived directly from concentration in the pore water (at./m^3) by multiplying by K_d. Closest to the fracture, concentrations in the pore water reflect directly the boundary condition, but deeper in the matrix, chain decay must be taken into account.

4.2 MODELLING TOOLS

In the present study, two codes formed the basic modelling toolbox. Numerical migration model FTRANS (INTERA 1983, Rasilainen 1989) was used to simulate the actual diffusion of natural radioactive decay chains within the rock matrix. Uranium-series disequilibria code URSE (Rasilainen & Suksi 1992, 1997) was used for independent uranium-series datings.

In this work the emphasis is on the validation of the matrix diffusion concept. The codes are, therefore, seen pragmatically as simple modelling tools, with the most important criterion being that they are verified, i.e. that they solve the basic equations correctly. But beyond that, the codes are not considered as research topics themselves. Consequently, the specific mathematical techniques applied in them are discussed only briefly below. Furthermore, from the mathematical point of view, the diffusion equation is relatively well-behaved.

FTRANS

FTRANS is a 2-dimensional code that can simulate groundwater flow, and transport of radioactive decay chains in porous or fractured medium. In the present work, the migration part of the code was employed, and of it, the porous medium approach. Diffusion, coupled with sorption, was assumed as the only migration mechanism in the rock matrix. The 1-dimensional transport equation applied in this work is based on the diffusion model in Eq. (13) and on chain decay in the form of a linear parabolic second order partial differential equation:

$$\frac{\partial}{\partial t}\Big[R_{p,i}\,\varepsilon_p\,C_{p,i}(z,t)\Big] = \frac{\partial}{\partial z}\bigg[D_e\,\frac{\partial C_{p,i}(z,t)}{\partial z}\bigg] - \lambda_i\,R_{p,i}\,\varepsilon_p\,C_{p,i}(z,t)$$

$$+ \ \lambda_{i-1}\,R_{p,i-1}\,\varepsilon_p\,C_{p,i-1}(z,t)$$

(27)

where t is time (s), z is the distance from the fracture surface (m), $C_{p,i}(z,t)$ is the concentration of nuclide i in pore water (at./m^3), $R_{p,i}$ is the retardation factor of nuclide i in the rock matrix [see Eq. (9)], and λ_i is the decay constant of nuclide i (1/s). Nuclide i - 1 is assumed to decay into nuclide i. In principle, diffusion is 3-dimensional, but due to practical limitations in matrix characterisation methods, we

have good experimental grounds only for 1-dimensional discussion, a fact which makes FTRANS suitable for these studies.

Actually, Eq. (27) represents a group of coupled differential equations with the chain decay generation term [last term in Eq. (27)] acting as the coupling factor; the number of equations in the group equals the number of nuclides in the decay chain. FTRANS solves Eq. (27) for the concentrations in the pore water $C_{p,i}(z,t = t_{sim})$, where t_{sim} is the simulation time (s). To facilitate direct comparison with the measured concentration profiles, $C_{p,i}(z,t = t_{sim})$ is converted to represent concentration in the rock matrix $C_{r,i}$ (at./kg) by multiplying with K_d value: $C_{r,i}(z,t = t_{sim}) = C_{p,i}(z,t = t_{sim}) \cdot K_{d,i}$.

Mathematically FTRANS is based on the finite element method (FEM). Time integration is based on two optional finite difference methods: either Crank-Nicolson, or fully implicit backward difference schemes; in the present work Crank-Nicolson time stepping was used. The numerical techniques of the code are shown in detail in INTERA (1983). FTRANS has been thoroughly verified in the INTRACOIN Project (SKI 1984, INTERA 1986), and in the INTRAVAL Project (Jackson 1994), and also in various in-house exercises (Rasilainen 1989, Vieno 1994).

FTRANS is well suited for the matrix diffusion problem at hand basically due to two factors. First, the description of heterogeneous matrix properties can be done easily; here the spatial resolution of the experimental methods, which provide the original data, is the limiting factor in the description. Second, the flexibility in handling initial and boundary conditions enables the simulation of various non-uniform and time-dependent systems, respectively; also in this case, the availability of reliable experimental data is the limiting factor in the practical simulation, not the degrees of freedom in the code.

FTRANS was further developed in the course of the work. The first conceptual improvement was the possibility to simulate an arbitrary 4-member decay chain instead of the original three members. Actually, if an external time-dependent source term is provided, then the decay chain length can be arbitrary. The second new conceptual feature was the option to handle arbitrary sorption isotherms.

Sorption isotherms are presented as nuclide-specific input tables [$K_d(C_p)$], and in the simulations K_d values are calculated continuously as a function of time. During each time step, the K_d values are calculated in all nodes by using linear interpolation. With this technique the original calculation logic of FTRANS can still be utilised, because essentially, the K_d values, that also originally could be space-dependent, are simply expanded to cover also time dependence: $K_d(z) \rightarrow K_d[C_p(z,t)]$. The non-linearity, introduced by sorption isotherms into the diffusion equation [Eq. (27)], is

approximated in a piece-wise manner assuming that the K_d is constant within each element for the duration of the time step.

URSE

Computer code URSE was developed in the course of this work to simulate the evolution of an arbitrary 4-member radioactive decay chain in a closed or an open system (Rasilainen & Suksi 1992, 1997). URSE was used in various radiometric dating studies of matrix diffusion, or in related decay chain systems to provide independent insight into the time scale for matrix diffusion simulations, see Fig. 6. Decay chain systems related indirectly to matrix diffusion can e.g. include uranium accumulated into fracture calcites, or α-recoil induced mass fluxes across mineral phases: recoil fluxes can e.g. be triggered by uranium accumulation into the system.

In a <u>closed system</u> mass flow is assumed to be instantaneous, after which the system is simply controlled by Bateman equations (Bateman 1910):

$$\frac{dC_i}{dt} = -\lambda_i C_i + \lambda_{i-1} C_{i-1} \tag{28}$$

where C_i is the concentration of nuclide i (at./m^3). Also here, nuclide i - 1 is assumed to decay into nuclide i. Instantaneous accumulation or release of material can be simulated by this model via the initial condition.

In an <u>open system</u> mass flows are assumed to be continuous, and for *continuous accumulation* of material, the Bateman equations are modified into

$$\frac{dC_i}{dt} = -\lambda_i C_i + \lambda_{i-1} C_{i-1} + R_i^+ \tag{29}$$

where R_i^+ is the constant accumulation rate of nuclide i (at./m^3/s). For *continuous release* of material the equation is

$$\frac{dC_i}{dt} = -\lambda_i C_i + \lambda_{i-1} C_{i-1} - r_i^- C_i \tag{30}$$

where r_i^- is the constant release factor of nuclide i (1/s).

Equations (29) and (30) are referred to as continuous accumulation and release models, respectively, because of an established terminology (e.g. Thiel et al. 1983, Latham & Schwarcz 1987, Alexander et al. 1990a), although both these open system

models can, strictly speaking, be used to simulate continuous accumulation or release of material, with an appropriate sign for the mass flow term. The real difference between the models is that in Eq. (29) the accumulation/release rate is constant in time, while in Eq. (30) it depends on the time-dependent concentration.

Each of the three submodels above [Eqs. (28) - (30)] are actually a group of coupled ordinary differential equations, with the number of equations equalling the number of members in the decay chain; the chain decay generation term acts as the coupling factor. An exact analytical solution was derived for the submodels. In the solution, no approximations were used concerning the radioactive half-lives of the nuclides, neither were any assumptions made concerning the magnitude or direction (i.e. accumulation/release) of mass flows of individual chain-members. Therefore, the analytical solutions can be regarded as general; the individual solutions were tested extensively against reported cases in the literature (Rasilainen & Suksi 1992).

The analytical solutions were programmed into the computer code URSE by applying the modularity principle, which makes the code very flexible in use. The rate of accumulation/removal of any nuclide is independent of that of the other members of the decay chain, allowing e.g. different mass flow directions (accumulation/release) for members within the same decay chain. If used in discretised form, the continuous accumulation submodel, Eq. (29), can approximate any form of accumulation/removal function. An unlimited number of basic mass flow episodes can be combined into a continuous mass flow scenario, because the output of one mass flow episode is used as the initial condition for the next one. For practical modelling, the properties of URSE offer, therefore, a versatile combination of accuracy and flexibility.

Besides matrix diffusion related studies, reported here, URSE has also been tested in studies of the stability of secondary uranium minerals (Finch et al. 1995, 1996).

5 MODEL TESTS USING NATURAL ANALOGUES

The model testing methodology formulated in the previous chapter was applied to in situ observations at two Finnish natural analogue sites: the uranium-thorium deposit at Palmottu, and a boulder sample near Hämeenlinna. The applications took the form of repeated model validation attempts using the data available at each time. This process of iterative validation attempts is believed to converge to a well-founded modelling concept. For both sites, the individual model tests are summarised in chronological order below, thus also documenting a learning process, with the first tests mainly focusing on the feasibility of the methodology.

Concerning the samples, the strategy was to start with only a few samples and study them as thoroughly as possible, rather than to try to progress immediately on a wide front. In other words, the strategy was to test the feasibility of the methodology before "production runs". Furthermore, the methodology comprises various theoretical (and experimental) aspects, and for practical reasons, these were tested and discussed by turns in the individual validation attempts, rather than all in one go.

The present work focuses on the model validation aspects in general, and on the simulation of concentration profiles in particular; the details of experimental methods fall outside the scope of this thesis. Independent USD dating of the matrix diffusion, or related decay chain systems, is emphasised in this study, because it can greatly support the matrix diffusion simulation.

5.1 PALMOTTU NATURAL ANALOGUE SITE

The natural analogue site at Palmottu in south-western Finland comprises a uranium-thorium ore deposit located in the granitic bedrock. The mineralisation extends from ground surface to at least the currently drilled depth of 250 m in an irregular and discontinuous geometry. The deposit contains about a million tonnes of uranium ore with the average grade being 0.1 %. The age of the deposit is approximately 1.7 - 1.8 Ga (Blomqvist et al. 1995).

