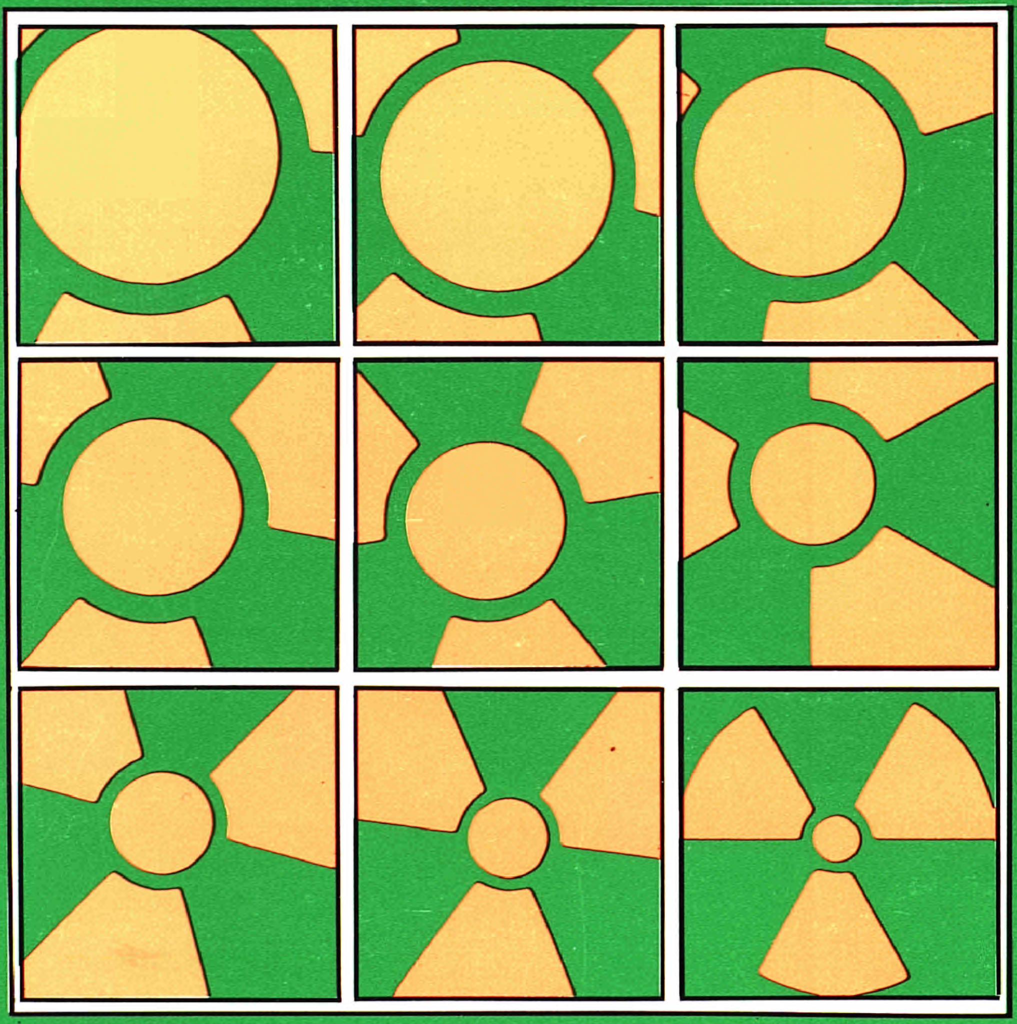
Commission of the European Communities

nuclear science and technology

Natural decay series radionuclide studies at the Needle's Eye natural analogue site



Report

EUR 13126 EN

5

Commission of the European Communities

nuclear science and technology

Natural decay series radionuclide studies at the Needle's Eye natural analogue site

A. B. MacKenzie,[1] R. D. Scott,[1] C. M. Houston,[1] P. J. Hooker[2]

[1] **Scottish Universities Research and Reactor Centre**
East Kilbride
Glasgow G75 OQU
United Kingdom
[2] **British Geological Survey**
Keyworth
Nottingham NG12 5GG
United Kingdom

Contract No FI1W/0073-UK

Topical report

Work carried out within the Mirage project of the
R&D programme on management and storage of radioactive waste

Directorate-General
Science, Research and Development

1991

Published by the
COMMISSION OF THE EUROPEAN COMMUNITIES

Directorate-General
Telecommunications, Information Industries and Innovation

L-2920 Luxembourg

Cataloguing data can be found at the end of this publication

Luxembourg: Office for Official Publications of the European Communities, 1991

ISBN 92-826-2347-5 Catalogue number: CD-NA-13126-EN-C

Printed in France

PREFACE

The Scottish Universities Research and Reactor Centre has been studying the Needle's Eye natural analogue site in Dumfries and Galloway District, southwest Scotland, in conjunction with the British Geological Survey (BGS), which has been co-ordinating the research programme. This work on a natural radioactive geochemical system has been carried out with the aim of improving our confidence in using predictive models of radionuclide migration in the geosphere. It has involved collaboration with the Ecole des Mines de Paris (Centre d'Informatique Géologique), Fontainebleau, for hydrogeological modelling. The natural analogue work jointly carried out has been supported by the Department of the Environment from July 1986 to March 1989 and by the Commission of the European Communities from July 1988 to September 1989 under the CEC shared-cost action MIRAGE II Project.

The Needle's Eye site lies within the Southwick Coast Reserve of the Scottish Wildlife Trust who kindly gave permission to sample for soils, sediments and waters for analysis.

This report is one of a series being produced from this effort and is concerned with the U/Th decay series characterisation of the hydrothermal mineral veins and the movement of these radionuclides into post-glacial flood plain deposits. Other reports and papers listed below give further details of the programme:

[1] HOOKER, P.J., MacKENZIE, A.B., SCOTT, R.D., IVANOVICH, M., BALL, T.K., BASHAM, I.R., BLOODWORTH, A.J., ROBERTS, P.D. : Natural analogues of radionuclide migration: reconnaissance study of sites (May 1985-March 1986). British Geological Survey Report, FLPU 86-6 (1986).

[2] HOOKER, P.J., CHAPMAN, N.A., MacKENZIE, A.B., SCOTT, R.D., IVANOVICH, M. in: Natural Analogues in Radioactive Waste Disposal (B. Côme and N.A. Chapman, Eds) CEC EUR 11037 EN (Graham & Trotman), 104-115 (1987).

[3] ROBERTS, P.D., BALL, T.K., HOOKER, P.J., MILODOWSKI, A.E. : A uranium geochemical study at the natural analogue site of Needle's Eye, SW Scotland. Mat. Res. Soc. Symp. Proc. **127**, 933-940 (1989).

[4] BASHAM, I.R., MILODOWSKI, A.E., HYSLOP, E.K., PEARCE, J.M. : The location of uranium in source rocks and sites of secondary deposition at the Needle's Eye natural analogue site, Dumfries and Galloway. British Geological Survey Technical Report WE/89/56 and DOE Report DOE/RW/89.091 (1989).

[5] HIGGO, J.J.W., FALCK, W.E., HOOKER, P.J. : Sorption studies of uranium in sediment-groundwater systems from the natural analogue sites of Needle's Eye and Broubster. British Geological Survey Technical Report WE/89/40 and DOE Report DOE/RW/89.072 (1989).

[6] SOUBEYRAN, R., LEDOUX, E., de MARSILY, G. : Modélisation du transfert d"analogues' naturels. Ecole des Mines de Paris (C.I.G.) progress report to 31.12.87, LHM/RD/88/11, 42pp (in French) (1988).

[7] DOUBLET, R., JAMET, Ph., SOUBEYRAN, R. : Hydrogéochimie du site de Needle's Eye - Premiere interprétations. Ecole des Mines de Paris (C.I.G.) progress report to 30.6.88, LHM/RD/88/59, 34pp (in French) (1988). Also in English as British Geological Survey Technical Report WE/89/55 and DOE Report DOE/RW/89.078 (1989).

[8] JAMET, Ph., LACHASSAGNE, P., DOUBLET, R. : Modélisation hydrogéochimique du site de Needle's Eye. Ecole des Mines de Paris (C.I.G.) progress report to 31.12.88, LHM/RD/89/66, 38pp (in French) (1989).

[9] JAMET, Ph., LACHASSAGNE, P., DOUBLET, R., LEDOUX, E. : Modelling of the Needle's Eye natural analogue. Ecole des Mines de Paris (C.I.G.) Report LHM/RD/89/81. Also as British Geological Survey Technical Report WE/89/64 and DOE Report DOE/RW/90.015 (1990).

[10] SCOTT, R.D., MacKENZIE, A.B., HOUSTON, C.M., HOOKER, P.J., BEN-SHABAN, Y.A. : Uranium transport and retardation at the Needle's Eye natural analogue site, southwest Scotland. Proceedings of the "Migration 89" Int. Conf., Monterey, CA, USA, Nov.6-10, 1989. Radiochimica Acta (in press).

ABSTRACT

Characterisation of the mechanisms, and rates, of the transport and retardation processes which affect radionuclides in the geosphere is of fundamental importance in far field considerations arising in safety assessments for proposed radioactive waste repositories. Moreover, application of speciation and transport codes to well defined natural geochemical processes is the only way of validating models used in such safety assessments under the complex environmental conditions operating over timescales appropriate to the requirements of radioactive waste disposal.

A study is described of the application of natural decay series radionuclides to the investigation of dissolution, transport and retardation processes affecting radionuclides in the environment around a uranium mineralisation in south west Scotland. A general geochemical description of the site is developed in which the radionuclide source term is characterised and the release rate of uranium from the vein is estimated. Dispersion of uranium for distances of up to 50m is observed in post glacial silts while the virtual insolubility and immobility of thorium under the same ambient conditions is confirmed. Three distinct retardation processes affecting uranium during groundwater transport are identified and characterised. Similarly two retardation mechanisms are identified for radium.

The information derived from this work will be used as input data by other groups involved in the application of speciation and transport codes.

CONTENTS

EXECUTIVE SUMMARY

In feasibility studies relating to the disposal of radioactive waste in underground repositories, the host rock, or far field, is identified as an important component in the multiple barrier system designed to restrict, to radiologically acceptable levels, the long term release of any of the waste radionuclides to the biosphere. Predictive modelling of the rate of radionuclide transport through the far field is critically dependent upon a thorough knowledge of the mechanisms and rates of geochemical, hydrological and geophysical processes operating in the relevant environment and upon the validity of computer codes used to describe these processes. A considerable research effort has therefore been devoted in recent years to "Natural Analogue Studies" with the aims of providing qualitative and quantitative descriptions of such far field processes and identifying suitable natural geochemical systems for testing computer codes under realistic, complex conditions operating over suitably long timescales.

This report describes a study of the distribution, geochemical behaviour and transport of natural decay series radionuclides in the environment around a uranium mineralisation vein at a location known as "The Needle's Eye" on the Solway Coast of South West Scotland. The work described here forms part of a larger co-ordinated programme which also involves geochemical, hydrological and geophysical studies by BGS and evaluation of the potential of this natural system for testing speciation and transport codes by BGS and the Ecole des Mines de Paris. The objectives of the natural decay series contribution to the study were:

1. to characterise the uranium and thorium isotopic composition of the vein material and thereby to assess the significance of the vein as a source of radionuclides to groundwaters in the area;

2. to investigate radionuclide concentrations in the groundwaters;

3. to investigate radionuclide concentrations in fracture lining minerals in water-bearing fissures in the granodiorite;

4. to characterise the dispersion of uranium series radionuclides on a scale of the order of 1m into the overlying soils from the line source of the vein;

5. to define the behaviour of uranium being transported by groundwater as it moves through the varying redox conditions in the different zones of the site;

6. to assess the extent of large scale dispersion of uranium into the silts of the floodplain of the Solway Firth.

Standard radiochemical methods were used in the work and were validated by analysis of standard reference material. Interpretation of the analytical data is based upon observations of variations in the

concentrations and activity ratios of the natural decay series radionuclides in samples of water, rock and soil from the site. A conceptual model has thus been developed to describe the geochemical behaviour and transport of uranium (and to a lesser extent of thorium and radium) in this system. The essential features of this model are as follows.

There is negligible dispersion of uranium or any of its descendant radionuclides into overlying soils from the line source of the vein. Significant dissolution of uranium and radium occurs when groundwater interacts with the vein and this leads to an increase in the specific activity of ^{238}U in the groundwater from about 0.01Bq l^{-1} to values in the range 0.3 to 0.74Bq l^{-1}. Retardation of both uranium and radium by uptake in carbon minerals lining fissures in the granodiorite occurs during transport and this, or some other mechanism, results in the retention within the granodiorite of most of the radium which is dissolved from the vein. Dissolution and transport of thorium is negligible in comparison with that of uranium. Most of the dissolved uranium (at least 80 to 90%) is removed from solution when the groundwater draining from the granodiorite interacts with a zone of anoxic, organic rich soil at the base of the cliff. The mechanism involved may simply be the reduction of uranium from the soluble 6+ oxidation state to the insoluble 4+ form or could involve active uptake of uranium by the organic matter. The uranium which remains in solution is subject to further retardation by uptake on Fe/Mn oxides as the groundwater drains across the Solway Firth floodplain silts.

The following major conclusions are drawn from the work.

1 The observed general behaviour of uranium, thorium and radium at this study site is consistent with the established geochemistry of these elements.

2 The vein material acts as a source of uranium and radium to groundwaters.

3 The probability of dissolution of uranium from the vein has an upper limit of about 5×10^{-5} y^{-1}.

4 Effectively zero dissolution of ^{230}Th from the vein was observed.

5 Groundwater transport has resulted in dispersion of uranium over distances of about 50m in the post glacial silts of the Solway floodplain.

6 Uptake of uranium and radium by carbonate minerals which line fracture surfaces in the rocks around the vein has been demonstrated to be a significant retardation process affecting these elements during groundwater transport. The rate of dissolution, transport and redeposition of radium in the rock system is rapid relative to a five year timescale. The efficiency of retardation of radium by this (or some other) mechanism appears to be greater than that of uranium.

7 The anoxic soil presents a highly efficient barrier to transport of uranium in groundwater with the efficiency of retention of uranium being at least 80 to 90%.

8 The cliff acts as a source of uranium (about an order of magnitude less than the vein) in areas remote from the main mineralisation at Needle's Eye.

9 Continuous retardation of uranium, by uptake on iron and manganese oxides, occurs as groundwater moves across the surface of the merse silts. The uranium removal process follows first order kinetics and is characterised by a halving distance for the groundwater concentration of uranium of 10m.

10 Upwards migration of radionuclides from the vein into overlying soils was not observed. The soil profiles in the immediate vicinity of the vein appear to have evolved dominantly as the result of groundwater leaching of radionuclides originally contained in the soil when it was deposited, with any dissolution and redeposition of radionuclides from the vein being a minor effect. Rapid (on a 5 year timescale) dissolution and redeposition of ^{228}Ra occurs in these soils, with the sulphide-sulphate system possibly exerting a control over radium solubility.

INTRODUCTION

In feasibility studies relating to the disposal of radioactive waste in underground repositories (eg NAGRA, 1985) the host rock, or far field, is identified as an important component of the multiple barrier system designed to restrict , to radiologically acceptable levels, the long term release of any of the waste radionuclides to the biosphere (IAEA, 1980; Chapman and McKinley, 1987; Roxburgh, 1987). Predictive modelling of the rate of radionuclide transport through the far field, upon eventual failure of the near field engineered barriers, is therefore an important feature of performance and safety assessments for proposed radioactive waste disposal repositories. Such modelling is critically dependent upon a thorough knowledge of the mechanisms and rates of geochemical, hydrological and geophysical processes operating in the far field environment, and upon the validity of computer codes (in particular speciation and transport codes) used to describe these processes. Some of the far field processes of importance in this context are, however, relatively poorly characterised and remain active areas of research at present (eg radionuclide speciation, sorption processes, matrix diffusion, redox front reactions and the possible influences of micro-organisms and colloids). Moreover, it is now widely accepted that, if possible, the computer codes used in safety assessments (derived largely from thermodynamic considerations in conjunction with the results of relatively simple laboratory-based experiments operating over, at most, a few years) should be validated by comparison with the effects of well defined natural geochemical processes operating in realistic environmental conditions over timescales of up to 10^7 years.

A considerable research effort has therefore been devoted to "Natural analogue studies" (Chapman et al, 1984) in recent years in an attempt to address such problems in radioactive waste disposal, both within the UK (eg Hooker et al, 1986; Hooker and Chapman, 1989) and internationally (eg Côme and Chapman, 1987; Côme and Chapman, 1988). The object of many of these studies has been the definition of numerical values for parameters such as diffusion coefficients or the characterisation of processes considered to be of importance in far field radionuclide transport and retardation. Such processes are generally considered in a generic, rather than site specific, way since it may be necessary to consider a variety of different far field environments and to accommodate potential changes in the far field conditions over long time periods. Examples of studies of this type are the investigation of radionuclide diffusion rates in the interstitial waters of saturated clays (MacKenzie et al, 1983; MacKenzie et al, 1984; Hooker et al, 1985) and studies of the effects of sorption and matrix diffusion processes on radionuclide transport in water bearing fractures in crystalline rocks (Smellie et al, 1986; Alexander et al, 1988; Alexander et al, 1989). In these latter studies, the radionuclides of the natural radioactive decay series (Figure 1) have proved to be particularly useful since the varying chemical behaviour of different nuclides in the decay chains can be used to investigate geochemical processes and, in suitable cases, the radioactive decay (or growth) of the nuclide involved can provide an insight into the rates of processes (Ivanovich and Harmon, 1982). As a further development of the natural analogue approach, a primary objective of recent programmes (eg The International Poços de Caldas Project; Côme and Chapman, 1987) has been to test speciation and transport codes against natural geochemical observations. This is, however, an extremely difficult task, with one of the main limitations being reconciliation of the rigorously defined conditions required for the models with the uncertainties involved in defining the processes operating in the natural system and the problems of producing a suitably comprehensive and reliable analytical database. Nevertheless, comparison with natural systems is the only option for validation of model codes under realistic, complex natural conditions over the timescales appropriate to radioactive waste disposal considerations.

The work described in this report involves a study of natural decay series radionuclides in the environment around a uranium mineralisation vein at a location known as 'The Needle's Eye' on the Solway coast of South West Scotland. The work reported here forms part of a larger programme, funded by the Department of the Environment and the Commission of the European Communities, with the aims of characterising processes of potential importance in the far field transport and retardation of radionuclides and of providing test cases for validation of speciation and transport codes. The overall programme thus entails a series of inter-related studies including, in addition to the present work, geochemical, hydrological and geophysical measurements by BGS and evaluation of the potential of this system for validation of speciation and transport codes by BGS and the Ecole National Superieure Des Mines De Paris.

THE NEEDLE'S EYE NATURAL ANALOGUE SITE

The existence of a series of uranium mineralisation veins in the Solway coastal area of South West Scotland was discovered during a car-borne gamma spectrometry survey of the area in the early 1960's. Some 60 locations containing detectable uranium mineralisation were identified during the survey (Miller and Taylor, 1966) and the present study site is centred upon the largest and most intensively studied of these veins, lying to the east of an ancient sea arch known as The Needle's Eye. The site is located on the edge of the Criffel granodiorite (Figure 2) where the intruded rocks of the pluton are faulted against Carboniferous rocks underlying the floodplain of the Solway Firth to the South. The edge of the granodiorite forms a distinct cliff and Miller and Taylor (1966) positively demonstrated the presence of the vein in the bedrock by excavations in the field at the top of the cliff, in the cliff face itself and beneath the post glacial flood plain deposits at the base of the cliff (known locally as The Merse).

Uranium occurs in the veins in the form of pitchblende along with associated mineralisation of other elements including Cu, Bi, Co, Ni, As and Sb. The age of the vein material was reported by Miller and Taylor (1966) to be 185 ± 20 million years, substantially more recent than the age of the Criffel pluton of 397 ± 2 million years (Halliday et al, 1980).

The bedrock and surface soil characteristics of the site are shown schematically in Figure 3 and the following sequence is encountered on moving from the area above the cliff towards the Solway Firth:

1 Inland from the cliff, the granodiorite bedrock is overlain by 1 to 2m depth of boulder clay. This area is grass covered and the fields are used for grazing cattle and sheep. A road forms the southern limit of this area, at the edge of the cliff. Groundwaters draining from these fields are channelled under the road via a conduit to form a small stream running to the west of the Needle's Eye.

2 The cliff, which is of variable steepness and is densely overgrown with trees and shrubs. At the foot of the cliff, the outcropping rock contains obvious water bearing fissures and, in places, overhanging rock forms shallow caves. A narrow band of scree forms the limit of the cliff area.

3 Along the base of the cliff is a band of waterlogged, organic-rich, anoxic soil of width varying from 5 to 10m. The organic rich material extends to a depth of about 1m and is underlain by a narrow layer (~ 10cm) of fine clay then a coarse gravel (identified by BGS as a fossil beach deposit).

4 Adjoining the organic, boggy area is a narrow belt of silt covered with a dense vegetation of trees and shrubs. This zone also has a variable width of some 5 to 10m and the soil depth is 1 to 2m. A small stream draining the organic soil at the base of the cliff emerges in this area.

5 The boundary of the floodplain of the Solway Firth is marked by a sharp transition in the vegetation from the trees and shrubs of zone 4 to the salt resistant grass of the Merse. This area consists of silt of depth 1 to 2m overlying carboniferous siltstones and extends for about 55m to the edge of the Southwick Water, a salt water inlet of the Solway Firth. The merse silts are cut by a number of small, meandering streams and those emerging from the field drain and organic bog described above merge before flowing into the Southwick Water.

The cliff area and the adjoining section of the Merse constitute a nature reserve owned by the Scottish Wildlife Trust. Prior permission for sampling was obtained by BGS from the Scottish Wildlife Trust and sampling was performed within agreed guidelines to avoid any detectable damage to the site or disturbance of the natural habitat.

Complementary studies by BGS have characterised the geochemical profile of the sediments at the base of the cliff and the major features of the hydrology of this area. Figures 4 and 5 show schematic representations of the findings of this work, with a notable feature being the artesian input of water at the base of the sediment.

The objectives of the natural decay series contribution to the study of this site were:

1 To characterise the uranium and thorium isotopic composition of the vein material and thereby to assess the significance of the vein as a source of radionuclides to groundwaters in the area.

2 To investigate radionuclide concentrations in the groundwaters.

3 To investigate radionuclide concentrations in fracture lining minerals in water bearing fissures in the granodiorite.

4 To characterise the dispersion of uranium series radionuclides on a scale of the order of 1m into the overlying soils from the line source of the vein.

5 To define the behaviour of uranium being transported by groundwater as it moves through the varying redox conditions in the different zones of the site defined above.

6 To assess the extent of large scale dispersion of uranium into the Merse silts.

The integration of the individual components of this work, along with the complementary work by BGS and the Ecole Des Mines, thus has the aim of producing a well characterised geochemical system with identified radionuclide transport and retardation processes which have the potential for testing speciation and transport codes. Preliminary reports of some of the other aspects of the study have already been presented elsewhere (Soubeyran et al, 1987; Roberts et al, 1988; Doublet et al, 1988; Breward and Peachey, 1988; Basham and Hyslop, 1989; Higgo et al, 1989).

ANALYTICAL METHODS

The uranium/thorium analysis, based upon the method of Bacon and Rosholt (1982), involved anion exchange separation of uranium and thorium from the samples followed by alpha spectroscopy. Sample weights of about 2g were used for soils and sediments and the samples were initially furnaced at 450°C to destroy organic matter. Thereafter an aliquot of a solution containing a known activity of ^{232}U, with its daughter ^{228}Th in transient equilibrium, was added as a yield tracer to the ashed sample. The spike solution used is a dilution of a primary ^{232}U/^{228}Th standard solution purchased from AERE Harwell. Total sample dissolution was then effected by acid digestions using HCl, HNO_3 and HF, with intermediate leaching of soluble material into 6M HCl. In the early stages of the work, digestions were performed in a Teflon beaker on a hotplate but, more recently, microwave oven dissolution methods have been employed (Nadkarni, 1984; Lamothe et al, 1986). Uranium and thorium were coprecipitated from the 6M HCl leaching solution with $Fe(OH)_3$ by addition of NH_4 OH, after which the precipitate was re-dissolved in 9M hydrochloric acid. Iron was removed by solvent extraction into di-isopropyl ether and, after heating to remove all residual traces of ether, the solution was allowed to cool to room temperature. Uranium was then extracted on a 6cm x 1cm^2 column of Bio-Rad AG1x8 anion exchange resin. The 9M HCl solution which was washed through the column was retained for thorium analysis, while the uranium was eluted from the column with 1.2M HCl. A second purification of the uranium was performed by a repeat extraction from 9M HCl onto AG1x8 resin and elution with 1.2M HCl after which the solution was taken to dryness, the residue re-dissolved in 8 drops of concentrated HCl and made up to 40ml with a solution of 3.75% (m/V) NH_4 Cl. The uranium was electrodeposited from this solution onto a stainless steel disc in a deposition cell based upon the design of Hallberg et al (1960). The uranium spectrum was recorded by means of a surface barrier detector and simple multichannel analyser system.

In the thorium analysis it is essential to remove all traces of Cl^- ion from the sample since the presence of even trace amounts can interfere with the subsequent anion exchange extraction. Thorium was therefore coprecipitated with $Al(OH)_3$ by addition of NH_4OH to the 9M HCl solution obtained above, using the natural Al in the sample. The $Al(OH)_3$ precipitate was thoroughly washed with distilled water then re-dissolved in HNO_3. Al $(OH)_3$ was re-precipitated, the precipitate washed with distilled water and then re-dissolved in the minimum volume of concentrated HNO_3, after which the concentration of the nitric acid was adjusted to 8M. Thorium was extracted from the 8M HNO_3 solution onto Bio Rad AG1x8 and was eluted using 1.2M HCl. The elution solution was taken to dryness and the residue dissolved in 8 drops of concentrated HCl and 40ml of 3.75% (m/V) NH_4 Cl solution for electrodeposition and alpha spectroscopy as described above for uranium.

Minor modifications of this method were required on occasions in order to produce suitably thin sources for alpha spectrometry, especially for the organic rich soils from zone 3 at the foot of the cliff. A further modification was required for certain samples in which the $^{228}Th/^{232}Th$ activity ratio was found to deviate significantly from unity. The conventional assumption required in the use of a ^{228}Th yield tracer is that, in the natural sample, the $^{228}Th/^{232}Th$ activity ratio is unity so that in the α-spectrum the sample contribution to the events in the ^{228}Th α-peak can be taken as being equal to the number of events in the ^{232}Th α-peak. Thus, in samples for which the $^{228}Th/^{232}Th$ ratio does not equal unity, an additional procedure for determination of this ratio is required, namely the analysis of unspiked samples. The effect of this correction, as opposed to the assumption of equilibrium, generally produces only a small change in the calculated thorium isotope activities since ^{232}Th and its descendants are present in the samples at low levels. Nevertheless the analysis of unspiked thorium samples has been introduced as a standard component of the analytical method at a minimal level of "screening "analyses for groups of similar samples and, where $^{228}Th/^{232}Th$ disequilibrium is revealed, the analysis is applied to all of the samples in the group.

Analysis of vein material followed the same general procedure as described above, but with the following modifications, necessitated by the very high specific activity of U:

(a) the sample weight was restricted to a few tens of mg;

(b) furnacing was not employed;

(c) the spike was not added at the beginning of the dissolution. In this case, in order to obtain compatible activities of uranium in the sample and in the amount of spike used, the sample was dissolved, the solution volume made up to 1l and the spike was added to a subsample of the solution which was then analysed and the initial sample composition calculated by proportion.

Water analyses were similar except that Al and Fe carriers were added and the samples were initially passed through 0.22 μm filters.

The accuracy of the method was evaluated by analysis of the Canadian Centre for Mineral and Energy Technology standard reference sandstone Dl-1a (CANMET, 1983), with results for spiked and unspiked analyses showing a satisfactory level of accuracy as indicated in Table 1. The accuracy of the method was further validated by comparison with other analytical methods (MacKenzie et al, 1986) and by a comprehensive interlaboratory comparison organised as part of the International Pocos de Caldas Project. Within-laboratory replicate analyses indicated that values for the precision of uranium and thorium analyses were about 5%, while the interlaboratory exercise indicated that if results from different laboratories were to be compared, uncertainties of about 6% and 8% should be applied to uranium and thorium analytical results respectively.

In addition to whole samples of sediment, some samples were also subjected to a sequential leaching analytical scheme, as described by Cook et al (1984), designed to indicate the association of radionuclides with different operationally defined constituents of the sediment (viz available, exchangeable, organic, oxides and residual).

RESULTS

The results for analysis of a sample of the bulk uranium vein material from the exposed section of the vein on the cliff at the Needle's Eye are shown in Table 2, along with the results for analysis of a sample of pitchblende separated from the vein. The specific activity of 2.48 x 10^6 Bq kg^{-1} of ^{238}U for the bulk vein material corresponds to a concentration of uranium of 20% by weight.

Only a limited number of water samples were analysed during the course of the study and a comprehensive programme of water analyses has not been possible as a result of restrictions on access to the site. Nevertheless, a systematic pattern does emerge when the ranges of values of uranium concentration and the $^{234}U/^{238}U$ activity ratios are considered in the context of the various zones of the site defined above. The results for the water analyses are summarised on this basis in Table 3. In all cases, ^{230}Th was not detectable.

Four samples of carbonate minerals (tufa) lining fractures in the hornfels and felsite rocks around the Needle's Eye were collected by BGS, Edinburgh and the results for analysis of these samples are given in Table 4.

Six sections were excavated by spade at the positions indicated in Figure 6 as Pits 1 and 5 in the anoxic zone, Sections 1, 2 and 3 in the merse area and 'intertidal section' in the course of the Southwick Water. Pits 1 and 5 were excavated to the level of the bedrock at 110cm and 65cm respectively. Section 3 was excavated to a depth of 55cm which marked the level of the water table at this location and at which rapid ingress of water prevented further excavation. The remaining three sections were each excavated to a depth of 1m. Pit 5 was sampled in 5cm vertical increments while all of the other sections were sampled in 10 cm vertical increments. The results for samples so far analysed from these various sections are presented in Tables 5-7 and results for analysis of a sample of offshore surface sediment from the north eastern basin of the Irish Sea are also contained in Table 7.

Two samples each from the intertidal section and from section 3 in the merse were also subjected to the sequential leaching scheme of Cook et al (1984) and the results of this exercise are shown in Table 8. A sample of surface (top 1cm) of soil was taken every 5m on a transect running from the mean high water mark of the Southwick Water inland for a distance of 55m as shown in Figure 6. The samples were analysed for uranium and thorium and, to provide complementary data, for radiocaesium, plutonium alpha emitting isotopes and ^{241}Am; the results are presented in Tables 9(a) and (b).

A pit, identified as NEP 2 in Figure 6, was excavated by BGS directly over the vein in the field at the top of the cliff and samples from three vertical profiles in the section were analysed for natural decay series radionuclides, with the sampling positions being shown in Figure 7 and the results in Tables 10 to 12.

DISCUSSION

Before a detailed discussion of the results, it is useful initially to consider some of the basic assumptions and methods of interpretation used in natural decay series studies of this type. Of fundamental importance is the assumption that uranium in the 6+ oxidation state is normally soluble in natural waters whereas uranium in the 4+ oxidation state and thorium (which occurs naturally only in the 4+ oxidation state) are highly insoluble in natural waters. This behaviour pattern is well established by observation of natural geochemical systems (Ivanovich and Harmon, 1982) and is supported by relatively simple chemical principles. Thus, U with an ionic potential of 8.22 (Mason, 1966; Henderson, 1982; Greenwood and Earnshaw, 1984) readily forms the uranyl ion (UO_2^{2+}) which is capable of forming soluble anionic complexes with naturally occurring ligands (eg $[UO_2\ (CO_3)_2]^{2-}$). In contrast, U^{4+} and Th^{4+} with respective ionic potentials of 4.49 and 4.25 are highly susceptible to hydrolysis, leading to precipitation of insoluble hydroxides in aqueous systems and to sorption on the surfaces of negatively charged mineral particles or organic matter (Wedepohl, 1978).

Isotopic fractionation of ^{238}U from ^{234}U is also of considerable importance and is considered to occur as a result of alpha recoil, oxidation and lattice destabilisation during the decay of ^{238}U, and possibly enhanced rates of etching along alpha particle tracks in minerals by natural waters, leading to the preferential removal of ^{234}U into solution relative to ^{238}U (Fleischer, 1980). Thus, uranium dissolution from minerals can be considered to occur as the result of two competing processes, namely bulk dissolution of the mineral and preferential 'recoil' loss of ^{234}U. Rapid bulk dissolution of minerals would result in groundwater ^{234}U/^{238}U activity ratios equal to unity whereas a slow rate of dissolution relative to 'recoil' loss of ^{234}U will give a groundwater ^{234}U/^{238}U activity ratio of greater than one and a corresponding ratio in the leached mineral of less than one. Groundwaters thus commonly have high ^{234}U/^{238}U ratios, as do minerals formed by deposition from groundwater within the last 10^6 years or so.

On the basis of these considerations, the following general observations can be made with respect to radionuclide activity ratios in rock (and soil etc) samples:

(a) If the ^{234}U/^{238}U activity ratio is less than one, 'recoil' loss of ^{234}U to groundwater has affected the sample. The greater the deviation of the ratio from unity, the slower is the rate of bulk dissolution of the mineral relative to the rate of recoil loss of ^{234}U.

(b) If the ^{234}U/^{238}U activity ratio is greater than one, deposition of uranium from groundwater has occurred within the last 10^6 years.

(c) If the ^{230}Th/^{234}U ratio is less than one, uranium deposition from groundwater is implied.

(d) If the ^{230}Th/^{234}U ratio is greater than one, uranium removal to groundwater is implied. A complicating factor can, however, apply in this situation in that if a sudden (relative to the half lives involved) deposition of uranium occurs with a ^{234}U/^{238}U activity greater than one, then ^{230}Th can grow in to a state of transient equilibrium (Friedlander et al, 1981) with the excess ^{234}U, to give a ^{230}Th/^{234}U ratio greater than unity.