Being located at various depths and geochemical conditions within the fractured bedrock, the deposit covers structurally, mineralogically and geochemically the same spectrum of physicochemical conditions as expected at disposal depth, and above, for a spent nuclear fuel repository in a crystalline bedrock.

The mineralisation is intersected by a regular mesh of parallel drill holes, that were drilled for ore prospecting purposes in the late 1970's and early 1980's. For this

reason they are of varying length. Natural analogue studies have been pursued at Palmottu since 1988, and the results of these investigations provide the general background information for the current matrix diffusion studies. The matrix diffusion samples taken for this study are shown in Fig. 7.
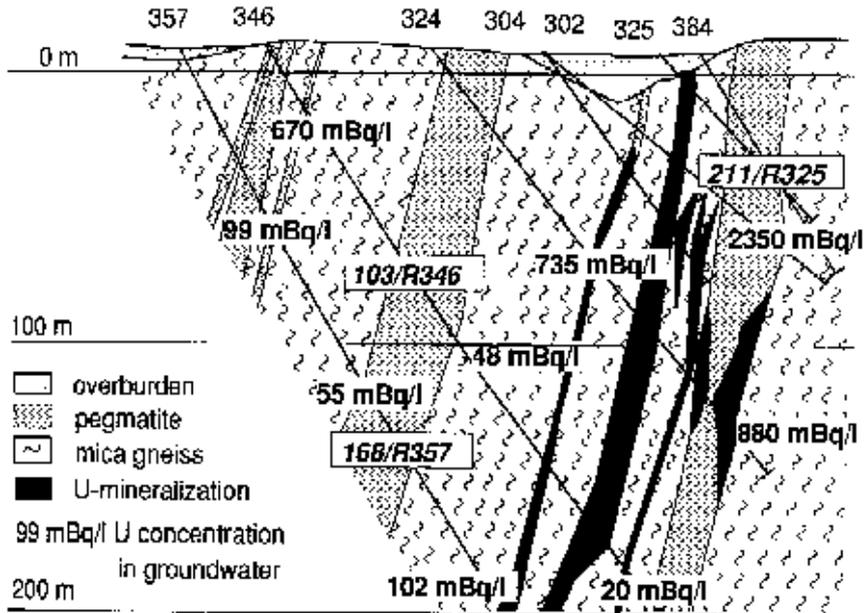
Fig. 7. Cross section of the bedrock along the line of the sampled drill holes at Palmottu. The letter 'R' in the sample codes (in italics) refers to the drill hole. Modified after Ahonen et al. (1994).

The drill core samples taken for this study were all from outside the mineralisation, so that it can be assumed, in line with the matrix diffusion concept, that the radionuclides have been transported along the fractures by the flowing groundwater, from which the subsequent diffusion into the rock matrix has taken place. All samples contain at least one fracture.

The measured concentrations of the readily dissolved uranium are shown in Fig. 8 as functions of distance from the fracture for the three matrix diffusion samples. In order to be able to compare the uranium concentrations in all rock samples discussed in this work, the respective uranium concentration distribution is also shown for the boulder sample. It can be seen that in samples 211/R325 and 103/R346 there is a clear uranium enrichment close to the fracture, in line with observations in many earlier natural analogue studies reported in literature. The boulder sample, in

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contrast, shows a clearly different pattern in that it contains a pulse-like concentration distribution. Sample 168/R357 is bounded by two fractures, and it does not show any concentration gradient.
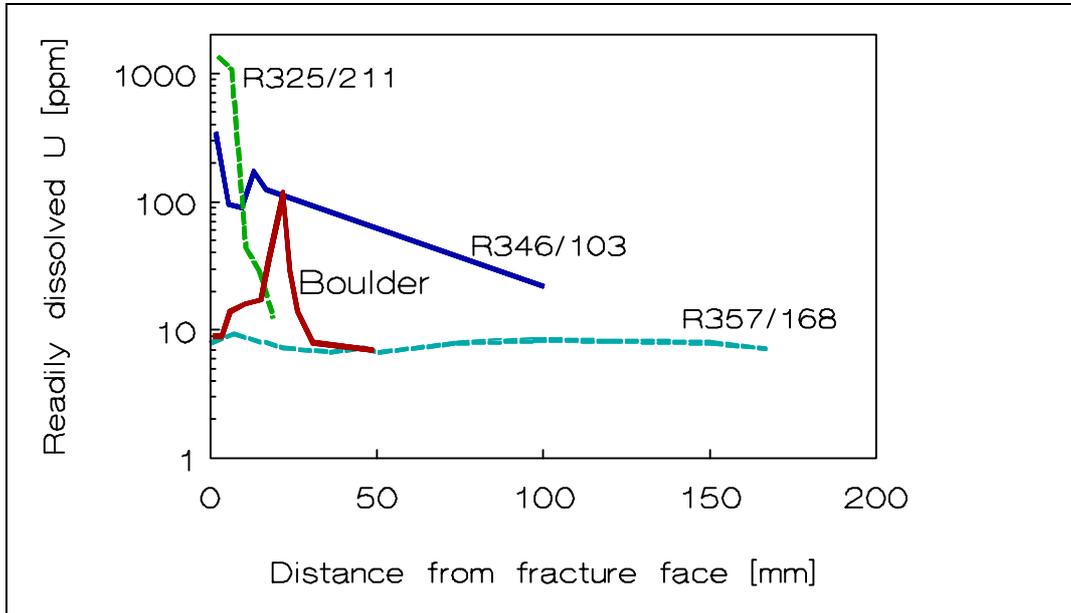
Fig. 8. Measured concentration distributions of the readily dissolved uranium vs. distance from the fracture in the three matrix diffusion samples (211/R325, 103/R346, and 168/R357). For comparison, the corresponding distribution is presented also for the boulder sample (Suksi et al. 1995). The concentrations for sample 211/R325 are based on selective subsampling of the uranium-containing minerals, while those of the others are whole rock values.

In the following model tests one should keep in mind that the experimental reference for sample 211/R325 represents, in fact, only the subsampled minerals. It can, however, easily be converted into a whole rock reference, which is conceptually in line with the model, by multiplying by the abundance of the subsampled minerals. The effect of this down-scaling will be assessed in the discussion of Publication 4.

Normally, matrix diffusion is considered as the only migration mechanism in a rock matrix. Notwithstanding, in order to test the possible significance of advection, as compared to diffusion, in the rock matrix at Palmottu, a simplistic analysis based on Darcy's law was conducted, see Appendix A; advection has earlier been suggested by Alexander et al. (1990a). In the analysis, the rock matrix was simply interpreted as an ideal porous medium with a determinable permeability, located at Palmottu with known hydraulic gradients. The site-scale hydraulic gradients were assumed to extend through the pore water in the rock matrix. The study indicated that, as

compared to diffusion, advection is probably a minor migration mechanism in the rock matrix, thus increasing the argument for a matrix diffusion case.

5.1.1 Tests with samples from Palmottu

Publication 1 (Appendix B) documents the first quantitative effort to interpret the concentration distributions in the rock matrix around water-carrying fractures at Palmottu. Therefore, the overall aim was to test the part of the concentration profile method that yields the experimental reference.
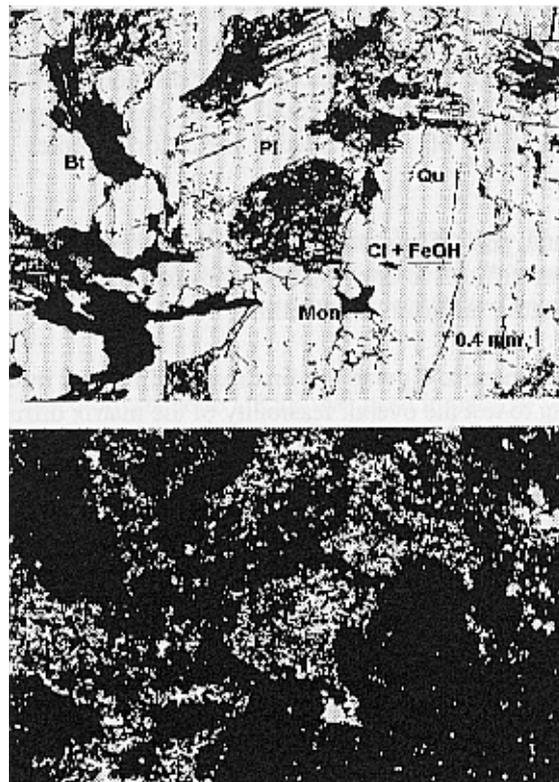
Fig. 9. Distribution of radioactivity in a subsample of sample 211/R325. The photomicrograph above shows the mineral composition: Qu = quartz, Pl = plagioclase, Cl + FeOH = intensely altered plagioclase grains containing clay minerals and iron oxyhydroxides, Bt = biotite, Mon = monazite. The respective autoradiograph below shows the distribution of α-activity (white points). Altered plagioclase and biotite appear to act as sinks for secondary activity, while quartz is practically free of activity.

Besides grain boundaries, radioactivity within the rock samples was observed to be concentrated in altered minerals, wherever present. These minerals, therefore, appear to act as strongly sorbing sinks along the connecting pore system, because they were more or less isolated and did not form continuous altered channels. The co-location of uranium enrichment and a zone of altered rock close to the fracture is, again, in line with observations in many earlier natural analogue studies. The actual distribution of α-activity within a subsample from sample 211/R325 is shown in Fig. 9.

Uranium-series disequilibria code URSE was developed and verified (Rasilainen & Suksi 1992). The modelling aim in this exercise was to test quantitatively the feasibility of the USD method in a matrix diffusion case; the idea was obtained from similar studies in the literature (e.g. Smellie et al. 1986a, Alexander et al. 1990a). The closed system model was used, as it is the simplest possible. The experimental data base comprised measured concentration profiles of decay chain 4n+2 for samples 211/R325 and 103/R346.

The experimental part of the concentration profile method worked well. It proved, however, difficult to draw matrix diffusion related conclusions without actually doing matrix diffusion simulations.

Publication 2 (Appendix C) was the first matrix diffusion modelling effort at Palmottu, aiming to test the overall feasibility of the matrix diffusion concept as a possible explanation for the measured concentration profiles.