A very useful method for presentation of natural decay series results for rock analysis is by plotting one radionuclide activity ratio against another. For example, Latham and Schwartz (1987) have used ^{234}U/^{238}U versus ^{230}Th/^{234}U plots in the investigation of uranium removal rates from igneous rocks. In the present work we have adopted the approach of Thiel et al (1983) and use plots of ^{234}U/^{238}U versus ^{230}Th/^{238}U. With the assumption of initial secular equilibrium conditions which have subsequently been perturbed by rock-water interaction, plots of this type can be used to identify samples which have been affected by uranium deposition or removal processes. Extension of this approach to include the possibility of continuous or sudden (relative to the ^{230}Th half life) discontinuous processes can, as discussed in detail by Alexander et al (1989), be used to identify those areas of the graph shown in Figure 8 which can be reached by operation of various processes.

Radium can also provide useful information in certain natural decay series studies since, with a single possible oxidation state of +2 and ionic potential of 1.48, it is a relatively soluble species in many natural aqueous systems. Removal of radium from solution generally occurs by coprecipitation in situations where species such as Ca CO_3 or $BaSO_4$ are being deposited. Thus, although radium itself is not directly affected by redox processes, it can be dissolved or precipitated under varying redox conditions affecting the sulphide-sulphate system.

The uranium analysis of the bulk vein material (Table 2) indicates a composition of about 20% by weight of uranium and the ^{230}Th/^{234}U activity ratio of 1.84, in conjunction with a ^{234}U/^{238}U activity ratio of unity indicates dissolution of total uranium from the vein material at a rate which is high relative to the rate of preferential 'recoil' loss of ^{234}U. By assuming an initial state of equilibrium which has been disturbed by the onset of the leaching process, values for the removal probability per unit time of a uranium atom can be derived as a function of the leaching time if this removal probability is assumed to be constant. For example, if a time of 12,000 years, corresponding to the end of the last period of glaciation, is taken as the time during which leaching of uranium has occurred, then a removal probability of 5×10^{-5} y^{-1} is obtained (ie. dissolution of 5×10^{-5}g of uranium/g of uranium in the vein/year). As discussed below, the appropriate leaching time is in fact likely to be much greater than 12,000 years so this leaching value should be regarded as an upper limit. The analysis of the vein material thus confirms that it acts as a source of uranium to groundwaters in the area.

The separated pitchblende shows a higher uranium concentration than the bulk vein material and has a ^{234}U/^{238}U activity ratio of 0.96 (average of two measurements) and a ^{230}Th/^{234}U activity ratio of 0.98 which is, given the analytical uncertainty, indistinguishable from unity. These results are consistent with the dissolution of uranium from the vein by groundwater since the bulk sample consisted of weathered material whereas the separated pitchblende was unweathered. It should, however, be noted that while any loss of uranium from the unweathered pitchblende had been insufficient to produce a detectable effect on the ^{230}Th/^{234}U activity ratio, loss of ^{226}Ra is evidenced by the ^{226}Ra/^{230}Th activity ratio of 0.79 for this sample.

The enrichment of uranium in groundwaters which interact with the rocks of the cliff area is clearly seen in the results shown in Table 3. If the ^{238}U concentration of 0.012 Bq l^{-1} for the field drain water is taken as the 'normal' groundwater concentration before interaction with the rocks of the cliff, then it is apparent that enrichments by factors of 25 to 62 are observed in the water draining from the cliff. It has been noted qualitatively that the uranium concentration in the water is inversely proportional to the flow rate, which in turn varies directly with the amount of rainfall. A further point of interest here is that the ^{234}U/^{238}U ratios for these waters have all given values of less than unity (uncertainties here and throughout are propagated 1σ errors arising from counting statistics). This suggests that the material presently acting as the source of uranium has previously been subject to leaching in which preferential loss of ^{234}U was occurring at a relatively high rate compared to total uranium dissolution but that at present, total dissolution is much more rapid ie. it is probable that (at least) a two stage leaching history applies to the source of uranium.

The single ^{226}Ra measurement for water draining through a fissure in the cliff gave a ^{226}Ra/^{234}U ratio of 0.08 indicating that, for this sample at least, some highly efficient retardation process is operating within the rock, preventing the effective release from the rock body of any ^{226}Ra initially dissolved from the vein material.

The results of the analysis of water from the organic rich soils suggest that uranium is removed from solution with an efficiency of about 98% when groundwater interacts with the highly reducing conditions in this area. The mechanism of retardation of uranium may simply involve reduction of uranium from the 6+ to the 4+ oxidation state or could involve an active uptake of the uranium by the organic matter. Fission track analyses being performed by BGS, Edinburgh, may provide more information on this topic (Basham and Hyslop, 1989).

If the uranium present in the waters draining from the anoxic area and appearing as surface drainage in the merse silts is regarded as being derived from the cliff area then the anoxic soil would appear to be about 80-90% effective in arresting the flow of uranium towards the merse. This is, however, likely to be an underestimate of the efficiency of the retardation since artesian input of water to the base of the sediments has been established by BGS and the auger hole result indicates that these rising waters may be enriched in uranium. There are therefore two potential sources of uranium for waters draining through the merse silts.

The uptake of radionuclides from solution in groundwater by minerals forming on the walls of water bearing fissures in rocks is a potential retardation process of considerable importance in far field transport considerations. The uptake of radionuclides by such minerals could involve a variety of mechanisms including reversible sorption, precipitation or physical trapping of radionuclides in the matrix of a growing mineral. The results contained in Table 4 for the four samples of carbonate scraped from the surfaces of fissures in the rocks around the Needle's Eye indicate that a highly active system of radionuclide dissolution, transport and retardation is operating within the rock system and that different processes may be effective within the individual fissures.

Thus in sample 1, from a fracture in the felsite just to the west of the Needle's Eye, a ^{238}U activity of 70.3 Bq kg^{-1} was observed along with a ^{234}U/^{238}U activity ratio of 0.41. This extreme disequilibrium between ^{234}U and ^{238}U indicates that recoil loss of ^{234}U from this material is highly efficient and that once ejected into the groundwater, there is a negligible return of the ^{234}U to the carbonate. To obtain this degree of efficiency for the preferential loss of ^{234}U requires that the uranium must be contained essentially on the surface of the carbonate. Moreover a time equivalent to at least three half lives of ^{234}U would be required to generate this degree of disequilibrium implying a leaching time of at least 7×10^5 years. Active rock-water interaction within this system for such a time would mean that the leaching rate derived above for uranium would be a considerable overestimate of the true value. Thorium analysis of the small amount of material available for this sample was unsuccessful so no information is available on the ^{230}Th content of the sample. ^{226}Ra, however, was found to be highly enriched in the carbonate material with a specific activity of 1704 Bq kg^{-1}, corresponding to a ^{226}Ra/^{234}U activity ratio of 59 (or a ^{226}Ra/^{238}U ratio of 24). Retardation of radium is clearly much more efficient in this system than is retardation of uranium and this may explain the above observation of the low ^{226}Ra/^{234}U activity ratio for water draining through fissures in the vicinity of the uranium vein. The ^{232}Th activity of 78.5 Bq kg^{-1} probably reflects the presence of small quantities of detrital rock fragments in the sample but the ^{228}Th/^{232}Th activity ratio demonstrates an active deposition of ^{232}Th daughters in this material. The observed enrichment of ^{226}Ra in the carbonate and the extremely low solubility of thorium strongly imply that ^{228}Ra is being actively incorporated in the carbonate where it decays to produce ^{228}Th.

Samples 2 and 3 were both collected from under the arch of the Needle's Eye. They have similar natural decay series radionuclide concentrations and activity ratios, with ^{238}U concentrations of 77.5 Bq kg^{-1} and 72.6 Bq kg^{-1} respectively, in conjunction with ^{234}U/^{238}U activity ratios of 0.87 and 0.85. The uranium in those samples therefore either had a ^{234}U/^{238}U ratio of less than unity at the time of deposition or else has undergone preferential loss of ^{234}U since deposition. Since the groundwaters in the cliff area have been found to have ^{234}U/^{238}U ratios of generally less than unity (Table 3), the uranium deposited in these carbonates probably did have an initial ^{234}U/^{238}U ratio of less than one but the values for the carbonates are lower than the corresponding ^{234}U/^{238}U values for the water samples, which implies that recoil loss of ^{234}U is probably a significant factor even if an initial deposition ratio of less than one is assumed. The ^{230}Th/^{234}U activity ratios of 0.38 and 0.18 for these samples confirm the active deposition of uranium, and the ^{230}Th which is present probably arises from the inclusion of small rock fragments in the sample, evidenced by the ^{232}Th activities of 11.7 and 7.5 Bq kg^{-1} respectively. The ^{226}Ra activities of 96 and 129 Bq kg^{-1} (representing ^{226}Ra/^{238}U ratios of 1.2 and 1.8) again indicate that radium is being more efficiently retained by the fracture lining materials than is uranium but the effect is much less pronounced for these samples than for sample 1. In the absence of appropriate water analyses, it is not possible to say whether this is a result of a lower efficiency for retention of radium or of a lower ^{226}Ra/^{238}U ratio in the waters passing through these fissures relative to the water in the fissure from which sample 1 was collected. Indirect evidence that the efficiency of retention of radium may be fairly similar in all three cases is provided by the ^{228}Th/^{232}Th activity ratios of 21.8 and 10.1 for samples 2 and 3 respectively, relative to a value of 19.7 for sample 1.

Carbonate sample 4 which was collected from a fissure in the shallow cave close to the location of the uranium vein shows the highest level of uranium enrichment, with a ^{238}U activity of 3614 Bq kg^{-1} and a ^{234}U/^{238}U activity ratio of 0.97 (which is very similar to the activity ratio values for water samples collected from this fissure system). The very low ^{230}Th/^{234}U ratio of 0.01 confirms that the uranium is effectively being transported and deposited in the absence of thorium, with the small activity of ^{230}Th being accounted for by traces of rock fragments in the sample (the presence of which is indicated by the low ^{232}Th activity of 3.4 Bq kg^{-1}). ^{226}Ra is present at much lower activities than uranium in this sample, with the ^{226}Ra activity of 79 Bq kg^{-1} corresponding to a ^{226}Ra/^{238}U ratio of 0.02. As discussed above for samples 2 and 3, this may well be the result of a low ^{226}Ra content in the water passing through the fissure rather than a reduced efficiency for retention of radium since the ^{228}Th/^{232}Th ratio of 172 implies an efficient uptake of ^{228}Ra in this sample.

In summary, therefore, the carbonate samples confirm that the vein is acting as a source of uranium and radium to groundwaters in the cliff area and that uptake of these species by fracture surface minerals can significantly retard their rate of transport through fissures. Uranium is most enriched in the carbonate sample collected close to the vein but is present at much lower concentrations in the samples from fissures more remote from the vein. Uranium is also preferentially enriched relative to ^{226}Ra in the sample from the vein area but the reverse situation is true for the more remote samples. The ^{228}Th/^{232}Th results imply that ^{228}Ra is also subject to dissolution, transport and deposition in this system, indicating that the rates of these processes are fast relative to the ^{228}Ra half life of 5.75y. Without water analysis data it is not possible to say whether the varying patterns of uranium and radium deposition in the carbonate represent different mechanisms or simply varying uranium to radium ratios in the waters in the different fissures.

The results for the SURRC Pits 1 and 5, presented in Tables 5 and 6 and shown graphically in Figures 9 and 10, demonstrate a very high efficiency for retention of uranium by the organic rich, anoxic soils at the base of the cliff, consistent with the above observations for groundwater. The profile for Pit 1 consists of a high water content section extending from the surface to about 40cm depth, with organic content of up to 72% and ^{238}U activities in the range 6500 to 9850 Bq kg^{-1}. The presence of ^{137}Cs from the surface to 40cm depth and the zero values for radiocarbon ages from the surface to 50cm depth indicate that this section of the soil is subject to rapid mixing relative to a 30 year timescale. The absence of ^{134}Cs from the mixed section implies a weapons testing fallout origin for the ^{137}Cs and indicates that this area is not subject to incursion by seawater from the Solway Firth, which does affect lower areas of the merse, as discussed below, and can be identified by ^{134}Cs/^{137}Cs ratios characteristic of the Sellafield discharge. (The samples discussed here were collected before deposition of fallout from the Chernobyl nuclear reactor accident). Below the mixed zone, uranium concentration and organic content show very similar trends of depth distribution, with a subsidiary maximum in each at 60 to 70 cm, and the ^{238}U activity and organic content in fact show a reasonable degree of correlation over the entire profile (linear correlation coefficient = 0.85). ^{234}U shows an identical depth distribution to ^{238}U in the profile, with an average ^{234}U/^{238}U ratio of 0.97 in the mixed zone (very similar to the activity ratio of waters draining into this area at present) but with an average value of 1.00 for the deeper sections. this small difference in the ^{234}U/^{238}U ratio between the two sections of the profile may simply be due to the increased proportion of inorganic material in the lower section but the results are also consistent with the BGS hydrological model with an input of artesian water at the base of the soil and the above observation of a ^{234}U/^{238}U activity ratio of 1.1 for water from the bottom of an auger hole in the merse.

^{232}Th activities in the Pit 1 profile range from below detection limit at the surface up to values of about 20 Bq kg^{-1} in the lower section of the profile. On the basis of a negligible dissolved state transport for ^{232}Th, the ^{232}Th concentration can be taken to indicate the amount of detrital mineral material in the soil. Any such detrital component in the soil will also contain some ^{230}Th but, despite this, all of the observed ^{230}Th/^{234}U ratios are very low (ranging from 0.0084 to 0.108) confirming that the uranium is being transported in solution in the virtual absence of thorium before it is taken up in the organic soils. The transport of ^{230}Th in mineral grains is also implied by the fact that ^{230}Th/^{234}U ages (Ivanovich and Harmon, 1982), calculated on the assumption of zero activity of ^{230}Th upon initial deposition of the soil, are too high relative to corresponding ^{14}C ages as shown in Tables 5 and 13.

The change in redox conditions affecting uranium as it is transported (initially, almost certainly in the 6+ oxidation state) in groundwaters which are highly oxygenated when they drain through the cliff area but which rapidly become anoxic upon interaction with the organic soil, would, on its own, be sufficient to cause reduction of U^{6+} to U^{4+}, with consequent rapid removal from solution (Wedepohl, 1978). However, the organic matter may play an active role in the uptake of uranium, and it has been suggested (Idiz et al, 1986) that humic and fulvic compounds can actively cause uptake of uranium in organic soils by complexation. Leventhal and Daws (1986) have also shown an association of uranium with aromatic hydrocarbons rather than aliphatic hydrocarbons in sediments. Moreover, consolidation of organic rich sediments can lead to effectively 'permanent' immobilisation of uranium, with the existence of fossil organic rich deposits containing elevated levels of uranium of ages of the order of 10^8 years being well established (Das, 1985).

Uranium fission track distribution studies in conjunction with scanning electron microscopy techniques are being used by BGS to investigate the role of organic matter in the retardation of uranium at this site. Initial results (Basham and Hyslop, 1989) indicate that organic matter is probably actively involved.

Pit 5 was located some 80m to the east of Pit 1, well away from the uranium vein, but uranium enrichment in this profile is once again apparent, although at a much lower level than observed in Pit 1. The characteristics of the concentration profiles for Pits 1 and 5 are in fact very similar and Pit 5 also shows a high organic and high water content upper layer enriched in uranium (with a maximum ^{238}U activity of 1065 Bq kg^{-1}) overlying a more inorganic layer with lower uranium content. ^{230}Th/^{234}U ratios are, once again, low (ranging from 0.088 to 0.31) suggesting uranium transport and retardation in the absence of ^{230}Th. The mobilisation of uranium from the cliff area with subsequent groundwater transport and deposition in the anoxic zone is thus clearly established at this location well away from the main location of uranium mineralisation at the Needle's Eye. Consequently the general cliff area must be regarded as a source of uranium for groundwaters in this area, or else there is an additional, and as yet unidentified, location of uranium mineralisation somewhere in the vicinity of Pit 5.

The manmade radionuclide concentrations and activity ratios observed in the surface transect samples (Table 9(a)) are characteristic of the Sellafield discharge and demonstrate that the silts being deposited in the merse are of marine origin from further south in the Irish Sea (MacKenzie et al, 1987). The natural decay series radionuclide concentrations and activity ratios of the sample collected on the mean high water mark (Table 9(b)) are very similar to those observed for the surface sediment of the Irish Sea (Table 7). There is, however, as shown in Figure 11 a systematic change in uranium concentrations and ^{230}Th/^{234}U ratios on moving inland, with ^{238}U concentrations reaching a maximum of 1078 Bq kg^{-1} in the sample from the 45m position on the transect which was adjacent to the small stream draining from the anoxic area. The $^{230}Th/^{234}U$ ratios show a change from values in excess of unity in the seaward section of the transect to values significantly less than unity from 30m inland to the end of the transect, with the lowest value of 0.020 being observed for the 45m sample which also showed the highest uranium concentration. The uranium/thorium system observed in the merse surface deposits therefore consists of at least two components, with Irish Sea silt, characterised by a $^{230}Th/^{234}U$ ratio of 1.9, $^{238}U/^{232}Th$ ratio of 0.93 and a ^{238}U concentration of 18.8 Bq kg^{-1}, being deposited and then being subject to addition of uranium with this contribution increasing on moving towards the Needle's Eye mineralization.

If we assume that the ^{232}Th in the surface transect samples is derived solely from Irish Sea silt and, that the relative activities of ^{232}Th, ^{238}U, ^{234}U and ^{230}Th for this material are characterised by those of the Irish Sea surface sediment sample (Table 7) then an Irish Sea sediment contribution can be subtracted from the total uranium concentration for each sample. The excess ^{238}U contributions calculated in this way are shown in Table 14 along with analogous ^{230}Th data and the resulting $^{230}Th/^{234}U$ ratios for the excess component. The influence of the stream draining the anoxic zone is again apparent in the very high excess ^{238}U value of 1071 Bq kg^{-1}, while the remaining results show an exponential increase in excess ^{238}U on moving towards the mineralization site, as shown in Figure 12. If the 45m sample is omitted, the remaining results plot on a straight line in the graph of ln (excess ^{238}U) against distance, with a correlation coefficient of 0.945, gradient 0.0695m^{-1} and intercept 1.25. This indicates that removal of uranium from solution in surface groundwaters in the merse follows first order kinetics and the exponential decrease in excess uranium concentration with distance is characterised by a removal, or retardation, coefficient of 0.0695m^{-1}, corresponding to a halving distance of 10m. The data in Table 14 reveal that throughout the length of the transect, a significant fraction of the uranium in the samples is in excess of that normally present in Irish Sea silt. Moreover, the data suggest that in several of the samples, all of the ^{230}Th can be accounted for by the Irish Sea contribution. The samples from 40, 50 and 55m, however, contain ^{230}Th well in excess of the values appropriate to the Irish Sea silt, which suggests incorporation of detrital material from a source other than the Irish Sea and probably indicates seaward movement of fragments of rock and minerals from the cliff area.

The results presented in Table 7 for the samples from the sections dug in the intertidal and merse areas (Figure 6) can be treated in the same way as the surface transect results and Table 15 shows the excess ^{238}U and ^{230}Th components for these samples. The intertidal samples show uranium values similar to the Irish Sea silt but have lower ^{230}Th concentrations and lower $^{230}Th/^{232}Th$ ratios. This may arise as the result of additional terrigenous detrital material transported by the Southwick Water to these sediments diluting the marine excess of ^{230}Th. The section 1 samples are all very similar to the Irish Sea silt with no indication of uranium deposition. This is consistent with the fact that ^{210}Pb dating plus Sellafield waste radionuclide profiles indicate that this area, in an eroded section of the merse, is accumulating at a rate of about 4cm y^{-1}. The section 2 samples show evidence of slight uranium deposition at the surface but not at depth and it is notable that the 100cm sample is much less enriched in ^{230}Th than present day Irish Sea silt. This could indicate either than the $^{230}Th/^{234}U$ ratio in the silt deposited from the Irish Sea has varied with time or alternatively that the material at 100cm depth in this section is from a different source from that at the surface. In the samples from section 3, there is clear evidence of uranium deposition at the surface and also at 80cm but not at the intermediate depth (40cm) sample. This deposition pattern is consistent with that predicted by the BGS hydrological model for the site which suggests that uranium deposition should occur at the surface and at depth in the sediment where groundwater flow from the cliff area occurs. Once again, the deeper samples from this section are less enriched in ^{230}Th than present day Irish Sea surface sediment. In all of the samples from the Merse sections, there is no evidence of any excess ^{230}Th deposition.

The final set of results relating to the merse sediments is for the sequential leaching study summarised in Table 8. The data relating to the intertidal sediment are much as would be expected, with a small amount of the uranium in the exchangeable, organic and oxide fractions but with about 80% in the detrital phase. In contrast, the samples from section 3 show 81.6% of the uranium in the surface sample and 20.2% in the 80cm sample to be associated with the oxide component.

In summary, therefore, the results for the merse samples indicate that uranium dispersion for distances of up to about 50m from the cliff takes place both on the surface of the sediments and at depths where groundwater flow occurs. Retardation of uranium in the surface silts occurs by a process of continuous removal, following first order kinetics and being characterised by a halving distance of about 10m. The evidence of the leaching experiment suggests that the sorption process may involve uptake on iron and manganese oxide species.

During the initial survey of this site in the early 1960's, Miller and Taylor (1966) excavated a section in the soil overlying the main uranium vein in the field at the top of the cliff. Beta-probe measurements in the overlying soil formed a pattern with a systematic decrease in activity on moving away from the vein as shown in the insert diagram in Figure 3. The cause of the observed pattern of beta-probe readings was not investigated, but one possibility was that uranium series nuclides could have been transported by groundwater movement away from the vein and deposited in the overlying soil in this pattern. The existence of such a system would have allowed the systematic investigation of natural decay series radionuclide movement and retardation processes operating over a distance of the order of 1m on a timescale of up to about 10^4y. The vein in the field at the top of the cliff was excavated along its total length during the 1960's survey and was consequently unsuitable for further study of this type. Attempts to locate the vein in the course of the present work in the merse area were unsuccessful so in an attempt to further investigate the possible movement of radionuclides from the vein into overlying soils, a pit NEP2 (Figure 6) was excavated over a smaller vein to the east of the main vein in the field at the top of the cliff.

The three profiles for NEP 2 (Figure 6) overlying the uranium vein in the field at the top of the cliff all show increasing uranium concentrations with increasing depth and, on first sight, these could be taken to relate to the vein as a source of uranium being deposited in the soil. Any such deposition of uranium would, however, result in a systematic increase in the $^{238}U/^{232}Th$ ratio with depth and, as shown in Table 18, this is not observed (with the possible exception of the higher value observed for sample 204). Moreover, the $^{230}Th/^{234}U$ ratios for the samples from this pit are all substantially greater than unity, indicating uranium removal, with increasing values at depth for this ratio suggesting a higher rate of uranium removal in the lower parts of the profiles. $^{234}U/^{238}U$ versus $^{230}Th/^{238}U$ plots (Thiel et al., 1983) for the three profiles from pit NEP 2 are shown in Figures 13 -15, with the uranium vein result also plotted for comparison in each case. The majority of the results lie in the complex process or uranium removal areas close to the vein sample. The two lowest samples from the 0cm and -60cm profiles are exceptions to this general pattern with both having very high $^{230}Th/^{238}U$ ratios, sample 221 (0cm profile) lying in the complex process area and 204 (-60cm profile) being in the uranium removal sector. Within the analytical uncertainties, the data are generally consistent with uranium removal at, or close to, equilibrium. The soil profiles therefore appear to have been generated by the effects of groundwater leaching of natural decay series radionuclides originally contained in the soil, rather than deposition of radionuclides transported from the vein. This mechanism would be consistent with the number of data points lying in the complex process zone. Further evidence of recent dissolution/deposition processes influencing the natural decay series radionuclides in these profiles is provided by the $^{228}Th/^{232}Th$ ratios which in all cases show an excess of ^{228}Th. Given the low probability of solution transport of ^{228}Th itself, the most likely cause of these ratios is the dissolution of the more soluble ^{228}Ra from some other source area followed by deposition in these soils. There is a tendency for higher $^{228}Th/^{232}Th$ ratios at shallower locations in the profile and this could suggest redox control of the ^{228}Ra distributions via the sulphide/sulphate system, with soluble behaviour of Ra under reducing conditions in the presence of sulphide but precipitation as the sulphate under more oxidizing conditions. The ^{228}Ra half life of 5.75 years indicates that the transport involved in this situation is rapid and suggests advective rather than diffusive movement, possibly as a result of drainage down the slope of the hill.

The general conclusion from the study of NEP 2 is therefore that the disequilibria observed in the natural decay series nuclides in the profiles do not bear a simple relationship with the vein as a source of uranium, but are more likely to have been produced by a complex set of processes including transport of nuclides from the vein, leaching of indigenous minerals in the soils, advective transport of soluble nuclides in the groundwater draining downslope and possibly redox reactions.

CONCLUSIONS

The following salient conclusions can be drawn from the above discussion:

1 The observed general behaviour of uranium, thorium and radium at this study site is consistent with the established geochemistry of these elements.

2 The vein material acts as an effective source of uranium and radium to groundwaters.

3 The probability of dissolution of uranium from the vein is about 5 x 10^{-5} y^{-1} on the assumption that leaching has been continuous since the end of the last period of glaciation (~12,000 years ago) but this is almost certainly a much lower value for the leaching time than the true value so this leaching probability is an upper limit.

4 Effectively zero dissolution of ^{230}Th from the vein was observed.

5 Groundwater transport has resulted in dispersion of uranium over distances of about 50m in the post glacial silts of the Solway floodplain.

6 Uptake of uranium and radium by carbonate minerals which line fracture surfaces in the rocks around the vein has been demonstrated to be a significant retardation process affecting these elements during groundwater transport. The rate of dissolution, transport and redeposition of radium in the rock system is rapid relative to a five year timescale. The efficiency of retardation of radium by this mechanism appears to be greater than that of uranium.

7 The anoxic organic soil presents a highly effective barrier to transport of uranium in groundwater, with the efficiency of retention of uranium being at least 80 to 90%.

8 The cliff acts as a source of uranium (about an order of magnitude less than the vein) in areas remote from the main mineralisation at Needle's Eye.

9 Continuous retardation of uranium, by uptake on iron and manganese oxides, occurs as groundwater moves across the surface of the merse silts. The uranium removal process exhibits first order kinetics and is characterised by a halving distance for the groundwater concentration of uranium of 10m.

10 Upwards migration of radionuclides from the vein into overlying soils was not observed. The soil profiles in the immediate vicinity of the vein appear to have evolved dominantly as the result of groundwater leaching of radionuclides originally contained in the soil when it was deposited, with any dissolution and redeposition of radionuclides from the vein being a minor effect. Rapid (on a 5 year timescale) dissolution and redeposition of ^{228}Ra occurs in these soils, with the sulphide - sulphate system possibly exerting a control over radium solubility.

The general features of the dissolution, transport and deposition of uranium (and to a lesser extent radium) have therefore been established for this study site and, in the context of a geochemical model, are reasonably well understood. A variety of dissolution, groundwater transport and retardation processes, of significance in far field transport considerations, have been identified and characterised. Continuing work on this project is being focussed upon further definition of these processes, with particular attention to uranium aqueous phase speciation, solid phase geochemical associations and quantitative characterisation of redox controlled reactions in the system. The next phase of the study will be carried out in close liaison with the modelling groups who will be attempting to apply speciation and transport codes both to some of the individual processes observed and to the overall transport of uranium at the site.

REFERENCES

REFERENCES

Alexander, W. R., Scott, R. D., MacKenzie, A. B. and McKinley, I. G., 1988. "A natural analogue study of radionuclide migration in a water conducting fracture in crystalline rock". Radiochimica Acta 44/45, 283-289.

Alexander, W. R., MacKenzie, A. B., Scott, R. D. and McKinley, I. G., 1989. "Natural analogue studies in crystalline rock: the influence of water-bearing fractures on radionuclide immobilisation in a granite rock repository." PSI Technical Report 87-08. Paul Scherrer Institute, Villigen, Switzerland.

Bacon, M. P. and Rosholt, J. N., 1982. "Accumulation rates of ^{230}Th, ^{231}Pa and some transition metals in the Bermuda Rise". Geochim. Cosmochim. Acta, 46, 651-666.

Basham, I. R. and Hyslop, E. K., 1989. "Uranium location studies at the Needle's Eye natural analogue site - a preliminary account" BGS Technical Report WG/89/6R. British Geological Survey, Edinburgh.

Breward, N. and Peachey, D., 1989. "The development of portable equipment to study physical and chemical phases in natural waters." DOE Report No: DOE/RW/88.102. Department of the Environment, London.

CANMET, 1983 "^{226}Ra in certified uranium reference ores DL-1a, BI-4a, DH-1a and BL-5." CANMET Report 93-9E. Canadian Centre for Mineral and Energy Technology, Ottawa.

Chapman, N. A., McKinley, I. G. and Smellie, J. A. T., 1984. "The potential of natural analogues in assessing systems for deep disposal of high level radioactive waste" EIR Report No 545, EIR, Wurenlingen, Switzerland.

Chapman, N. A. and McKinley, I. G., 1987. "The geological disposal of nuclear waste." John Wiley Ltd. Chichester.

Côme, B. and Chapman, N. A., (Eds.) "Natural analogues in radioactive waste disposal." Graham and Trotman Limited, London.

Côme, B. and Chapman, N. A., 1988 (Eds.) "CEC natural analogue working group. 3rd meeting. Snowbird near Salt Lake City (USA)". CEC Report EUR 11725 En. Commission of the European Communities, Brussels.

Cook, G. T., Baxter, M. S., Duncan, H. J., Toole, J. and Malcolmson, R., 1984. "Geochemical associations of plutonium in the Caithness environment." Nucl. Instr. Methods. Phys. Res. 223, 517-522.

Das, N., 1985. "Geochemical studies of the Caithness flags". PhD Thesis, University of Glasgow.

Doublet, R. Jamet, P. and Soubeyran, R., 1988. "Modelling transfer in natural analogues." CEC Report LHM/RD.88/59. Ecole des Mines de Paris.

Fleischer, R. L., 1980. "Isotopic disequilibrium of uranium: alpha-recoil damage and preferential solution effects." Science, 207, 979-981.

Friedlander, G., Kennedy, J. W., Macias, E. S. and Miller, J. M., 1981. "Nuclear and radiochemistry" 3rd Edition. John Wiley and Sons, New York.

Greenwood, N. N. and Earnshaw, A., 1984. "Chemistry of the elements" Pergamon Press, Oxford.

Hallberg, L., Brise, H., Anderson, S. and Telc. A., 1960. "Determination of ^{55}Fe and ^{59}Fe in blood." Int. J. Applied Radiat. Isotopes, 89, 100-108.

Halliday, A. N., Stephens, W. E. and Harmon, R. S., 1980. "Rb-Sr and oxygen isotopic relationships in three zoned Caledonian granitic plutons, Southern Uplands, Scotland: evidence for varied sources and hybridisation of magmas." J. Geol. Soc. London, 137, 329-348.

Henderson, P., 1982. "Inorganic Geochemistry" Pergamon Press Oxford.

Higgo, J. J. W., Falck, W. E. and Hooker, P. J., 1989. "Sorption studies of uranium in sediment-groundwater systems from the natural analogue sites of Needle's Eye and Broubster." BGS Technical Report WE/80/40. British Geological Survey, Keyworth.

Hooker, P. J., MacKenzie, A. B., Scott, R. D., Ridgway, I. M., McKinley, I. G. and West, J. M., 1985. "A study of long term (10^3 - 10^4y) elemental migration in saturated clays and sediments (Part 3)". BGS Report FLPU 85-9. British Geological Survey, Keyworth.

Hooker, P. J., MacKenzie, A. B., Scott, R. D., Ivanovich, M., Ball, T. K., Basham, I. R., Bloodworth, A. J. and Roberts, P. D., 1986. "Natural analogues of radionuclide migration: reconnaissance study of sites (May 1985-March 1986)." BGS Report FLPU 86-6, British Geological Survey, Keyworth.

Hooker, P. J. and Chapman, N. A., 1989. "UK natural analogue co-ordinating group: second annual report." DOE Report No: DOE/RW/89.021. Department of the Environment, London.

Idiz, E. F., Carlisle, D. and Kaplan, I. R., 1986. "Interaction between organic matter and trace metals in a uranium rich bog, Kern County, California, USA." Applied Geochem., 1, 573-590.

International Atomic Energy Agency, 1980. "Underground disposal of radioactive wastes." Vols I and II. IAEA, Vienna.

Ivanovich, M. and Harmon, R. S., 1982. (Eds) "Uranium series disequilibrium: applications to environmental problems." Oxford University Press, Oxford.

Lamothe, P. J., Fries, T. and Consul, J. J., 1986. "Evaluation of a microwave oven system for the dissolution of geological samples." Anal. Chem., 58, 1881-86.

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

Leventhal, J. S. and Daws, T. A., 1986. "Organic geochemical analysis of sedimentary organic matter associated with uranium." Applied Geochem., 1, 241-247.

MacKenzie, A. B., Scott, R. D., McKinley, I. G. and West, J. M., 1983. "A study of long term (10^3-10^4y) elemental migration in saturated clays and sediments (Part 1)." BGS Report FLPU 83-6. British Geological Survey, Keyworth.

MacKenzie, A. B., Scott, R. D., Ridgway, I. M., McKinley, I. G. and West, J. M., 1984. "A study of long term (10^3-10^4y) elemental migration in saturated clays and sediments." BGS Report FLPU 84-11. British Geological Survey, Keyworth.

MacKenzie, A. B., Scott, R. D. and Smellie, J. A. T., 1986. "A comparison of neutron activation and alpha spectroscopy analyses of thorium in crystalline rocks." J. Radioanal. Nucl. Chem. Letters, 103, 321-330.

MacKenzie, A. B., Scott, R. D. and Williams, T. M., 1987. "Mechanisms for northwards dispersal of Sellafield waste". Nature, 329, 42-45.

Mason, B., 1966. "Principles of Geochemistry" 3rd Edition. John Wiley and Sons, New York.

Miller, J. M. and Taylor, K., 1966 "Uranium mineralisation near Dalbeattie, Kirkcudbrightshire." Bull. Geol Surv. Great Britain, 25, 1-18.

Nadkarni, N. A., 1984. "Applications of microwave oven sample dissolution in analysis." Anal. Chem., 56, 2233-37.