Migration code FTRANS was further developed to handle an arbitrary 4-member decay chain. Homogeneous and heterogeneous matrix concepts, and time-dependent as well as time-independent boundary conditions were tested. The heterogeneous matrix concept comprised an altered zone close to the fracture, with increased porosity and diffusivity, followed by a virgin zone deeper in the rock matrix. The K_d values used were simply obtained by dividing the respective concentrations in the rock matrix by those measured in the groundwater.

The experimental data base included measured concentration distributions for decay chains 4n+2 and 4n+3 (sample 211/R325), and uranium-series measurements in groundwater at Palmottu as well as reported data for other sites in Finland. Otherwise, the model input data were derived from literature, and they were considered reasonable as such. A model calibration for decay chain 4n+2 using a homogeneous rock matrix concept and time-independent boundary condition is shown in Fig. 10.
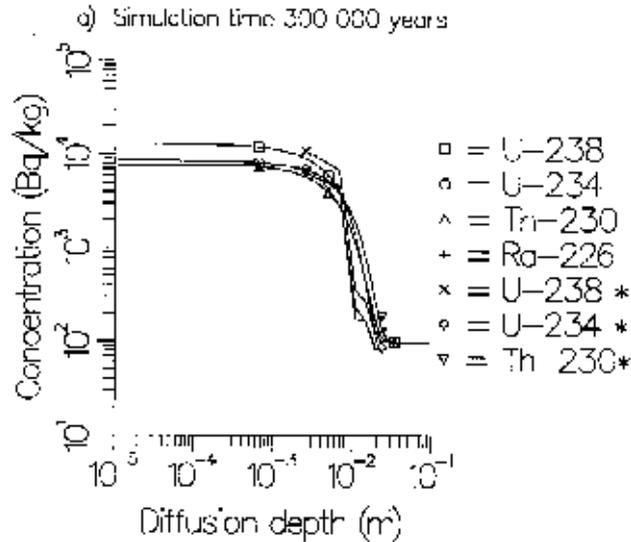
Fig. 10. Model calibration for decay chain 4n+2 in sample 211/R325 applying a homogeneous rock matrix concept and time-independent boundary condition. Simulation time is 300 000 a. The measured concentration profiles are denoted with asterisks (*).

Uranium-series disequilibria code URSE was used in parallel with FTRANS to simulate a time-dependent boundary condition. The aim of this scenario was to outline the effect of repeated glaciations on the concentration profiles. Uranium concentrations in groundwater were varied synchronously with glaciation cycles, with the variation between glaciation and interglacial being two orders of magnitude (current local variation at Palmottu).

The model calibration exercise was successful, and indicated that matrix diffusion can be the reason for the observed concentration profiles. The hypothetical "glaciation scenario" indicated that periodical changes in the boundary condition are smoothed effectively deeper in the concentration profile ($\geq$ 5 mm from fracture surface), because diffusion is very slow, due to the high K_d values used (e.g. 13 m^3/kg for uranium), and long-term average concentrations seem to control the process.

Publication 3 (Appendix D) was a direct continuation to the previous study, with the aim of scanning in more detail the possibilities for matrix diffusion modelling, and with an eye to input data availability, as well as identifying areas for more detailed studies in the future.

Migration code FTRANS was used for matrix diffusion simulations applying a heterogeneous rock matrix concept. The experimental data base consisted of that of

the previous study, and of measured values for ε_p (0.1 - 0.2 %) and D_e (2 - 3 $\cdot$ 10^{-13} m^2/s) for the rock matrix with the bounding values representing the virgin and altered zones, respectively, and mineralogical analysis of the rock matrix. Measured sorption data were not available, and, therefore, sorption was studied by means of sensitivity analysis. An extensive intercomparison study of methods for porosity measurements was initiated in order to obtain quality controlled porosity data for the matrix diffusion model (Rasilainen et al. 1996). USD code URSE was used to date radiometrically the measured uranium accumulation within a fracture calcite sample removed from the same fracture surface (sample 211/R325), see Fig. 11.
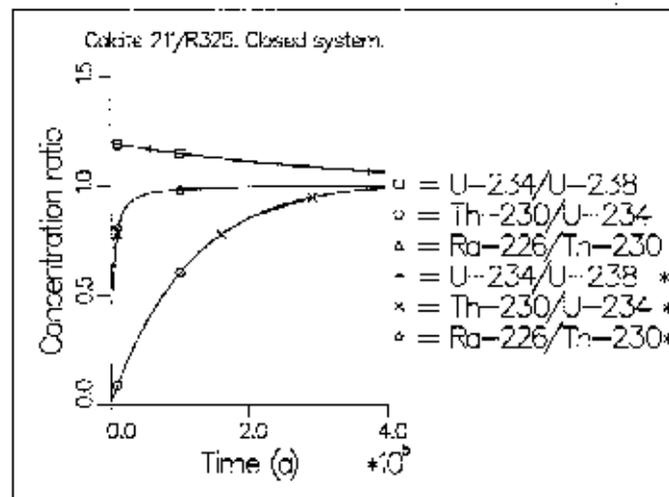
Fig. 11. Uranium-series disequilibria dating of fracture calcite in sample 211/R325. The measured activity ratios, denoted with asterisks (*), are projected on the respective simulated curves; the range between the symbols on the curves expresses the experimental error bar. For Ra-226/Th-230 activity ratio, only the upper end of the error bar is shown. For U-234/U-238 and Th-230/U-234 activity ratios, the error bars overlap on the time axis, indicating consistent system ages around 200 000 a.

Rough agreement was obtained between measured and simulated concentration profiles, and the need for systematic sorption studies was noted clearly. Matrix diffusion simulations and USD dating of the calcite were in overall agreement concerning the time scale (200 000 a).

Publication 4 (Appendix E) was a systematic continuation to Publication 3, and it concentrated specifically on the reliability and availability of sorption data.

Migration code FTRANS was further developed to handle arbitrary sorption isotherms. Matrix diffusion simulations were done by applying in parallel K_d and sorption isotherm $K_d(C)$ concepts for uranium, and a heterogeneous rock matrix concept. The experimental data base consisted of that of the previous publication (sample 211/R325), and sample-specific measured K_d values supported by mechanistic sorption modelling for uranium ($3 \cdot 10^{-2}$ m^3/kg). The sorption isotherm for uranium, based on current and earlier batch experiments, is shown in Table 2. Values for ε_p (0.1 - 0.2 %) and D_e (2 - $3 \cdot 10^{-13}$ m^2/s) with the bounding values representing the virgin and altered zones in the rock matrix, respectively, were cross-checked by measuring them with a set of different non-destructive methods. The comparison of measured and simulated concentration profiles of decay chain 4n+2 is given in Fig. 12 for a K_d scenario.

Table 2. The sorption isotherm of uranium used in matrix diffusion simulation.

Uranium concentration (mol/l)	K_d (m^3/kg)
10^{-9}	$9 \cdot 10^{-2}$
10^{-7}	$3 \cdot 10^{-2}$
10^{-6}	$2 \cdot 10^{-2}$

The stability of the bulk enrichment was tested in a sensitivity study by setting the bulk enrichment as a non-uniform initial condition, and letting matrix diffusion act on the concentration distributions. In other words, it was assumed, for the moment, that the whole measured concentration profile is mobile.

Uranium-series disequilibria code URSE was used in an attempt to date the bulk enrichment of radionuclides close to the fracture. α-recoil was tested preliminarily as the mass exchange mechanism, and as the explanation for the radioactive disequilibrium observed within the bulk enrichment.
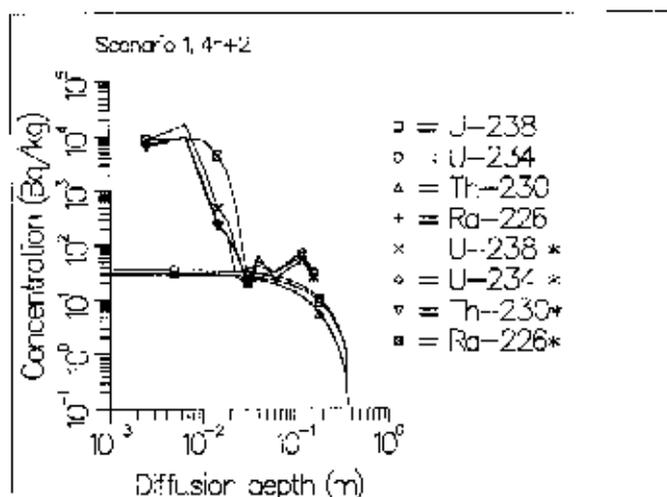
Fig. 12. Comparison of simulated and measured concentration profiles for sample 211/R325. All matrix properties were measured by independent means. The measured profiles up to the depth of 3 cm is referred to as the 'bulk enrichment'.

Matrix diffusion alone could not explain the measured bulk enrichment within the altered rock closest to the fracture (0 - 3 cm); the difference between measured and simulated concentrations was nearly three orders of magnitude. This difference, however, exaggerates the mismatch slightly, because the measured concentrations represent solely the subsampled minerals, while the simulated concentrations represent whole rock values. Therefore, to obtain the conceptually comparable discrepancy, one must down-scale the measured concentration profile with the abundance of the subsampled mineral (ca. 15 %, see Publication 3). In doing so, the discrepancy is decreased to nearly two orders of magnitude, which is still a marked difference. Beyond the surface zone, deeper in the virgin unaltered rock matrix (> 3 cm), the observed concentrations were, however, roughly in line with the model. The sorption isotherm used for uranium improved the model fit only marginally at the edge of the concentration profile. The thinness of data base available for mechanistic sorption modelling, in this case surface complexation modelling, was observed.

The sensitivity study, testing the stability of the bulk enrichment, indicated unequivocally that the whole bulk enrichment can not be mobile in the sense of the matrix diffusion model. If it were, the strong concentration gradients would have been levelled out within about 200 000 a.