NAGRA, 1985. "Project Gewahr 1985". NAGRA, Baden, Switzerland.

Roberts, P. D., Ball, T. K., Hooker, P. J. and Milodowski, A. E., 1988. "A uranium geochemical study at the natural analogue site of Needle's Eye, S W Scotland." Proc. 12th symp. "Scientific basis for nuclear waste management." MRS (in press).

Roxburgh, I. S., 1987 "Geology of high level nuclear waste disposal." Chapman and Hall, London.

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

Souberyan, R., Ledoux, E. and de Marsily, G., 1988. "Modelling transfer in natural analogues". Report no. LHM/RD/88/11. Ecole des Mines de Paris.

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

Wedepohl, K. H. 1978 (Ed) "Handbook of Geochemistry. Vo.l II/5. Uranium" Springer-Verlog. Berlin.

TABLES

A. SPIKED ANALYSIS (specific activities in Bq kg^{-1})

^{238}U	^{234}U	$^{234}U/^{238}U$	^{230}Th	$^{230}Th/^{234}U$	^{232}Th
1400 ± 33	1427 ± 33	1.02 ± 0.02	1423 ± 40	1.00 ± 0.03	300 ± 12

These activities correspond to a uranium concentration of 114 ± 3 ppm and a thorium concentration of 74.5 ± 3 ppm.

B. UNSPIKED URANIUM RATIO ANALYSES

Analysis number	$^{234}U/^{238}U$
1	1.00 ± 0.02
2	1.01 ± 0.02

CERTIFIED VALUES

Uranium concentration : 116 ppm
Thorium concentration : 76 ppm
^{226}Ra specific activity : 1400 Bq kg^{-1}
$^{226}Ra/^{238}U$ activity ratio : 0.980

Table 1 **Analytical results and certified values for the reference sandstone DI-1A (CANMET, 1983).**

Nuclide	Concentration (MBq kg^{-1})	
	Bulk Vein Material	Separated Pitchblende
^{238}U	2.48 ± 0.07	4.29 ± 0.28
^{234}U	2.56 ± 0.08	4.17 ± 0.27
^{230}Th	4.70 ± 0.18	4.10 ± 0.15
^{226}Ra	-	3.22 ± 0.93

	Activity Ratio	
	Bulk Vein Material	Separated Pitchblende
$^{234}U/^{238}U$	1.03 ± 0.04	(a) 0.97 ± 0.03 (b) 0.94 ± 0.03
$^{230}Th/^{234}U$	1.84 ± 0.09	0.98 ± 0.06

Table 2 **Uranium and thorium isotope data for vein material and separated pitchblende from the mineralization at Needle's Eye**

$^{234}U/^{238}U$ ratio: (a) spiked
(b) unspiked

Pitchblende sample separated from crushed, washed vein material using heavy liquid (sodium polytungstate) separation followed by hand picking of the pitchblende (separation performed by E Hyslop, BGS, Edinburgh)

^{226}Ra determination by gamma spectroscopy.

Field Above Cliff		
Field drain	$[^{238}U]$ =	0.012 Bq l^{-1}
	$^{234}U/^{238}U$ =	1.15 ± 0.08
Cliff		
Water draining through fissures in cliff	$[^{238}U]$ =	0.3 - 0.74 Bq l^{-1}
	$^{234}U/^{238}U$ =	0.91 ± 0.04
		0.97 ± 0.02
	^{226}Ra =	0.022 Bq l^{-1} (single analysis)
Anoxic Organic-Rich Soil		
Surface drainage into anoxic area	$[^{238}U]$ =	0.80 Bq l^{-1}
	$^{234}U/^{238}U$ =	0.96 ± 0.03
Interstitial water from 5cm depth in soil	$[^{238}U]$ =	0.015 Bq l^{-1}
(Very large uncertainty ≃20%; isotopic activity ratio 1.3 ± 0.3)		
Merse Silts		
Surface drainage	$[^{238}U]$ =	0.03 - 0.19 Bq l^{-1}
	$^{234}U/^{238}U$ =	0.95 - 1.06 (± 0.06)
Sample from bottom of auger hole	$[^{238}U]$ =	0.26 Bq l^{-1}
	$^{234}U/^{238}U$ =	1.11 ± 0.04

Table 3 Summary of uranium specific activities and isotopic activity ratios for water samples from the Needle's Eye area.

Sample	^{238}U	^{234}U	$^{234}U/^{238}U$	^{232}Th	$^{228}Th/^{232}Th$	^{230}Th	$^{230}Th/^{234}U$	^{226}Ra
1	70.3±9.8	28.8±6.1	0.41±0.10	78.5±10.9	19.7±4.5	ND	ND	1704±356
2	77.5±4.2	67.8±3.9	0.87±0.06	11.7±1.1	21.8±3.8	25.6±1.6	0.38±0.03	96±25
3	72.6±2.7	61.6±2.5	0.85±0.03	7.5±0.4	10.1±0.9	11.1±0.6	0.18±0.01	129±32
4	3614±95	3521±92	0.97±0.01	3.4±0.6	172±71	21.2±1.7	0.01±0.001	79±19

Table 4 **Natural decay series radionuclide analyses for fracture lining materials from fissures in the hornfels and felsite at the Needle's Eye analogue study site.**

Specific activity units: Bq kg^{-1}

^{226}Ra determined by gamma spectroscopy.

Samples (provided by E Hyslop, BGS, Edinburgh):

1. From joint surfaces in blocky felsite to the west of the Needle's Eye.
2. From fractured hornfels under the Needle's Eye
3. From fractured felsite under the Needle's Eye
4. From fractured felsite in cave to the east of the Needle's Eye - the same fissures from which the water samples identified as 'cliff' in Table 3 were collected.

DEPTH (cm)	WET:DRY RATIO	% LOSS OF WEIGHT ON IGNITION	% ORGANIC MATTER	% PYRITE	^{137}Cs cps kg^{-1}	^{14}C AGE YEARS BP	^{238}U Bq kg^{-1}	^{234}U Bq kg^{-1}	^{234}U/^{238}U	^{230}Th	^{230}Th/^{234}U	^{232}Th
0-10	5.10	86.3	72	0.31	0.93	NA	6500±133	6320±133	0.97±0.01	90±7	0.0142±0.0007	ND
10-20	6.64	83.0	69	0.29	0.75	0	7220±183	6970±167	0.97±0.01	58±4	0.0084±0.0005	5.0±1.7
20-30	5.62	60.6	62	0.28	0.22	0	9850±350	9683±350	0.98±0.01	127±5	0.0131±0.0005	8.7±1.3
30-40	4.18	47.3	38	0.10	0.28	0	6570±183	6280±167	0.96±0.02	155±5	0.025 ±0.001	11.1±1.2
40-50	2.69	24.8	29	0.12	ND	0	506± 15	493± 15	0.97±0.03	42±2	0.085 ±0.004	16.7±0.8
50-60	3.07	30.8	26	0.11	ND	505	982± 40	970± 40	0.99±0.02	46±2	0.047 ±0.002	15.7±0.8
60-70	4.22	45.2	36	0.28	ND	520	4050±117	4030±117	1.00±0.02	85±5	0.021 ±0.001	21.0±2.2
70-80	3.40	34.4	37	0.29	ND	605	1180± 28	1143± 28	0.97±0.01	41±2	0.035 ±0.001	16.3±1.0
80-90	2.54	21.2	19	0.30	ND	670	463± 10	470± 10	1.01±0.01	47±3	0.100 ±0.005	18.2±1.5
90-100	2.90	25.4	25	0.18	ND	790	633± 18	630± 18	0.99±0.01	44±2	0.070 ±0.003	11.8±1.2
100-110	1.91	9.2	8	0.09	ND	NA	295± 10	300± 10	1.02±0.02	33±1	0.108±0.005	18.0±1.0

TABLE 5 Analytical results for samples from a vertical section in SURRC Pit 1 at the Needle's Eye natural analogue study site.

NA = not analysed
ND = not detected

DEPTH (cm)	WET:DRY RATIO	% LOSS OF WEIGHT OF IGNITION	^{238}U Bq kg^{-1}	^{234}U Bq kg^{-1}	^{234}U/^{238}U	^{230}Th Bq kg^{-1}	^{230}Th/^{234}U	^{232}Th Bq kg^{-1}
0-5	8.06	80.2	152± 4	153±4	1.00±0.02	37.2±1.7	0.24 ±0.009	6.2±0.7
5-10	7.41	84.9	170± 4	168±4	0.99±0.02	34.8±1.7	0.21 ±0.008	5.3±0.5
10-15	6.54	78.3	362±12	330±12	0.91±0.02	49.7±1.7	0.15 ±0.005	11.5±0.7
15-20	5.31	64.4	815±20	773±20	0.98±0.02	80.5±3.2	0.10 ±0.003	13.8±1.0
20-25	3.34	48.5	1065±37	1018±35	0.96±0.02	89.7±3.3	0.088±0.003	15.3±1.0
25-30	4.32	45.1	1040±35	1002±33	0.96±0.02	96.5±5.3	0.096±0.005	19.7±2.0
30-35	3.35	29.4	293±13	277±13	0.94±0.04	36.7±1.5	0.13 ±0.006	16.0±0.8
35-40	3.94	33.8	453±13	442±13	0.97±0.02	46.3±2.0	0.105±0.004	16.8±1.0
40-45	3.96	33.8	463±10	447±10	0.96±0.01	46.3±2.0	0.104±0.004	21.0±1.2
45-50	3.46	39.2	410±13	393±13	0.96±0.02	NA	NA	NA
50-55	4.46	42.1	432±10	428±10	0.99±0.02	42.2±2.5	0.098±0.005	14.5±1.5
55-60	1.73	5.9	57± 1	55± 1	0.96±0.02	17.2±0.8	0.31 ±0.01	20.8±0.8

TABLE 6 **Analytical results for samples from a vertical section in SURRC Pit 5 at the Needle's Eye natural analogue study site.**

NA = not analysed

Sample	^{238}U	^{234}U	$^{234}U/^{238}U$	^{232}Th	^{230}Th	$^{230}Th/^{234}U$
Intertidal Section						
Surface	15.5 ± 0.4	13.8 ± 0.8	0.89 ± 0.06	16.3 ± 0.8	17.0 ± 0.8	1.23 ± 0.09
50cm	12.5 ± 0.7	13.6 ± 0.8	1.09 ± 0.09	12.0 ± 0.6	17.6 ± 0.9	1.29 ± 0.10
100cm	11.8 ± 0.5	10.8 ± 0.4	0.92 ± 0.05	12.3 ± 0.3	13.1 ± 0.3	1.21 ± 0.05
Merse Section 1 (7.5m)						
Surface	13.9 ± 0.4	13.0 ± 0.3	0.94 ± 0.03	17.5 ± 0.5	28.0 ± 0.7	2.15 ± 0.07
50cm	16.8 ± 0.5	14.9 ± 0.3	0.89 ± 0.03	16.8 ± 0.6	28.7 ± 0.7	1.93 ± 0.06
100cm	15.9 ± 0.6	15.4 ± 0.3	0.97 ± 0.04	17.5 ± 0.6	27.1 ± 0.6	1.76 ± 0.06
Merse Section 2 (15m)						
Surface	20.2 ± 0.7	18.5 ± 0.5	0.92 ± 0.04	16.0 ± 0.6	28.3 ± 0.8	1.53 ± 0.06
50cm	19.7 ± 0.6	17.5 ± 0.5	0.89 ± 0.04	18.5 ± 0.9	-	-
100cm	14.7 ± 0.5	14.6 ± 0.3	0.99 ± 0.04	17.8 ± 0.9	16.4 ± 0.7	1.12 ± 0.06
Merse Section 3 (30m)						
Surface	33.8 ± 1.2	33.5 ± 0.9	0.99 ± 0.04	20.5 ± 0.6	36.8 ± 1.2	1.10 ± 0.05
25cm	19.9 ± 1.2	20.1 ± 1.2	1.01 ± 0.09	21.7 ± 1.0	23.4 ± 1.0	1.16 ± 0.09
55cm	47.3 ± 3.0	43.2 ± 2.8	0.91 ± 0.08	18.0 ± 1.0	16.0 ± 0.8	0.37 ± 0.03
Irish Sea						
Surface Sediment	18.8 ± 0.9	18.3 ± 0.8	0.97 ± 0.05	20.3 ± 1.6	34.9 ± 2.3	1.91 ± 0.15

TABLE 7 **Uranium and thorium concentrations and isotopic activity ratios for selected samples from Netherclifton Merse sections (Figure 6) plus a sample of surface silt from the north eastern basin of the Irish Sea**

Concentration Units: Bq kg^{-1}

Sample	% of Uranium Associated with Different Soil Components				
	Available	Exchangeable	Organics	Oxides	Residual
Intertidal Section					
Surface	0	4.5	4.0	7.6	83.8
100cm	0	5.4	6.6	8.7	79.2
Merse Section 3					
Surface	0.5	0	7.0	81.6	10.7
55cm	0.25	3.2	2.0	20.2	71.3

Sequential Leaching Scheme:

Fraction	**Leaching Solution**
Readily available	0.5M $CaCl_2$
Exchangeable/adsorbed	0.5M acetic acid
Organic bound	0.1M tetra sodium pyrophosphate
Fe/Mn oxides	0.1M oxalic acid/0.175M ammonium oxalate
Residual	HNO_3/HCl/HF

TABLE 8 **Uranium association with different soil fractions for samples from Netherclifton Merse and Intertidal sections**

Distance Inland from Mean High Water Level (m)	$^{137}\mathrm{Cs}$	$\frac{^{134}\mathrm{Cs}}{^{137}\mathrm{Cs}}$	$^{239,240}\mathrm{Pu}$	$\frac{^{238}\mathrm{Pu}}{^{239,240}\mathrm{Pu}}$	$^{241}\mathrm{Am}$
0	804 ± 25	0.012 ± 0.003	206 ± 16	0.20 ± 0.02	206 ± 28
5	746 ± 24	0.013 ± 0.004	155 ± 10	0.22 ± 0.02	222 ± 24
10	1945 ± 57	0.009 ± 0.001	254 ± 14	0.22 ± 0.02	419 ± 42
15	2371 ± 69	0.007 ± 0.001	297 ± 15	0.18 ± 0.01	486 ± 49
20	3347 ± 95	0.007 ± 0.001	378 ± 29	0.20 ± 0.02	700 ± 68
25	1952 ± 59	0.008 ± 0.001	304 ± 22	0.20 ± 0.02	548 ± 55
30	2135 ± 62	0.006 ± 0.001	195 ± 12	0.24 ± 0.02	419 ± 45
35	1961 ± 61	0.007 ± 0.002	167 ± 12	0.20 ± 0.02	304 ± 35
40	1532 ± 51	0.009 ± 0.002	130 ± 9	0.26 ± 0.03	236 ± 35
45	1549 ± 54	0.013 ± 0.004	BDL	BDL	159 ± 30
50	845 ± 31	0.011 ± 0.004	60 ± 4	0.20 ± 0.02	81 ± 18
55	144 ± 8	BDL	12 ± 1	0.16 ± 0.03	BDL

Table 9(a) Radionuclide specific activities and isotopic activity ratios for surface soil samples from a 55m transect running from the Southwick Water towards the Needle's Eye (Figure 6)

Distance Inland from Mean High Water Level (m)	$^{238}\mathrm{U}$	$\frac{^{234}\mathrm{U}}{^{238}\mathrm{U}}$	$^{232}\mathrm{Th}$	$^{230}\mathrm{Th}$	$\frac{^{230}\mathrm{Th}}{^{234}\mathrm{U}}$
0	18.2 ± 0.5	0.89 ± 0.03	22.4 ± 0.8	35.8 ± 1.9	2.21 ± 0.13
5	24.2 ± 0.7	1.08 ± 0.04	19.3 ± 0.8	30.9 ± 1.7	1.18 ± 0.07
10	27.8 ± 0.5	0.89 ± 0.02	17.7 ± 0.6	28.7 ± 1.7	1.16 ± 0.07
15	23.2 ± 0.5	1.00 ± 0.03	25.3 ± 0.8	38.1 ± 2.3	1.65 ± 0.10
20	33.8 ± 0.9	0.98 ± 0.04	24.2 ± 0.8	42.4 ± 2.7	1.28 ± 0.09
25	29.7 ± 0.4	0.99 ± 0.02	18.5 ± 1.0	35.7 ± 2.5	1.21 ± 0.09
30	45.5 ± 2.2	1.03 ± 0.07	16.1 ± 0.5	28.6 ± 1.9	0.61 ± 0.05
35	35.5 ± 1.7	1.06 ± 0.05	12.6 ± 0.3	22.4 ± 1.5	0.60 ± 0.05
40	49.4 ± 2.4	0.99 ± 0.07	9.8 ± 0.2	27.1 ± 1.8	0.55 ± 0.05
45	1078 ± 46	1.00 ± 0.06	8.0 ± 0.2	21.6 ± 0.7	0.020±0.001
50	219 ± 4	1.01 ± 0.03	12.0 ± 0.2	49.3 ± 1.6	0.22 ± 0.01
55	218 ± 4	1.01 ± 0.02	20.2 ± 1.2	126 ± 5	0.57 ± 0.02

Table 9(b) **Radionuclide specific activities and isotopic activity ratios for surface soil samples from a 55m transect running from the Southwick Water towards the Needle's Eye (Figure 6)**

Sample	^{238}U	^{234}U	^{234}U/^{238}U	^{232}Th	^{230}Th	^{230}Th/^{234}U	^{228}Th/^{232}Th
NEP 216	13.8 ± 0.5	13.6 ± 0.5	0.98 ± 0.03	11.3 ± 0.7	21.8 ± 1.0	1.60 ± 0.06	-
NEP 217	14.3 ± 0.6	15.0 ± 0.6	1.04 ± 0.04	12.5 ± 0.6	19.9 ± 0.9	1.33 ± 0.06	1.73 ± 0.06
NEP 218	17.4 ± 1.0	20.0 ± 1.0	1.15 ± 0.07	18.3 ± 0.9	26.8 ± 1.2	1.34 ± 0.07	1.48 ± 0.13
NEP 219	18.6 ± 0.7	19.9 ± 0.7	1.07 ± 0.03	20.2 ± 1.1	32.8 ± 1.5	1.65 ± 0.07	1.73 ± 0.06
NEP 220	21.0 ± 0.8	20.0 ± 0.8	0.95 ± 0.04	25.8 ± 1.4	39.0 ± 1.8	1.95 ± 0.09	1.01 ± 0.05
NEP 221	23.5 ± 0.8	25.5 ± 0.9	1.08 ± 0.04	23.7 ± 1.0	76.2 ± 2.1	2.99 ± 0.09	1.51 ± 0.06

Table 10 **Natural decay series radionuclide specific activities and isotopic activity ratios for samples from the 0cm (above vein) profile for NEP 2 (Figures 6 and 7)**

Specific Activity Units: Bq kg^{-1}

Sample	^{238}U	^{234}U	$^{234}U/^{238}U$	^{232}Th	^{230}Th	$^{230}Th/^{234}U$	$^{228}Th/^{232}Th$
NEP 211	13.8 ± 0.6	14.0 ± 0.6	1.03 ± 0.05	12.3 ± 0.6	18.8 ± 0.8	1.34 ± 0.06	1.68 ± 0.06
NEP 212	14.9 ± 0.5	16.3 ± 0.5	1.09 ± 0.03	9.8 ± 1.5	18.7 ± 2.1	1.14 ± 0.12	1.83 ± 0.27
NEP 213	15.1 ± 0.5	15.2 ± 0.5	1.01 ± 0.03	13.6 ± 0.5	26.2 ± 0.8	1.73 ± 0.04	1.80 ± 0.27
NEP 214	17.0 ± 0.6	17.4 ± 0.7	1.02 ± 0.04	15.2 ± 0.5	25.0 ± 0.7	1.44 ± 0.04	1.05 ± 0.14
NEP 215	17.2 ± 0.7	18.6 ± 0.8	1.08 ± 0.05	15.3 ± 0.7	29.5 ± 1.0	1.58 ± 0.06	1.17 ± 0.11

Table 11 **Natural decay series radionuclide specific activities and isotopic activity ratios for samples from the -20cm profile for NEP 2 (Figures 6 and 7)**

Specific Activity Units: Bq kg^{-1}

Sample	^{238}U	^{234}U	$^{234}U/^{238}U$	^{232}Th	^{230}Th	$^{230}Th/^{234}U$	$^{228}Th/^{232}Th$
NEP 200	13.6 ± 0.6	12.8 ± 0.6	0.94 ± 0.04	10.4 ± 0.5	15.9 ± 0.6	1.24 ± 0.05	1.89 ± 0.08
NEP 201	15.6 ± 0.7	16.5 ± 0.7	1.05 ± 0.04	17.9 ± 1.6	25.5 ± 2.0	1.54 ± 0.11	1.79 ± 0.26
NEP 202	15.8 ± 0.4	16.1 ± 0.4	1.02 ± 0.02	15.1 ± 1.0	24.7 ± 1.3	1.53 ± 0.07	1.47 ± 0.18
NEP 203	17.5 ± 0.5	18.6 ± 0.5	1.06 ± 0.02	20.0 ± 1.1	30.8 ± 1.4	1.65 ± 0.08	1.26 ± 0.10
NEP 204	49.8 ± 2.0	45.4 ± 1.9	0.91 ± 0.04	26.5 ± 1.4	192.2 ± 5.4	4.16 ± 0.15	1.78 ± 0.14

Table 12 **Natural decay series radionuclide specific activities and isotopic activity ratios for samples from the -60cm profile for NEP 2 (Figures 6 and 7)**

Specific Activity Units: Bq kg^{-1}

DEPTH (cm)	APPARENT AGE (y)
0-10	1550
10-20	900
20-30	1400
30-40	2700
40-50	9600
50-60	5300
60-70	2300
70-80	3900
80-90	11400
90-100	6900
100-110	12700

TABLE 13 Apparent age of samples from the profile in Pit 1, at the Needle's Eye natural analogue site on the assumption of ^{230}Th being totally absent at the time of the deposition of the soil.

Distance Inland from Mean High Water Mark (m)	Excess ^{238}U	$\frac{\text{Excess } ^{238}\text{U}}{\text{Total } ^{238}\text{U}}$ x100%	Excess ^{230}Th	$\frac{^{230}\text{Th}}{^{234}\text{U}}$ for Excess
0	-2.6	-	-2.7	-
5	6.3	26	-2.5	-
10	11.3	41	-1.7	-
15	-0.3	-	-5.3	-
20	11.2	33	0.8	0.09
25	12.5	42	3.9	0.31
30	30.5	67	0.9	0.03
35	23.7	67	0.7	0.03
40	40.3	81	10.3	0.25
45	1071	99	7.8	0.007
50	208	95	28.7	0.14
55	199	91	91.3	0.45

Table 14 Excess ^{238}U and ^{230}Th in Netherclifton surface transect samples relative to Irish Sea silt

Concentration Units: Bq kg^{-1}

Sample	Excess ^{238}U	$\frac{\text{Excess } ^{238}U}{\text{Total } ^{238}U}$ x100%	Excess ^{230}Th	$\frac{^{230}Th}{^{234}U}$ for Excess
Intertidal Section				
Surface	0.3	1.9	-11.0	-
50cm	1.3	10.4	-3.0	-
100cm	0.4	3.4	-8.0	-
Merse Section 1 (7.5m)				
Surface	-2.4	-	-2.0	-
50cm	1.2	7.1	-0.2	-
100cm	-0.4	-	-3.0	-
Merse Section 2 (15m)				
Surface	5.3	26	0.8	0.20
50cm	2.5	13	-	-
100cm	-1.9	-	-14.2	-
Merse Section 3 (30m)				
Surface	14.7	14	1.5	0.10
40cm	-0.3	-	-13.9	-
80cm	30.6	65	-14.9	-

Table 15 Excess ^{238}U and ^{230}Th in Netherclifton intertidal and merse section samples relative to Irish Sea silt

Concentration Units: Bq kg^{-1}

Sample	$^{238}U/^{232}Th$ Activity Ratio
200	1.31 ± 0.08
201	0.87 ± 0.16
202	1.05 ± 0.11
203	0.88 ± 0.11
204	1.88 ± 0.26
211	1.11 ± 0.07
212	1.51 ± 0.28
213	1.11 ± 0.05
214	1.12 ± 0.05
215	1.12 ± 0.07
216	1.22 ± 0.09
217	1.14 ± 0.07
218	0.95 ± 0.07
219	0.92 ± 0.06
220	0.81 ± 0.05
221	0.99 ± 0.05

Table 16 **$^{238}U/^{232}Th$ activity ratios for samples from pit NEP 2 (Figures 2.1 and 2.2)**

FIGURES

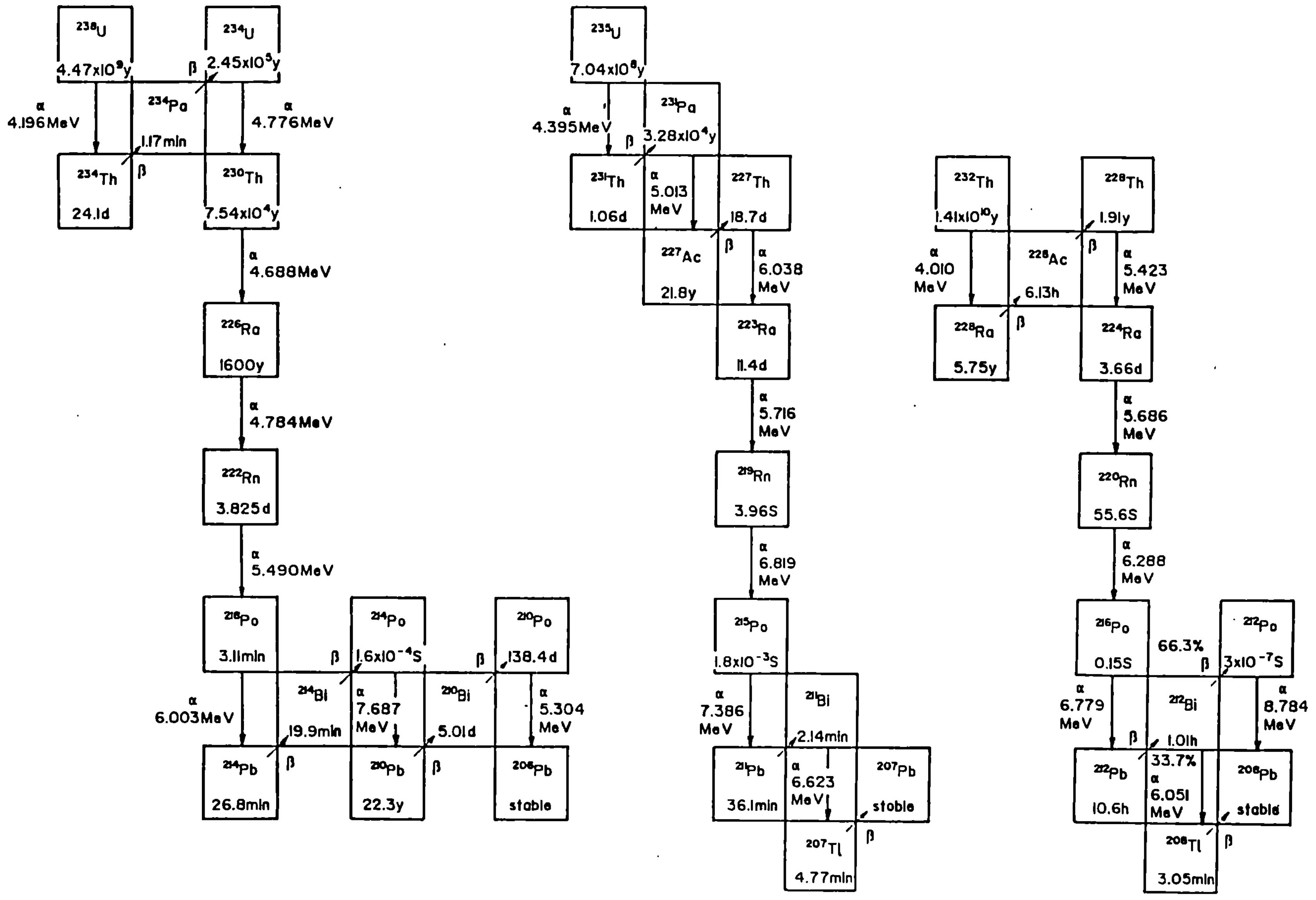
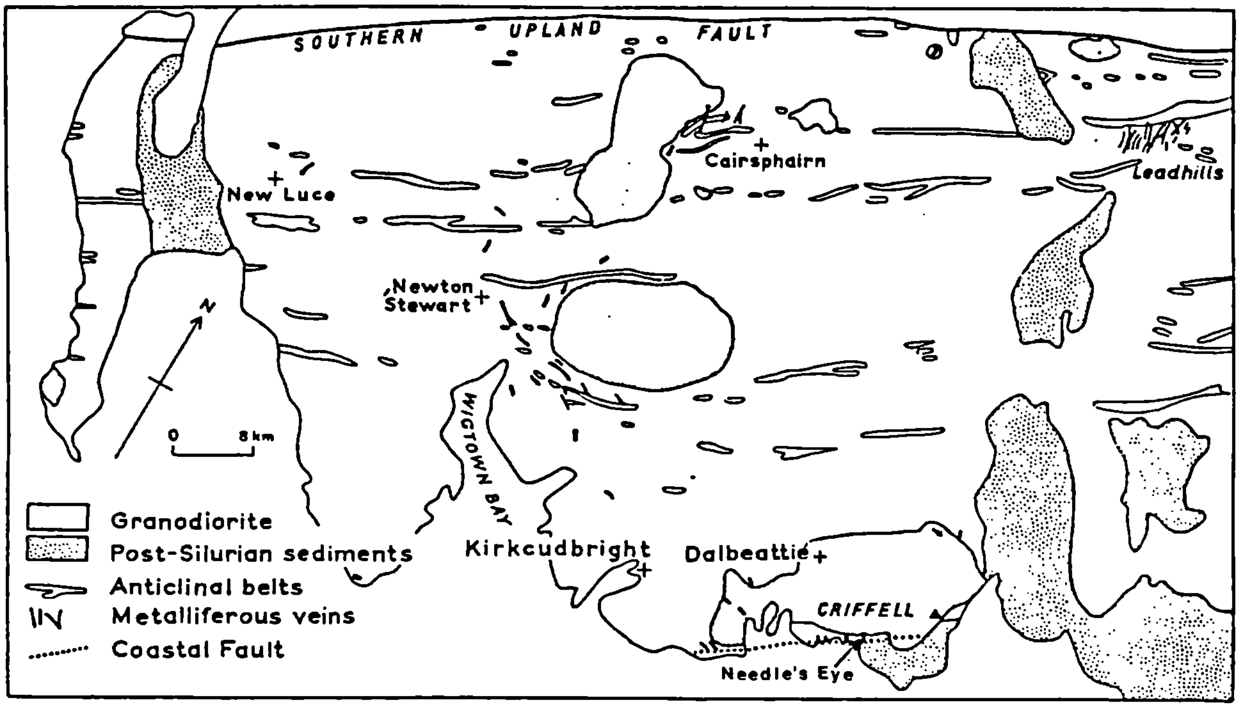
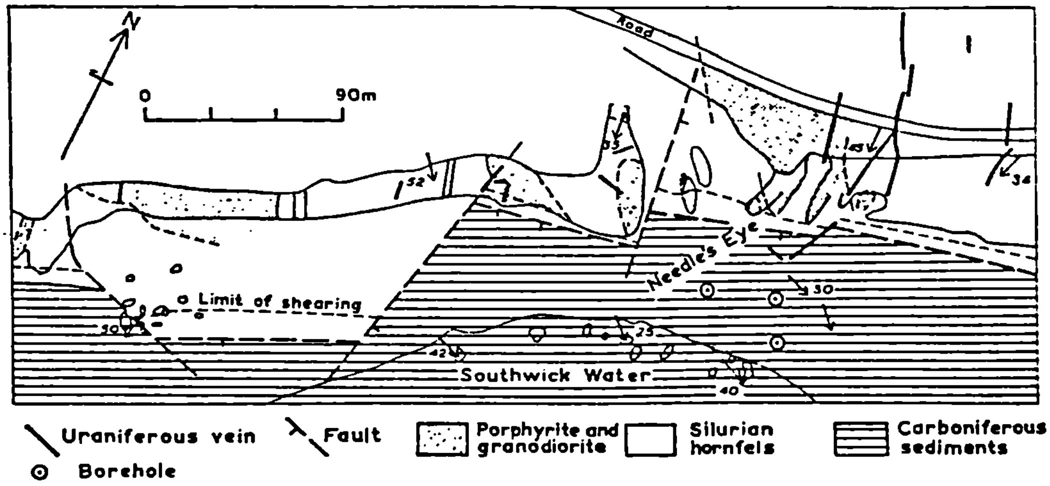


Figure 1 The natural radioactive decay series

Figure 2 Maps showing the location of the Needle's Eye natural analogue site



Sketch map of the western Southern Uplands, showing the distribution of mineral veins (from Miller & Taylor 1966).



Geological sketch map of Southwick cliffs and shore at Needle's Eye (from Miller & Taylor).

Figure 3 Schematic diagram of bedrock and surface soil characteristics of the Needle's Eye natural analogue site. Insert (top right) is a reproduction of beta probe readings in soils overlying the vein obtained by Miller and Taylor in the original 1960's survey.