α-recoil could explain the observed radioactive disequilibrium within the bulk enrichment; radiometric dating, however, requires supporting information. The measured concentration profiles of short-lived daughters Ra-226 and Pa-231

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extended clearly deeper into the rock matrix than those of their respective parents. This is "illogical" assuming a common source in the fracture. The idea of a secondary source within the bulk enrichment was, therefore, suggested as a possible explanation for this behaviour; α-recoil could, in principle, act as the release mechanism.

The previous seemingly successful model calibrations in Publications 2 and 3 (cf. Fig. 10) indicated clearly that a generic input data base may lead to false conclusions. Publication 2 was based on a purely generic, and Publication 3 still on a partly generic data base; only Publication 4 has a complete site-specific data base.

By definition, the matrix diffusion model represents only the mobile inventory with K_d as the sole attachment mechanism on pore surfaces. Therefore, the clear discrepancy observed indicates that the sequential extraction method, used to obtain the measured concentration profiles, was too aggressive and dissolved additional inventories from the rock matrix other than the adsorbed ones (represented by K_d), and a clear need for further development was observed. Sorption data appeared absolutely essential in explaining the measured concentration profiles; in fact, the conclusion of over-aggressive extractions was based on the discrepancy between K_d-enabled and measured concentrations. The batch experiments were done on the same rock sample as the extractions, and sorbing phases in the rock matrix are preserved in crushing, however destructive the crushing process may otherwise be. Therefore, batch experiments provided a useful reference for the extractions.

Publication 5 (Appendix F) studied the possibility to use α-recoil as an independent radiometric dating method in order to support matrix diffusion modelling. At the same time it also acted as a preparatory concept feasibility exercise for including the α-recoil mechanism explicitly into the classical matrix diffusion concept.

Uranium-series disequilibria code URSE was used to simulate the evolution of decay chain section U-238$\rightarrow$U-234$\rightarrow$Th-230 under recoil-induced U-234 and Th-230 fluxes. Open system approximations were used to test isotopic enrichment and depletion concepts. The experimental data base consisted of measured uranium-series data for samples 209 (R325/43.60 m), 218 (R337/67.40 m), 221 (R330/101.10 m), 168/R357, and 211/R325. USD datings for two calcite samples (218 and 221) that had been studied preliminarily earlier were also available. A detailed USD dating result of the bulk enrichment of sample 211/R325 is shown in Fig. 13.
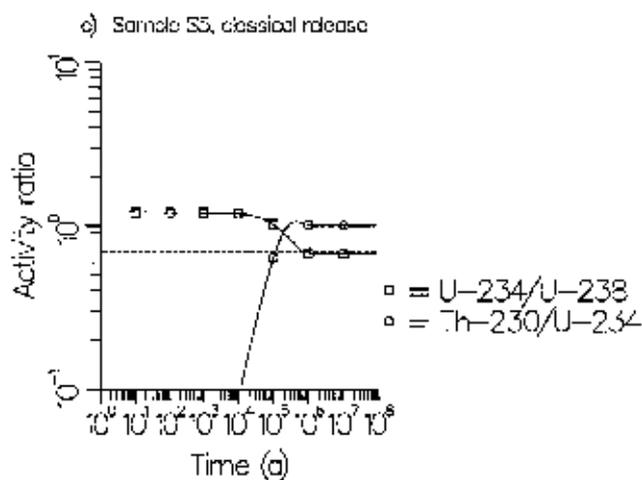
Fig. 13. Uranium-series disequilibria dating of the bulk enrichment in sample 211/R325 applying α-recoil as the mass exchange mechanism. The dashed horizontal line is the measured U-234/U-238 activity ratio. The model age of the system is ≥ 1 Ma, i.e. the system appears to be in steady state.

α-recoil gave a satisfactory explanation for the measurements in four cases out of five, thus indicating obvious dating potential. For radiometric dating applications, however, a more detailed recoil flux determination is necessary; in this exercise the fluxes were estimated theoretically. The fact that the bulk enrichment in sample 211/R325 appears to be in steady state, supports the earlier conclusion of an old and largely immobile inventory.

Publication 6 (Appendix G) was an elaboration of the observed discrepancy between measured concentrations in the rock matrix obtained by sequential extractions, and the concentrations that can be sustained by sorption equilibrium, cf. discussion of Publication 4 above.

The sorption concept used in the matrix diffusion model (i.e. K_d) was discussed in an effort to increase the selectivity of sequential extractions to extract only the adsorbed radionuclide inventories. The idea of partially irreversible sorption was suggested as an explanation for the observed discrepancy, see Fig. 14.

The experimental data base consisted of batch experiment and sequential extraction results for samples 211/R325, 103/R346, and 168/R357 from Palmottu, and for the boulder sample from near Hämeelinna.
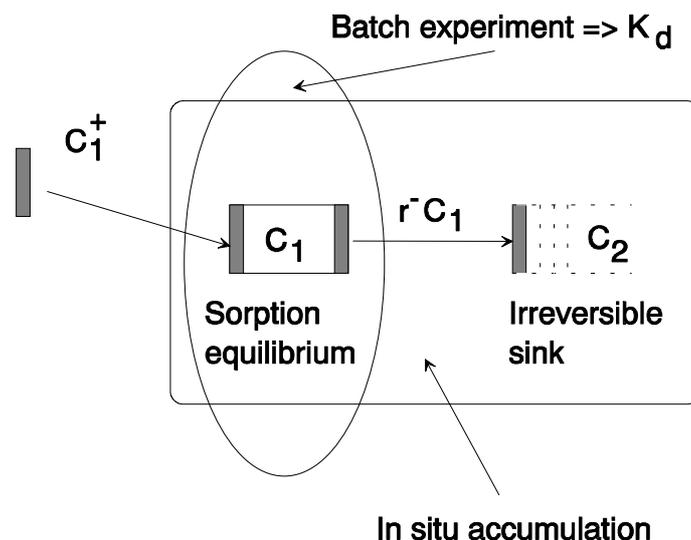
Fig. 14. The concept of partially irreversible sorption. Fraction r^- (1/a) of the concentration in sorption equilibrium (C_1) is removed to the irreversible sink (concentration C_2); an equal mass flow (C_1^+) from groundwater replaces the irreversibly removed inventory to maintain sorption equilibrium.

The simplistic model in Fig. 14 yields an in situ accumulation that consists of a mobile concentration in sorption equilibrium (C_1), and a co-located immobile concentration in the irreversible sink (C_2). At first, there is only C_1, and C_2 starts from zero accumulating at a constant slow rate. Qualitatively, the in situ accumulation concept in Fig. 14 appears to correspond to the observed situation at Palmottu. In the figure it is also indicated that batch experiments (i.e. K_d's) only record the inventory in sorption equilibrium. Assuming 99.99 % reversible sorption, i.e. $r^- = 10^{-4}$ 1/a, results in $C_2 = 100 \cdot C_1$ after one million years, i.e. the immobile inventory completely dominates in the in situ accumulation.

Against this background, it is understandable that over-aggressive extractions yield concentrations higher than those indicated by batch experiments. As C_2 is proportional to time, the above simplistic concept also explains why *recent* accumulations do not yield overly high concentrations, however aggressively extracted they may be, as observed with the boulder sample.

Quantitative model testing requires, essentially, that the concept of radionuclide attachment on the rock matrix behind the experimental reference equals the theoretical concept in the simulation model. It is important to see that the in situ accumulation, K_d (representing the model), and phase-selective extractions all address partly different aspects of radionuclide attachment. Therefore, the intersection of these three aspects appears essential from the model testing point of view, see Fig. 15.
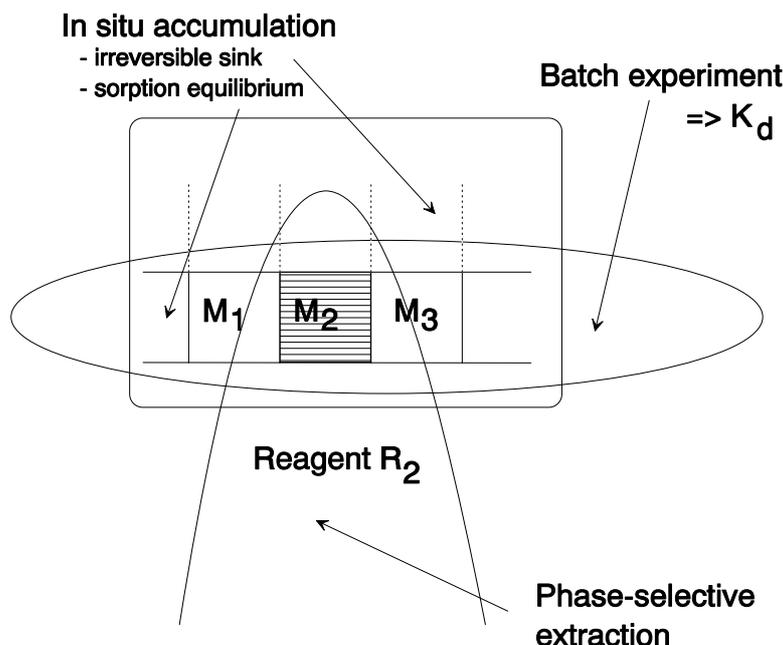
Fig. 15. Intersection of in situ accumulation, batch experiment, and phase-selective extraction concepts when comparing measured and simulated concentrations in a natural analogue. M_1, M_2, and M_3 stand for different fast sorption mechanisms. In this example, reagent R_2 in the phase-selective extraction is assumed to be selective for sorption mechanism M_2, but some accidental extraction occurs, too.

The in situ accumulation of radionuclides in a natural analogue may contain mobile (in sorption equilibrium) and immobile (irreversible sink) inventories. Batch experiments scan all the fast sorption mechanisms, and only them, and give as a result a weighted average of the individual mechanism-specific K_d values. Phase-selective extractions use chemicals that are selective for a certain phase (which can be linked to a certain fast sorption mechanism), but they may release accidentally other phases, too (cf. Fig. 15). For the model testing to be conceptually rational, the extraction should scan all the fast sorption mechanisms - as detected also by batch experiments - and only them.

In general terms, quality assurance in sequential extractions is of fundamental importance to the testing of the matrix diffusion model: without a reliable experimental reference, quantitative model testing is pointless. This conclusion applies, of course, to all migration studies applying natural analogues.