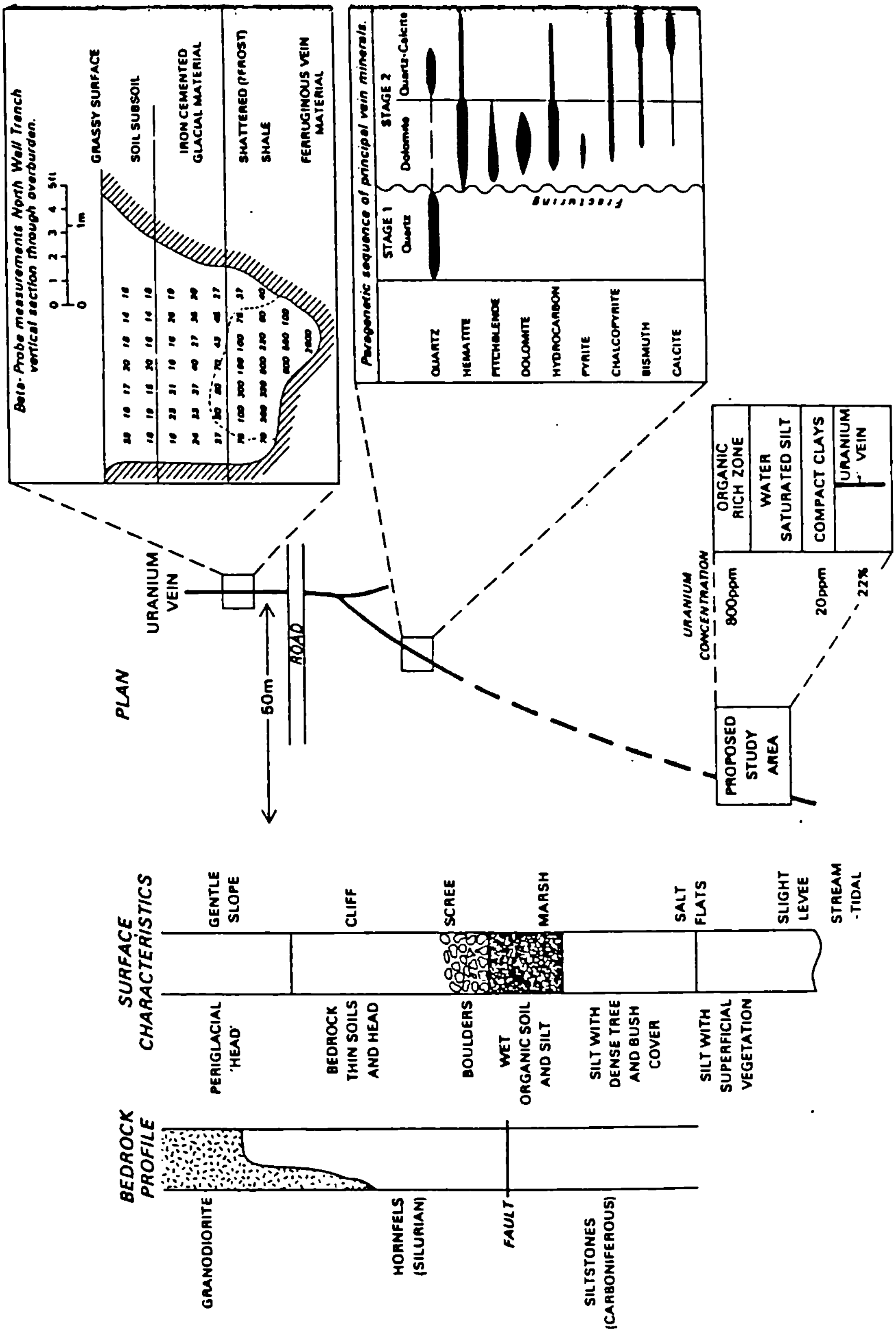
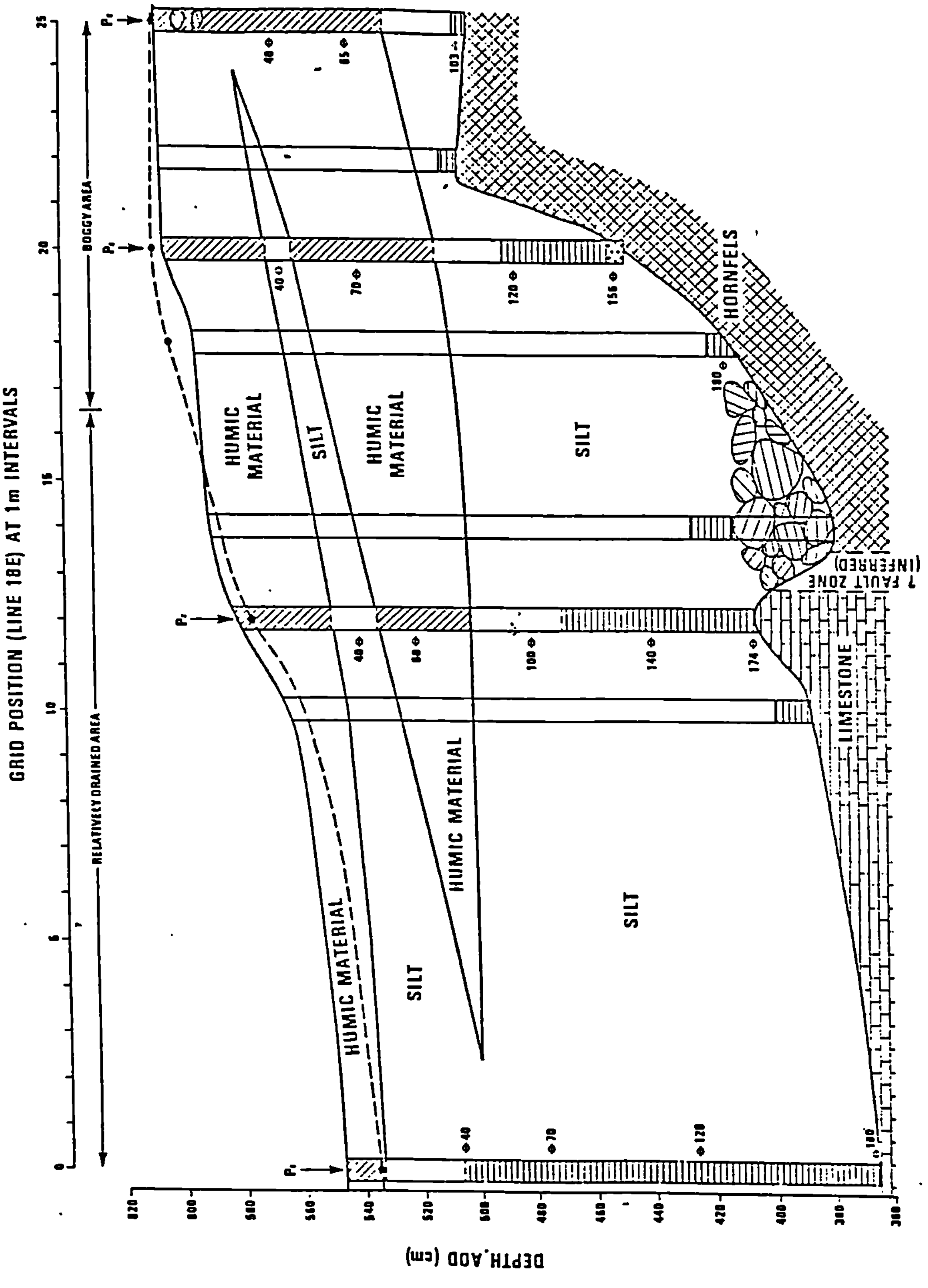


Figure 4 BGS schematic diagram of the sedimentary sequence at the base of the cliff at the Needle's Eye natural analogue site



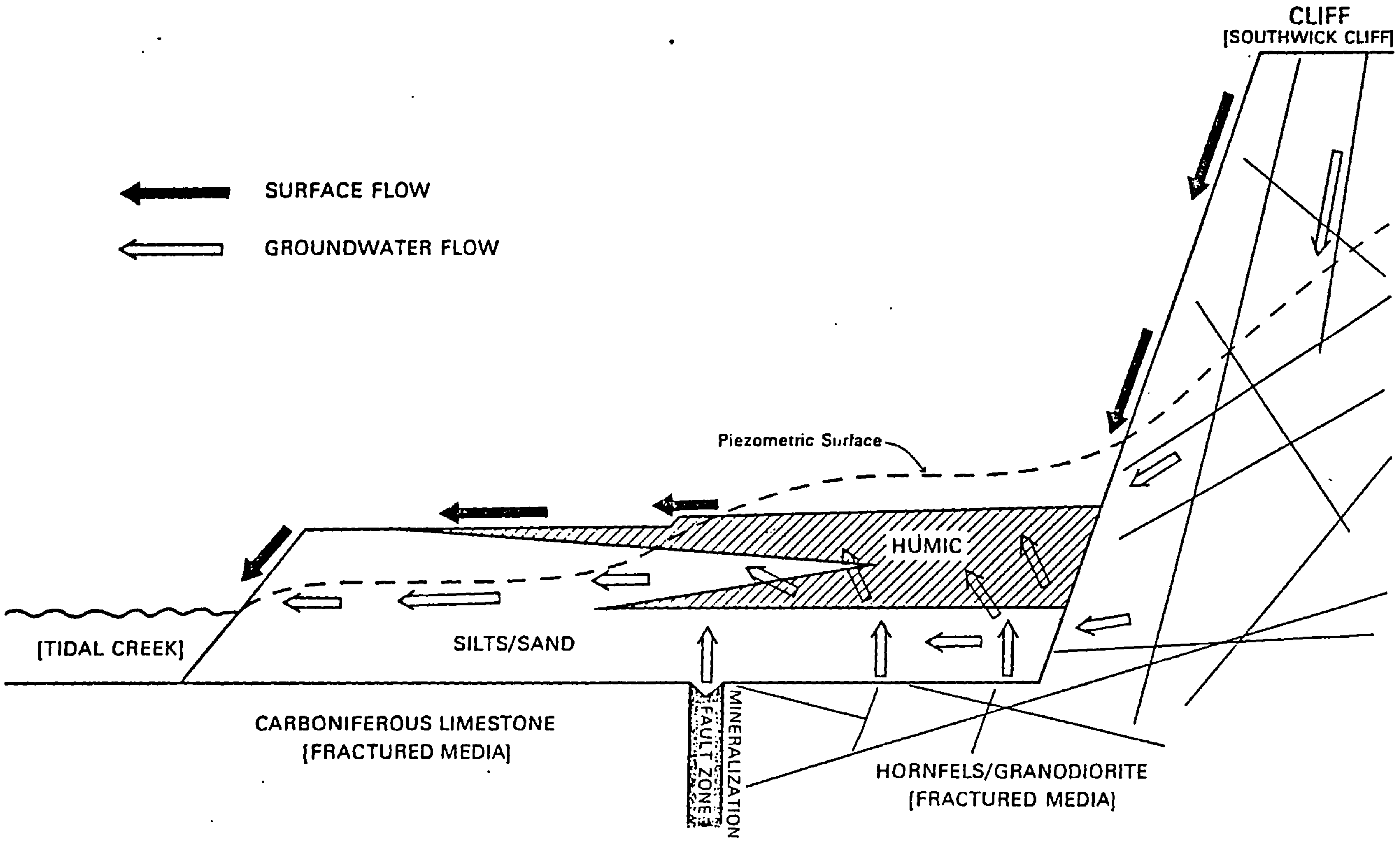


Figure 5 BGS schematic diagram showing the main hydrological features of the Needle's Eye natural analogue site

Figure 6 Schematic diagram of the Needle's Eye natural analogue site showing the locations from which samples were collected

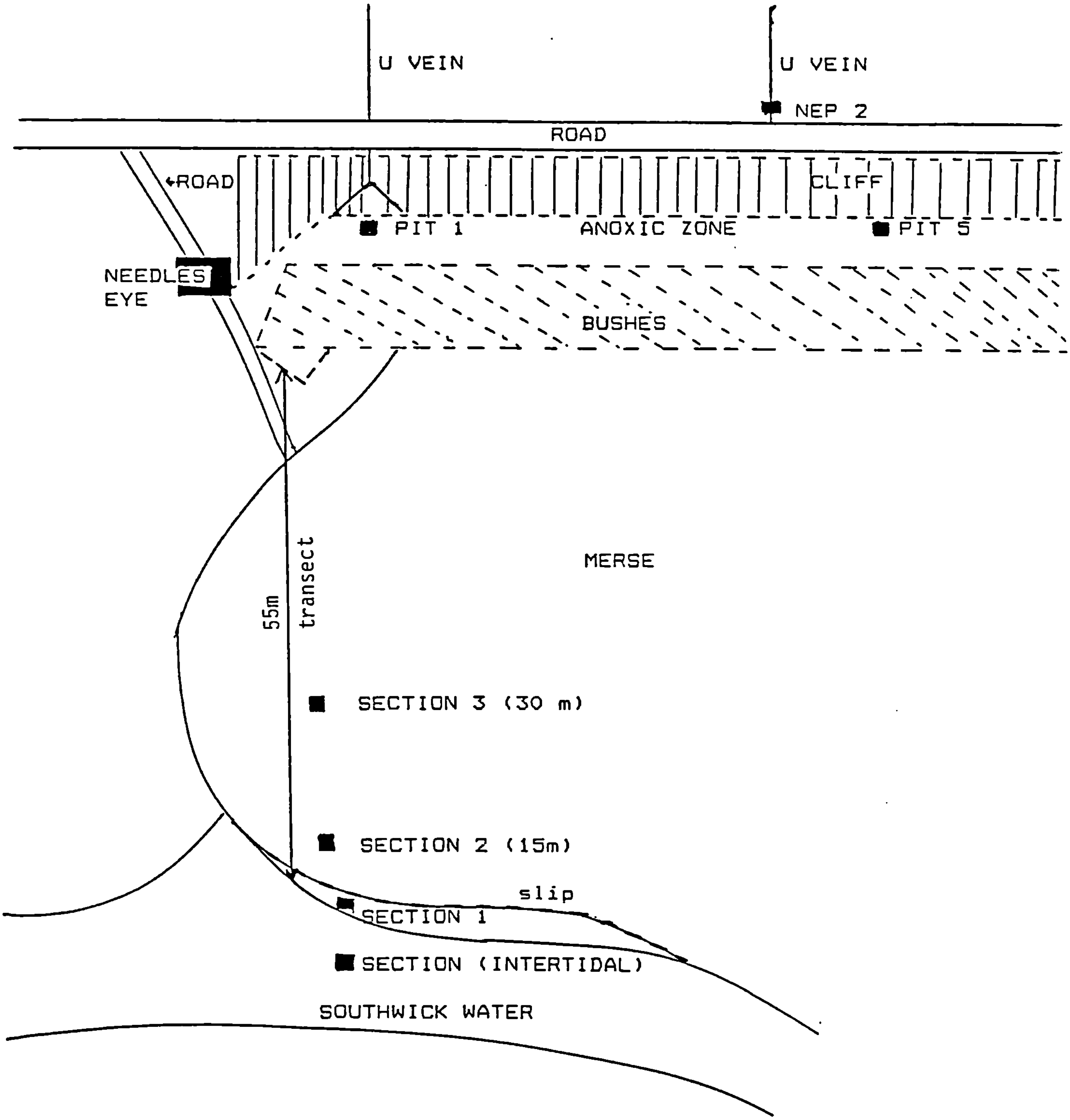


Figure 7 Sample locations in Needle's Eye pit NEP2

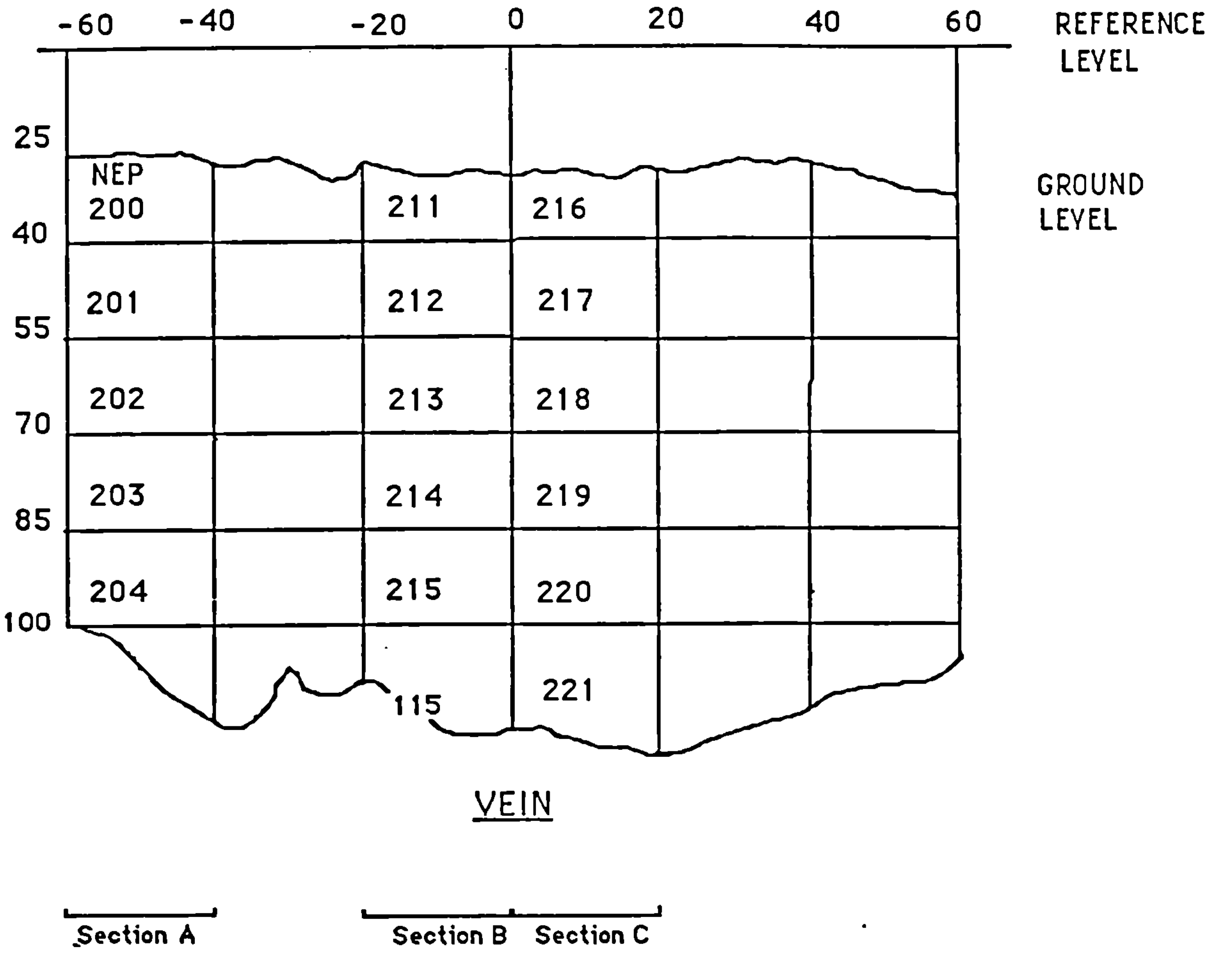


Figure 8 Diagram showing uranioum behaviour in a plot of $^{234}U/^{238}U$ versus $^{230}Th/^{238}U$ for rock samples (Based upon Thiel et al (1983) and Alexander et al (1989)