5.1.2 Supporting studies

In parallel with the quantitative model tests at Palmottu, supporting experimental rock matrix characterisation studies were organised in order to provide quality controlled input data for the simulation model. Below, a brief description is given of

two separate studies that both focused on quantifying the physical diffusion properties of the rock matrix.

An **interlaboratory comparison** study was conducted for six methods used in Finland to measure the effective rock matrix porosity (ε_p). Three different versions of the water immersion technique, a tracer elution method, a helium gas method, and a C-14-PMMA method were tested (Rasilainen et al. 1996). The aim of the study was twofold: first, to compare different experimental techniques for future applications, and second, to actually obtain quality controlled data for the model testing. Rock samples for the study were obtained from a homogeneous unaltered drill core section at Palmottu very close to matrix diffusion sample 168/R357.

All methods proved to be comparable in their accuracy, and the selection of methods for future applications can, therefore, be based on practical considerations. For instance, the helium gas method is extremely fast as compared to the other methods, which are based on experiments in liquid phase. The measured comparable values for ε_p were very close to each other, between 0.2 - 0.3 %. The tracer elution and the helium gas methods also measured D_e values, and they varied between $1 - 7 \cdot 10^{-13}$ m^2/s.

A **partly altered drill core** section (length 78 mm) from Palmottu, close to sample 211/R325, was characterised for its diffusion properties (Hartikainen et al. 1996). The characterisation was done using the helium gas method. The aim of the study was, besides characterising the rock sample, to study the relationship between ε_p and D_e, and to test the effect of sample thickness on the measured values.

The method employed in this approach was to perform ε_p and D_e measurements for the whole rock sample, then cut the sample into two and do the measurements again, and to repeat the sequential cutting and measuring procedure for all subsamples twice more. Finally the original drill core section was cut into eight slabs, and we had subsequent measured data for altogether 15 partly overlapping rock samples (whole sample, 2 half samples, 4 quarter samples, and 8 eighths of the sample). The experimental approach was enabled by the fastness of the helium gas method.

The general results indicated directly the existence of a continuous pore network throughout the whole length of the drill core section, thus supporting the classical non-limited matrix diffusion concept. Diffusion properties along the rock sample varied considerably from the virgin to the altered part of the sample: 0.03 - 4 % for ε_p and $6 \cdot 10^{-15} - 2 \cdot 10^{-13}$ m^2/s for D_e, respectively, see Fig. 16. As compared to the matrix diffusion samples, the alteration in this rock sample was exceptionally strong.
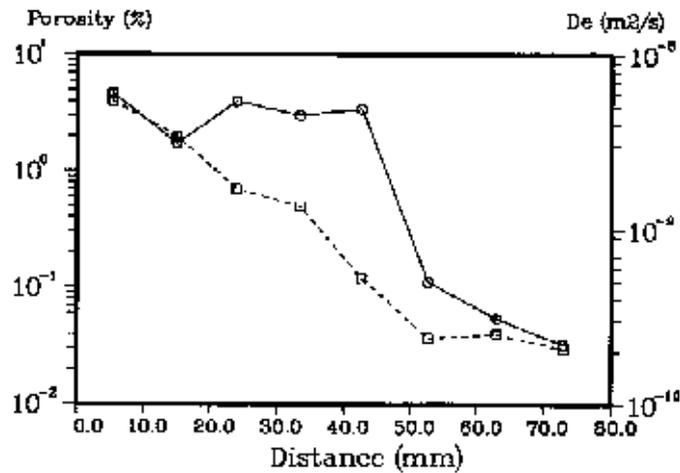
Fig. 16. Effective porosity ε_p (dashed line) and effective diffusion coefficient D_e (full line) as a function of distance from the fracture surface (Hartikainen et al. 1996). The altered end of the sample is on the left hand side. The D_e values represent helium gas in nitrogen gas, acting as the carrier, and these values are converted into heavier molecules in water phase by dividing by 35 000, see e.g. Rasilainen et al. (1996) for conversion details.

The relationship between ε_p and D_e did not appear to follow any constant function, rather the two parameters appeared to be relatively independent of each other, see Fig. 16. Sample thickness of less than 1 cm seemed to open some new connections at the dense unaltered part of the drill core section, as indicated by increasing D_e values.

5.2 BOULDER SAMPLE NEAR HÄMEENLINNA

The boulder was found on top of a morainic hill in the Kolkanmäki area close to the town of Hämeenlinna in southern Finland. The study area is covered with glacial till and more sorted sediments. In contrast to the multi-targeted natural analogue studies at Palmottu, where matrix diffusion is only one research area among others, the granitic boulder sample is studied specifically as a matrix diffusion analogue. Another difference is that uranium accumulation within the boulder is apparently recent (postglacial) as compared to the very old ore deposit at Palmottu.

The postulated accumulation history of uranium in the boulder is stepwise, in line with USD datings and the glacial history of the site. In-diffusion (100 a) was caused by uranium-rich waters that discharged onto the boulder at the end stage of glaciation. The subsequent out-diffusion (50 a) was caused by the Yoldia Sea stage

during which the boulder was submerged in the sea. The final isolated chain decay stage (10 000 a) began when the boulder, together with its surroundings, rose above sea level due to land uplift. This stage continued, actually, until the moment of sampling.
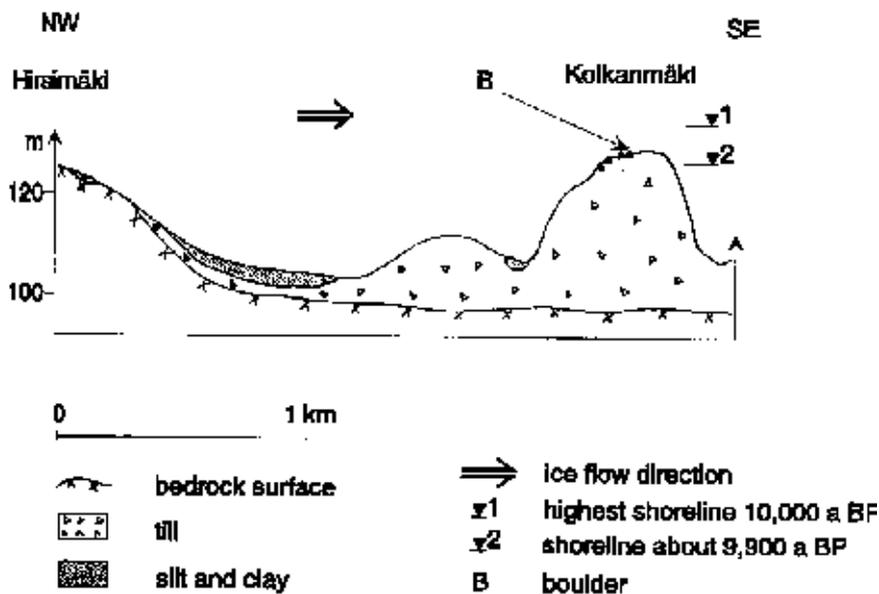
Fig. 17. Cross section of the geological surroundings of the boulder sample. The boulder (B) is assumed to have been transported by the ice to its current location.

The mineralogy of the boulder was used in an effort to locate the parent rock, and taking into account the known direction of ice flow at the site, 312 - 316° (NW - SE), the only reasonable granite outcrop with the same mineralogical composition (microcline granite) was found in Hirsimäki, see Fig. 17. Notwithstanding, areal gamma radiation mapping shows a local maximum at the Kolkanmäki site, but, interestingly, not at the outcrop. It appears, therefore, probable that the parent rock of the boulder is located in the soil-covered area between Hirsimäki and Kolkanmäki.

Deglaciation took place in the Hämeenlinna region about 10 000 a ago. The highest shoreline of the subsequent Yoldia sea stage at Hämeenlinna was 133 m above the current sea level. As the highest point of Kolkanmäki, and the location of the boulder, is only 2 - 3 m lower, it can be approximated that the boulder was below the Yoldia sea level for 50 - 100 a. Estimates of ice velocities towards the margin vary from a few to tens of m/a. This rate means a travel time of 50 - 500 a for the

boulder over the estimated distance of 1 - 2 km. At least part of this time the boulder was in wet conditions near the basal layers of the ice.

5.2.1 Tests with the boulder sample

Publication 7 (Appendix H) was the first quantitative effort to test the matrix diffusion model in a case with apparently recent uranium accumulation in the boulder sample. The case was tempting as a natural analogue, because the glacial history of the site was relatively well known.

Migration code FTRANS was used to simulate matrix diffusion of decay chains 4n+2 and 4n+3. A time-dependent boundary condition was applied in order to simulate the known glacial history of the site. A homogeneous matrix concept was used in the simulations. The experimental data base comprised measured concentration profiles, quality controlled sample-specific values for ε_p (0.1 - 1 %) and D_e ($1 - 3 \cdot 10^{-12}$ m^2/s) measured by a set of different methods, and K_d values for uranium ($1 \cdot 10^{-2}$ m^3/kg) obtained from batch experiments. A comparison of simulated and measured concentration profiles for decay chain 4n+2 is shown in Fig. 18.

Uranium-series disequilibria code URSE was used to obtain an independent radiometric dating of the accumulated matrix diffusion system. URSE simulations tested open, and initially open but later closing systems, with the closing system mimicking the final isolated chain decay stage. From the glacial history of the site we know that the uranium accumulation must be at least 10 000 a old, because that is the time the boulder has been on dry land.

Matrix diffusion could roughly explain the observed concentration distributions within the rock sample. Independent USD dating yielded a picture of the time scale consistent with the diffusion modelling. The well-bounded case enabled the derivation of a minimum value for apparent diffusivity *in situ* for the boulder: D_a (in situ) $\geq 4.5 \cdot 10^{-16}$ m^2/s. The measured concentration profiles were obtained by very aggressive aqua regia extractions, but in this case there was no discrepancy between extractions and sorption data, cf. discussion of Publication 6 above.
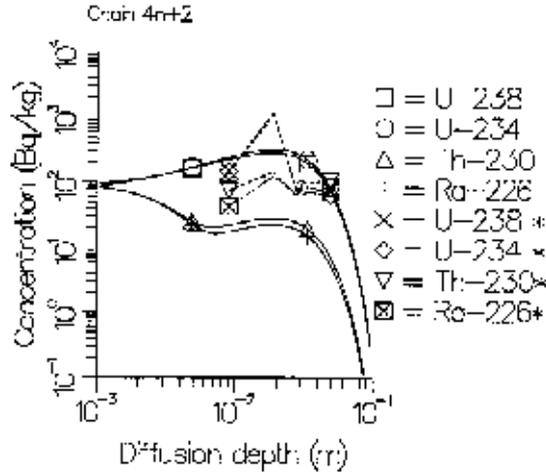
Fig. 18. Comparison of simulated and measured (*) concentration profiles for decay chain 4n+2. The simulations comprise consecutive in-diffusion (100 a), out-diffusion (50 a), and chain decay stage (10 000 a).

Publication 8 (Appendix I) was a direct continuation to the previous study with the aim to discuss quantitatively the accuracy of the USD method in radiometric dating. The study was enabled by the preceding successful matrix diffusion modelling exercise.

Uranium-series disequilibria code URSE was used to simulate the evolution of decay chains 4n+2 and 4n+3. The earlier modelled matrix diffusion case was used as the reference for the USD simulations: the time- and space-dependent migration process was simplified to a case of time-dependent net mass flows. Closed, open, and multistage systems were tested for radionuclide accumulation. The detailed multistage systems represented the known reference, including consecutive periods of continuous accumulation, partial release, and a closed system stage. The experimental data base was the same as in the previous publication. The results of the most detailed multistage simulation are shown in Fig. 19.

The exercise showed clearly that detailed knowledge of the mass flows involved, i.e. of the sequence of events, increases considerably the accuracy and consistency in USD dating. In the most detailed dating, the error (relative difference from the real age of the reference) was ≤ 2 %. In this case, the small difference is the error of the *USD method* in the studied diffusive system, because input errors were expressly excluded from this theoretical study. The absolute accuracy of USD dating obviously depends on how accurately the evolution of the system can be reconstructed using the net mass flows.
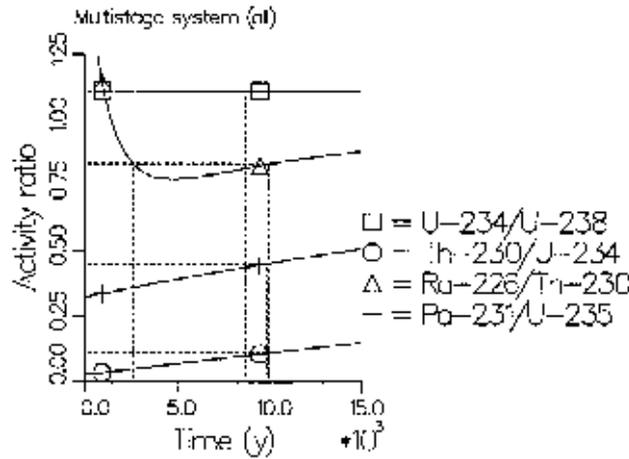
Fig. 19. Uranium-series disequilibria dating of the accumulated decay chain 4n+2 and 4n+3 activities using a multistage model for all radionuclides. The sequence of nuclide accumulation consisted of consecutive in-diffusion (100 a), out-diffusion (50 a), and chain decay stages. The real age of the matrix diffusion reference was 10 150 a. The dashed lines project the activity ratios of the reference on the time axis via the respective simulated curves. The first system age for the Ra-226/Th-230 activity ratio reflects the in-diffusion of unsupported Ra-226, which, of course, decays according to the radioactive decay coefficient of Ra-226.

5.3 TECHNICAL LIMIT TO THE MODEL TESTING

It is technically quite a demanding task to distinguish only the adsorbed inventory in the rock matrix. The yield of an extraction depends namely at the same time on the reagent used, the phase to be extracted and the element in that phase, as well as on the extraction time. Therefore, "blind" application of extraction techniques can easily lead to experimental artefacts. The extraction problem has also been acknowledged by other authors (e.g. Alexander et al. 1990a).

In some rock samples there are many overlapping tracks of successive uranium accumulations, e.g. around fractures that have been hydrothermally active. The distribution of radionuclides in a rock sample is usually non-uniform, and the mobile inventory is only one component of the total inventory, as has also been noted by other authors (e.g. Heath 1995).

Based on Publication 6, it appears that for some rock samples at Palmottu, e.g. for those containing old radionuclide inventories, there is a risk that artefacts in the extractions make the experimental reference inconsistent with the modelling concept. For the moment, therefore, the emphasis in model testing at Palmottu must be shifted from simulations to quality assurance of the extractions.

5.3.1 Beyond the limit

The question about possible artefacts in the experimental reference has delayed the final model tests at Palmottu. The concentration profiles measured so far for the matrix diffusion samples 211/R325, 103/R346, and 168/R357 (Suksi et al. 1995, cf. also Fig. 8) must, therefore, be validated by an improved extraction technique, which is still under development. For this reason, a finished testing strategy for studying the role of α-recoil in matrix diffusion is presented below, although the test has not yet been carried out.

In Publication 5 it was shown with USD simulations that α-recoil is capable of producing activity ratios U-234/U-238 < 1 in the rock matrix, cf. Fig. 13. In that study the recoiling atoms were simply assumed to be transported away from the system, with pore water acting as the carrier.

It is, however, possible to link the α-recoil induced mass flows explicitly into matrix diffusion simulations, and thereby to obtain a better general picture of the system. The mass flow takes place from the rock matrix into the pore water, and, therefore, it can be described simply by introducing an extra source term in the form of a flux boundary condition within the rock matrix, see Fig. 20. The possible role of α-recoil in USD profiles has been qualitatively suggested by other authors also (e.g. Smellie et al. 1986a, Alexander et al. 1990a). α-recoil has been considered in natural analogue studies in non-granitic surroundings also (Skagius et al. 1993).
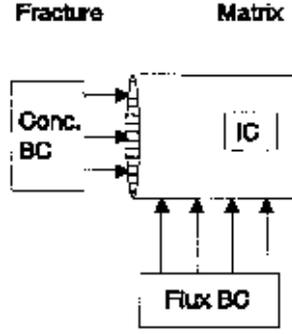
Fig. 20. The modified conceptual model for matrix diffusion to incorporate α-recoil. The standard concentration boundary condition (Conc. BC) at the fracture represents nuclide concentrations in the flowing groundwater. The extra flux boundary condition (Flux BC) in the rock matrix represents the α-recoil induced mass flow from the bulk enrichment. The initial condition (IC) represents the initial radionuclide concentrations in the pore water.

The extra flux boundary condition in the rock matrix can be derived from the measured bulk enrichment, cf. Fig. 12. First the bulk enrichment is averaged

$$C_{m,i}^{ave} = \frac{\int_0^{z_b} C_{m,i}(z)dz}{z_b} \tag{31}$$

where $C_{m,i}^{ave}$ is the averaged concentration of nuclide i in the bulk enrichment (Bq/kg), $C_{m,i}(z)$ is the measured concentration of nuclide i in the bulk enrichment (Bq/kg) at distance z (m), and z_b is the range of the bulk enrichment from the fracture (m). The total activity of nuclide i in the bulk enrichment can now be obtained from

$$A_{m,i}^{ave} = C_{m,i}^{ave} \, m_b \tag{32}$$

where $A_{m,i}^{ave}$ is the measured total activity of nuclide i in the bulk enrichment (Bq) and m_b is the mass of the drill core sequence (of length z_b) containing the bulk enrichment (kg). In this case, the rock samples are cylindrical drill core sections and the mass can be simply obtained from $m_b = \rho_s(1-\varepsilon_p)\pi d^2 z_b/4$, where d is the diameter of the drill core (m). $A_{m,i}^{ave}$ equals the total rate of disintegrations of nuclide i within the bulk enrichment. Assuming that fraction χ of the disintegrations is directed towards the pore water in the rock matrix, the total release rate of nuclide i can be assessed:

$$q_{i,tot} = \chi \lambda_i A_{m,i-1}^{ave} \qquad (33)$$

where $q_{i,tot}$ (Bq/s) is the total flow of nuclide i into the pore water. In Eq. (33) nuclide i - 1 is, as always, assumed to disintegrate into nuclide i. Now the flux boundary condition can be formulated

$$q_{i,j}(t) = \frac{(z_j - z_{j-1})}{z_b} q_{i,tot} \qquad (34)$$

where $q_{i,j}$ is the release rate (Bq/s) of nuclide i in location z_j (m), z_j denotes the discretised source locations along the z-axis, representing actually source length (z_j - z_{j-1}). Here, a uniform line source (of length z_b) was assumed for simplicity. After a change of variables (Bq → at.), this extra flux boundary condition can be applied to simulate quantitatively the effect of α-recoil on matrix diffusion by the code FTRANS.

5.4 DISCUSSION OF MAIN RESULTS

What do the results mean?

In order to avoid over- or understatements, the results obtained must be put into their proper context. This means that the general features of natural analogue studies in supporting a model must be taken into account, because they provide the overall perspective for this work also.

Natural analogue studies are like all experiments in that the quality of the original experimental data controls the rigour of model testing. Due to the long time periods considered in natural analogues, initial and boundary conditions are difficult to quantify in detail, which results in a larger inherent uncertainty than e.g. in laboratory experiments. Thus, a wider "error bar" is unavoidable, and, therefore, an agreement within, say, an order of magnitude between measured and simulated results can be considered acceptable in the case of natural analogues, provided the respective trends are similar. On the other hand, even a perfect curve fit does not prove much, if it is based only on model calibration.

As compared to recently reported natural analogue studies on matrix diffusion, the current study provides a more quantitative and model testing oriented approach, and consequently also more quantitative results. The systematic testing methodology enabled the testing to be extended to the current technical limits of the experimental methods used, in particular those providing the experimental reference and rock matrix properties. This, in turn, enabled the identification of

key factors, which had not received much quantitative attention in the previously reported natural analogue studies, namely quality assurance of the experimental reference and comprehensive site-specific data base. Understanding the long-term attachment of nuclides on pore surfaces proved to be crucial for both the experimental reference and the simulations.

Due to the interdisciplinary nature of the current study, the most important aspects linked to the iterative model testing process are discussed one at a time below. Some central observations are, therefore, looked at from different viewpoints, which contributes to a more versatile discussion.

Test methodology

The rigour of the current in situ tests depends essentially on two factors. First, how well the measured concentration profiles represent matrix diffusion in situ; in other words, how well the extraction technique used traces the matrix diffusion response in the rock matrix. Second, how well the simulations represent matrix diffusion in situ; in other words, how well the measured input data capture the in situ conditions.

The simulation of matrix diffusion was performed applying in parallel 1-dimensional matrix diffusion modelling, and USD dating. The parallel simulations are sensible, because the two modelling techniques are mutually independent and can, therefore, support each other. The parallel modelling approach is a new combination of the two, as such established techniques, as far as the author is aware. By studying two independent decay chains (4n+2, 4n+3) one can obtain more reliable conclusions than by using only one decay chain, because the respective chain-specific results can support each other.

The model tests performed showed the general feasibility of the concentration profile method. The repeated model validation attempts documented a learning process that converged relatively fast to identification of important further development needs. The strategy to use only a few carefully selected samples proved reasonable, because a great number of samples generates added value only after the testing approach applied to the samples is validated.

The model testing approach proved feasible, but the extractions yielding the measured concentration profiles need some fine-tuning. Due to the discrepancy observed, the emphasis at Palmottu has been shifted to experimental studies to ensure extractions free of artefacts. This shift of emphasis, in fact, demonstrates the strength of the iterative model validation process, in which any observed inconsistency forces one to critically review all aspects of the system, theoretical as well as experimental.

The shift of emphasis at Palmottu also illustrates the development potential of the test methodology. As it is now, the testing was supported by the best experimental methods available. For instance, the matrix characterisation methods used are technically well established with relatively limited room for further development. The extraction technique, that yields the measured concentration profiles, in contrast, has more adjustable parameters, and it can also be combined with batch experiments; therefore, the extraction technique has more improvement potential. Thus, there are realistic prospects of more detailed model tests with this methodology in the future.

Input data for matrix diffusion model

Of the matrix characterisation data, the physical diffusion parameters (ε_p, D_e) can be obtained quite reliably, according to the quality control studies performed, see also Siitari-Kauppi et al. (1994). The variation of the physical diffusion properties is usually moderate, while that of sorption (K_d) can be orders of magnitude, according to sensitivity studies applying surface complexation modelling. Therefore, obtaining reliable and representative sorption data is of utmost importance in matrix diffusion testing. The importance of sorption stems also from the fact that both the simulation model and the extraction method must be based on a sound, and mutually consistent understanding of the long-term attachment of radionuclides on pore surfaces, as demonstrated by the discrepancy at Palmottu.

Concerning specifically the heterogeneous matrix properties, the numerical code FTRANS, used for diffusion simulations, can readily describe heterogeneity in a discretised manner. The resolution of this discretised description depends directly on the overall resolution of the original experimental data (ε_p, D_e, K_d).

Besides matrix properties, the diffusion model needs time, and initial as well as boundary conditions as input. Time and matrix properties together control the depth of the simulated concentration profile, while boundary and initial conditions provide the concentration gradient, i.e. the driving force for diffusion. The USD method provides a possibility of independent radiometric dating of the matrix diffusion system itself, or related systems such as e.g. fracture calcites. The problem remaining is, however, that, although the evolution of a radioactive disequilibrium in a decay chain system can be dated, the system itself, if other than the matrix diffusion system, is linked only indirectly to matrix diffusion.

Lessons from the model tests

The most important lesson learned at Palmottu is that the respective concepts of radionuclide attachment on pore surfaces must be the same in the extraction method yielding the measured concentration profile, and in the simulation model. The

marked difference between measured and simulated concentrations, observed at Palmottu, appears to be caused by a discrepancy in the respective attachment concepts. This indicates, in turn, a clear need to improve the extraction method; of course, the model may have to be improved, too, but to obtain reliable grounds for it, the input data and the experimental reference must first be quality controlled.

The bulk enrichment closest to the fracture (0 - 3 cm), showing the largest difference between measured and simulated concentrations, appears to be largely immobile, as indicated unequivocally by the numerical sensitivity studies. Despite the immobility, the bulk enrichment must, however, be open to mass exchange, as indicated directly by the observed radioactive disequilibria. α-recoil could explain the measured U-234/U-238 activity ratio of about 0.6. The bulk enrichment can, therefore, technically act as a secondary radionuclide source within the rock matrix with α-recoil being the release mechanism. The bulk enrichment appears very old, as indicated by the steady state conclusion obtained in the USD dating.

Beyond the bulk enrichment and the altered rock zone, deeper in the virgin unaltered rock matrix (> 3 cm), the correspondence between measured and simulated concentration profiles was, however, relatively good. The simulations, therefore, indicate that matrix diffusion can penetrate the altered zone into the virgin rock, because a heterogeneous matrix concept, including altered and virgin zones, was used, and the respective zone-specific matrix properties were quality controlled.

Another major lesson learned at Palmottu is that a comprehensively site-specific data base is indispensable in quantitative model testing. This was demonstrated in the repeated successful model calibrations that, starting from a completely generic input, used an increasingly site-specific data base. Only after all input data had been measured independently, could the discrepancy mentioned above be distinguished. Therefore, even a partly generic data base may lead to false conclusions.

In contrast to the old uranium accumulations at Palmottu, the recent accumulation within the boulder showed good agreement between measured and simulated concentration profiles. In addition, independent USD dating provided an exceptionally consistent picture of the uranium accumulation history, which was well in line with the matrix diffusion scenario. Thus, a coherent picture of uranium accumulation could be obtained from three sources of information: glacial history of the site, matrix diffusion simulations, and USD dating. The case was, actually, so well defined that it could be separately used to study the accuracy of the USD method.

In order to understand why the discrepancy was observed at Palmottu but not in the boulder, and also the nature of the discrepancy, the concept of partially irreversible

sorption was suggested. It must, however, be kept in mind that, for the time being, this concept is a working hypothesis that, of course, must be validated by independent tests. Considering the slow accumulation of the irreversible sink, laboratory tests may have difficulties in observing the inevitably small mass losses from the adsorbed inventory. Of special interest to be studied, are factors that control the irreversible accumulation, because, obviously, unlimited accumulation is not possible.

Conclusions of the modelling concept

The current model tests did not indicate any needs to adjust the classical matrix diffusion model. The final tests at Palmottu are still unfinished, however, but the results from the boulder support the classical modelling concept. Of course, there are differences between measurements and simulations, but they can be explained by uncertainties in the input data, or by an erroneously high measured concentration profile due to over-aggressive extractions.

Against the current test experience, the proposal of a limited matrix diffusion concept, made repeatedly in earlier matrix diffusion studies (cf. Section 3.3), appears insufficiently founded. First, the concentration profiles, that are the basis of the conclusion, should be proven to represent only the mobile inventory, which obviously has not been done. Second, the range of the concentration profile should be proven to be limited by some other factor than by time, which is the limiting factor in the classical "unlimited" concept. These kinetic considerations were missing; in addition they would require a complete site-specific data base for the diffusion model, of which there was no mention. Third, limited matrix diffusion is often argued to be controlled by the enhanced porosity of an altered zone close to the fracture. The diffusivity characterisation study of the partly altered drill core section from Palmottu, however, showed directly that the continuous pore system extends easily beyond the altered zone (Hartikainen et al. 1996).

Recommendations for future work

The model tests above indicate clearly that recent uranium accumulations are easier to interpret than old ones, mainly for two reasons. First, the matrix diffusion response is technically easier to extract, and second, initial and boundary conditions are easier to quantify. The probability of disturbing mass flow events, that would mask the matrix diffusion response, increases namely with time in an evolving natural system. These events are difficult to distinguish and subsequently quantify from the integrated response. Therefore, the fact that they can be excluded, or at least reduced in number, makes recent systems extremely valuable test beds both for model testing and experimental studies.

The discrepancy at Palmottu delayed the final model testing, because the measured concentration profiles must first be validated by an improved extraction technique,

which is still under development. The improvements needed appear achievable, however, and, therefore, the model tests at Palmottu can be resumed, probably very soon. In addition to testing the classical modelling concept, a new model testing plan was formulated in this work for studying quantitatively the role of α-recoil in long-term matrix diffusion.

6 CONCLUSIONS

Matrix diffusion was studied in situ at two Finnish natural analogue sites: a uranium-thorium deposit at Palmottu in south-western Finland, and a boulder sample near Hämeenlinna in southern Finland. Both sites show elevated natural uranium concentrations. The model testing strategy at both sites was to do iterative model validation attempts with the data available at each time.

A methodology based on systematic comparison of measured and simulated concentration profiles was developed for the model tests. Long-lived natural decay chains 4n+2 and 4n+3 were studied as in situ tracers. The modelling approach utilises 1-dimensional matrix diffusion simulations in parallel with uranium-series disequilibria (USD) dating. This parallel modelling offers a new versatile approach to study in situ matrix diffusion of the two decay chains. Besides the matrix diffusion system itself, USD dating can be done on e.g. fracture calcites. All simulations were done applying verified codes. The possibility of advection to generate concentration profiles in the rock matrix at Palmottu was studied quantitatively, and found marginal, which, for its part, increases the argument for matrix diffusion being responsible for the in situ concentration profiles.

The systematic methodology enabled the rigour of the model tests to be extended to the current technical limits of the experimental methods used. This applies both to the chemical extractions yielding the measured concentration profiles of the two decay chains, and the input for the simulation model. The input data were obtained from independent experimental studies applying well-established methods, which ultimately makes the model testing genuine. Separate quality control studies were conducted for rock matrix porosity and diffusivity data.

The most important lesson learned at Palmottu is that the measured concentration profiles and the simulation model must be based on the same concept of radionuclide attachment on pore surfaces. This was illustrated by the fact that the measured concentrations were much higher than the simulated ones, indicating that the phase-selective extractions, used to obtain the measured concentration profiles, were over-aggressive, extracting additional inventories from the pore surfaces other than those in sorption equilibrium. This conclusion was supported by the fact that the matrix diffusion model, by definition, represents exclusively mobile inventory having K_d as the only attachment concept; furthermore, the K_d values used were based on batch experiments on the same rock samples. The discrepancy observed thus indicates a clear need to improve the extraction methods.

Another lesson learned at Palmottu is that a comprehensively site-specific data base for the simulation model is a necessity in quantitative model testing. The repeated

successful model calibrations with a combination of generic and site-specific input data demonstrated clearly that even a partly generic data base may lead to false conclusions.

In contrast to the old uranium accumulations at Palmottu, the recent accumulation in the boulder sample showed good correspondence between the measured and simulated concentration profiles. In addition, the independent USD dating of the matrix diffusion system provided an exceptionally consistent picture of the accumulation history, well in line with the matrix diffusion simulations. The well-defined boulder case could also be separately used to demonstrate the good accuracy of the USD dating method.

In order to understand the nature of the discrepancy at Palmottu, and also the absence of discrepancy in the boulder case, the concept of partly irreversible sorption was introduced. In this concept, in situ accumulation of a radionuclide consists of a mobile inventory in sorption equilibrium (represented by K_d), and a co-located slowly accumulating immobile inventory. Therefore, in an old system, an over-aggressive extraction can easily extract also the immobile inventory that has grown dominant, as appears to be the case at Palmottu. In a young system, however, the mobile inventory may still dominate, which would explain the good match between the measured and simulated concentration profiles in the boulder, despite the very aggressive extraction used.

The experiences above indicate clearly that recent uranium accumulations are easier to interpret than old ones, mainly for two reasons. Matrix diffusion response is easier to trace experimentally, and boundary conditions for simulations are easier to reconstruct. It appears, therefore, that recent uranium systems are worth actively looking for as natural analogues.

The model tests performed indicate no need to adjust the classical matrix diffusion concept. Due to the discrepancy mentioned above, however, final model tests at Palmottu have been postponed. On the other hand, the boulder tests support the matrix diffusion model unequivocally. Thus, for instance, the current tests do not support the concept of limited matrix diffusion that has repeatedly been proposed in earlier natural analogue studies of matrix diffusion.

The fact that improvement needs in extraction techniques were noted at Palmottu, actually demonstrates the power of the iterative model validation process, which exposes all aspects of the system, theoretical as well as experimental, to repeated critical   reviews.

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ON THE POSSIBILITY OF ADVECTION
IN ROCK MATRIX AT PALMOTTU
- COMPARISON WITH DIFFUSION

Background

This simplistic discussion is based on assuming that Darcy's law, describing advection, applies to the rock matrix. In other words, it is assumed that the site-scale hydraulic gradient extends through the pore water in the rock matrix. A rock matrix is assumed to be an ideal isotropic porous medium, and, therefore, the effective pore network available for advection is the same as for diffusion.

Advection in a rock matrix is studied by comparing it with diffusion, using real site-scale hydraulic gradients obtained from Palmottu, as well as real sample-scale laboratory-derived rock matrix data (permeability, ε_p, D_e, K_d). The aim of this exercise is to obtain an upper boundary for the extent of advection in the rock matrix, and, therefore, upper boundary values were also chosen for the permeability of the rock matrix and for the hydraulic gradient. If this exaggerated estimate of the extent of advection is smaller than the realistic extent of diffusion, then advection most probably is not an important migration mechanism in the rock matrix, and no further consideration is necessary.

Advection

Groundwater flow in a porous medium is usually described by Darcy's law (see e.g. Bear 1979), which in a general 3-dimensional case can be expressed as

$$\vec{q} = -[K]\nabla h \qquad (1)$$

where $\vec{q}$ is the Darcy velocity (m/s), [K] is the hydraulic conductivity tensor (m/s) and ∇h is the hydraulic gradient, i.e. hydraulic head difference per unit length. In the case perpendicular to a surface, Darcy velocity can be visualised as the water flux (volumetric flow per unit area) across that surface ($m^3/m^2/s$). The real groundwater velocity is obtained from Darcy velocity by dividing it by the effective porosity:

$$\vec{v} = \frac{\vec{q}}{\varepsilon_p} \qquad (2)$$

where $\vec{v}$ is the flow velocity (m/s) and ε_p is the effective porosity of the medium.

1-dimensional discussion simplifies notation, and in this notation the absolute value of the effective distance moved by a sorbing nuclide i within the matrix during time t, can be described as

$$z_A = \frac{vt}{R_{p,i}} = \frac{K\nabla ht}{\varepsilon_p R_{p,i}} \tag{3}$$

where z_A is the effective distance moved due to advection (m), t is time (s), and $R_{p,i}$ is the retardation factor of nuclide i in the rock matrix, described as

$$R_{p,i} = 1 + \frac{K_{d,i}\rho_s(1-\varepsilon_p)}{\varepsilon_p} \tag{4}$$

where $K_{d,i}$ is the sorption-induced distribution coefficient of nuclide i (m^3/kg) and ρ_s is the density of the rock material (kg/m^3). Hydraulic conductivity of the porous medium is defined by (e.g. Bear 1979)

$$K = k\rho g / \mu \tag{5}$$

where k is the permeability (m^2) depending only on the geometrical structure of the rock matrix, ρ is the density of water (kg/m^3), g is the acceleration due to gravity (m/s^2), and μ is the dynamic viscosity of water (Pas).

Matrix diffusion

Molecular diffusion in a 1-dimensional system (rock matrix in this case) is usually described by Fick's second law, which for homogeneous matrix properties can be expressed as

$$\frac{\partial C_{p,i}(z,t)}{\partial t} = D_a\frac{\partial^2 C_{p,i}(z,t)}{\partial z^2} \tag{6}$$

where $C_{p,i}$ is the concentration of nuclide i in the porewater (at./m^3), z is the distance from fracture surface (m), t is time (s), and D_a is the apparent diffusion coefficient (m^2/s). D_a can be expressed as

$$D_a = \frac{D_e}{\varepsilon_p R_{p,i}} = \frac{D_e}{\varepsilon_p + K_{d,i} \rho_s (1 - \varepsilon_p)} \tag{7}$$

where D_e is the effective diffusion coefficient (m^2/s) of the rock matrix (assumed identical for all nuclides). The analytical solution to Eq. (6), assuming $C_{p,i}(z = 0,t) = C_{p,i}^0$ and $C_{p,i}(z,t = 0) = 0$, can be formulated as (Neretnieks 1980)

$$C_{p,i}(z,t) = C_{p,i}^0 \, erfc(\frac{z}{2\sqrt{D_a t}}) \tag{8}$$

The effective diffusion depth into the rock matrix during time t can be defined as the centre of gravity of the concentration profile:

$$z_D = \frac{1}{C_{p,i}^0} \int\limits_{z=0}^{\infty} C_{p,i}(z,t) dz \tag{9}$$

where z_D is the effective diffusion depth from the fracture surface (m). For the analytical solution in Eq. (8), z_D can be approximated (Neretnieks 1980) as

$$z_D \approx 1.13\sqrt{D_a t} = 1.13\sqrt{\frac{D_e t}{\varepsilon_p R_{p,i}}} \tag{10}$$

From Eqs. (3) and (10) one can easily derive the ratio of effective advection distance/effective diffusion depth:

$$\frac{z_A}{z_D} = \frac{K\nabla h}{1.13\sqrt{\varepsilon_p R_{p,i} D_e}}\sqrt{t} \tag{11}$$

Equation (11) was used to calculate the z_A / z_D ratios shown in Table 1. Conservative but reasonable values were used as input. Permeability of the rock matrix was measured for three rock samples from Palmottu (adjacent to rock samples 211/R325, 103/R346, and 168/R357, respectively) using the helium gas technique (Hartikainen et al. 1996). The permeability used here ($k = 1 \cdot 10^{-18}$ m^2) was the highest value measured; the respective hydraulic conductivity is derived from Eq. (5). The value for dynamic viscosity for water ($\mu = 1$ mPas) was derived from Lide (1990). The hydraulic gradient used ($\nabla h = 5$ %) is slightly above the highest inter-hole head-level gradient measured at Palmottu, no attenuation with depth was assumed.

Table 1. Effective advection distance/effective diffusion depth ratio (z_A / z_D) vs. time.
$\nabla h = 5 \cdot 10^{-2}$, $\varepsilon_p = 2 \cdot 10^{-3}$, $k = 1 \cdot 10^{-18}$ m^2, $\mu = 1$ $mPas$, $\rho = 1\ 000$ kg/m^3, $K = 1 \cdot 10^{-11}$ m/s, $D_e = 2 \cdot 10^{-13}$ m^2/s, $K_d(uranium) = 3 \cdot 10^{-2}$ m^3/kg, $\rho_s = 2\ 700$ kg/m^3.

Time (a)	Advection distance / Diffusion depth
10^1	$2.0 \cdot 10^{-3}$
10^2	$6.2 \cdot 10^{-3}$
10^3	$2.0 \cdot 10^{-2}$
10^4	$6.2 \cdot 10^{-2}$
10^5	$2.0 \cdot 10^{-1}$
10^6	$6.2 \cdot 10^{-1}$

It can be seen in Table 1 that, for the times considered, diffusion is the dominating migration mechanism in the rock matrix, and that with increasing time this relative dominance decreases. This is due to the fact that effective diffusion depth is proportional to the square root of time, while the effective advection distance is directly proportional to time. The time range considered in Table 1, although limited, covers well a continuous evolution period of a natural analogue. The reason for this is that at Finnish latitudes repeating glaciations have changed the hydraulic gradients fundamentally, during the last 1 000 000 years at a rate of about once in 100 000 a (e.g. Eronen & Olander 1990), and thus any hydraulic gradient could last at most 100 000 a. This applies, of course, to the concentration gradients, too. Taking further into account the conservative input data for the advection model in this exercise, the results in Table 1 indicate clearly that at Palmottu, advection is most likely not comparable to diffusion as a migration mechanism in a rock matrix.

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