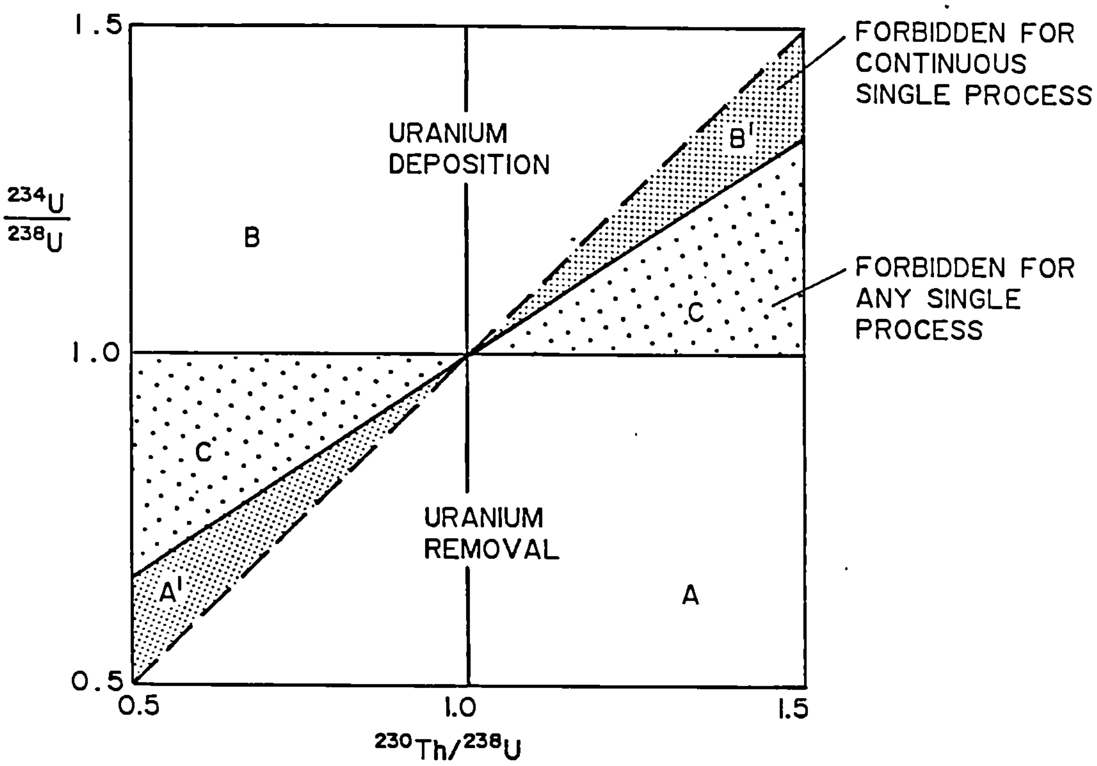
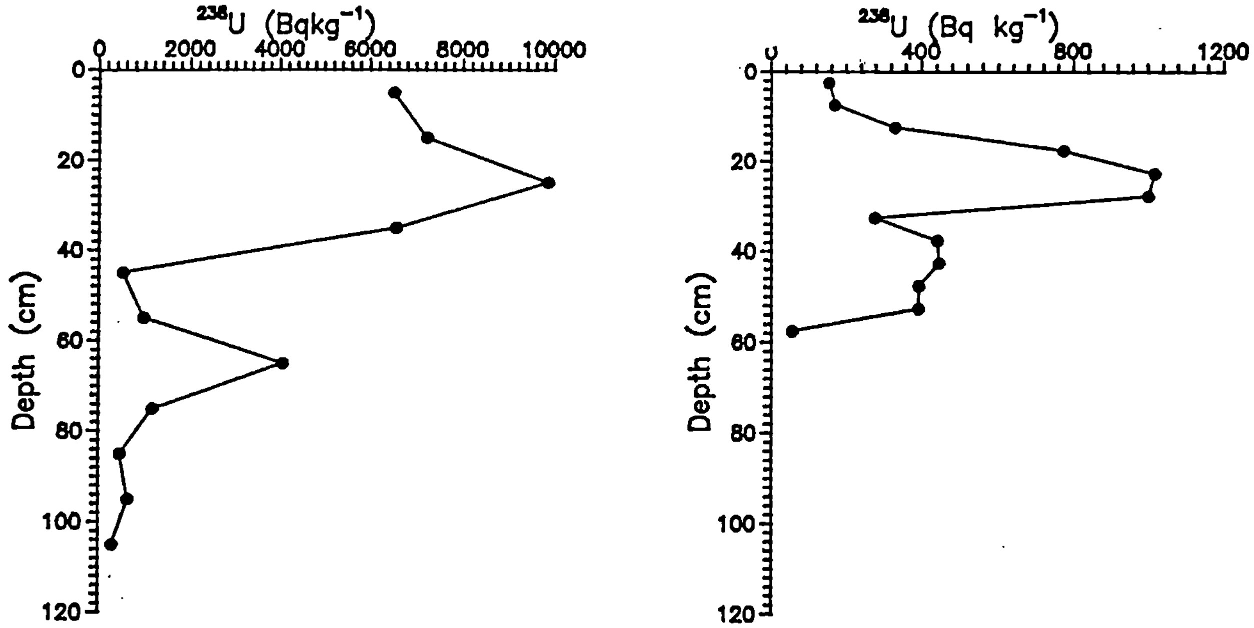
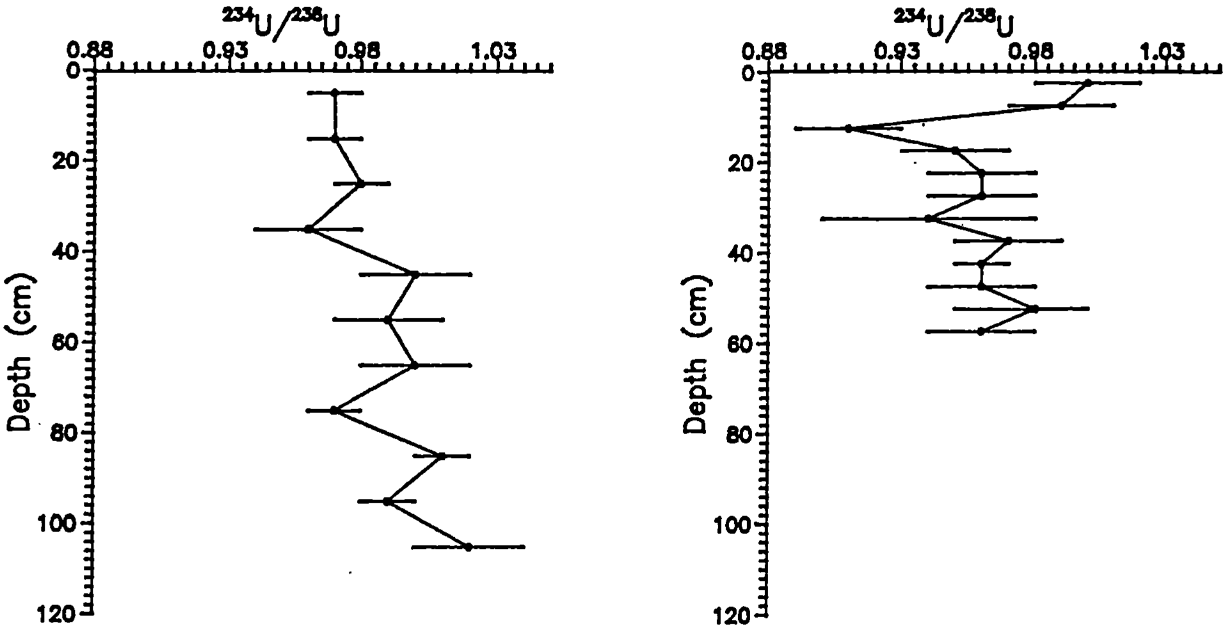


Figure 9 ^{238}U concentrations and ^{234}U/^{238}U activity ratios for SURRC pits 1 and 5 at the Needle's Eye natural analogue site



SURRC PIT 1 SURRC PIT 5



SURRC PIT 1 SURRC PIT 5

Figure 10 % loss of weight on ignition and $^{230}Th/^{234}U$ activity ratios for SURRC pits 1 and 5 at the Needle's Eye natural analogue site

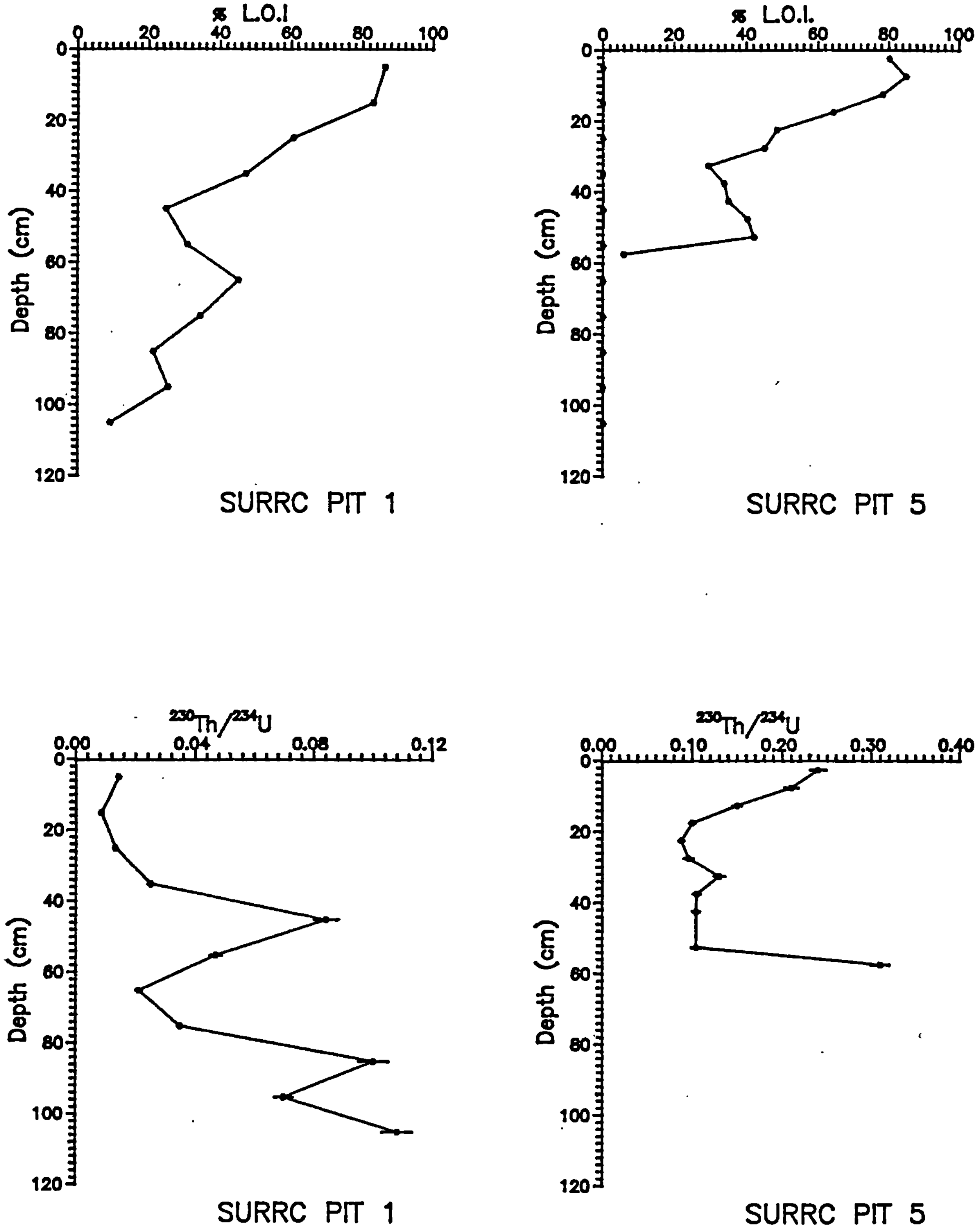
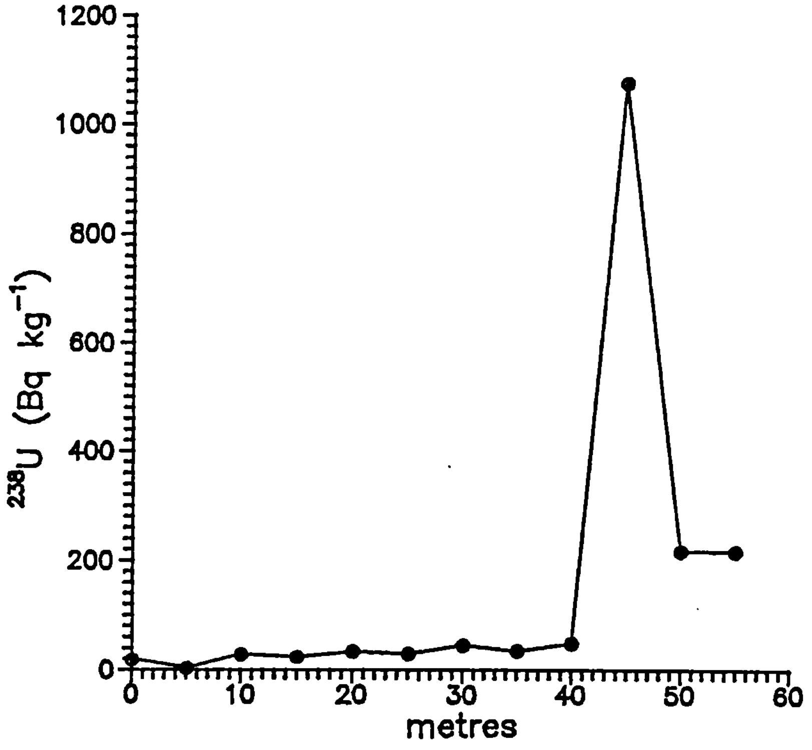
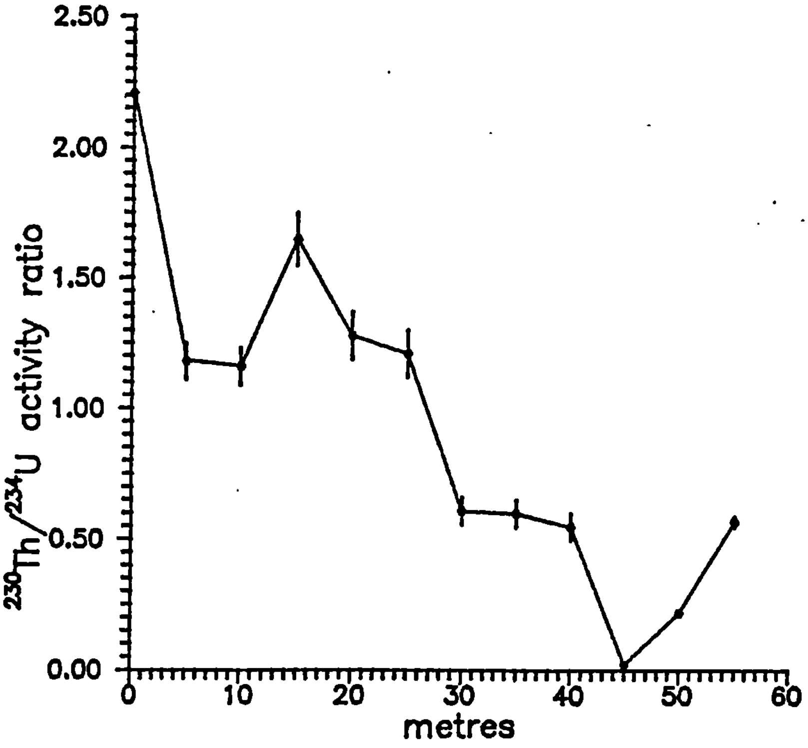


Figure 11 ^{238}U, concentrations and ^{230}Th/^{234}U activity ratios for samples from the surface transect (Figure 6) at the Needle's Eye natural analogue site.

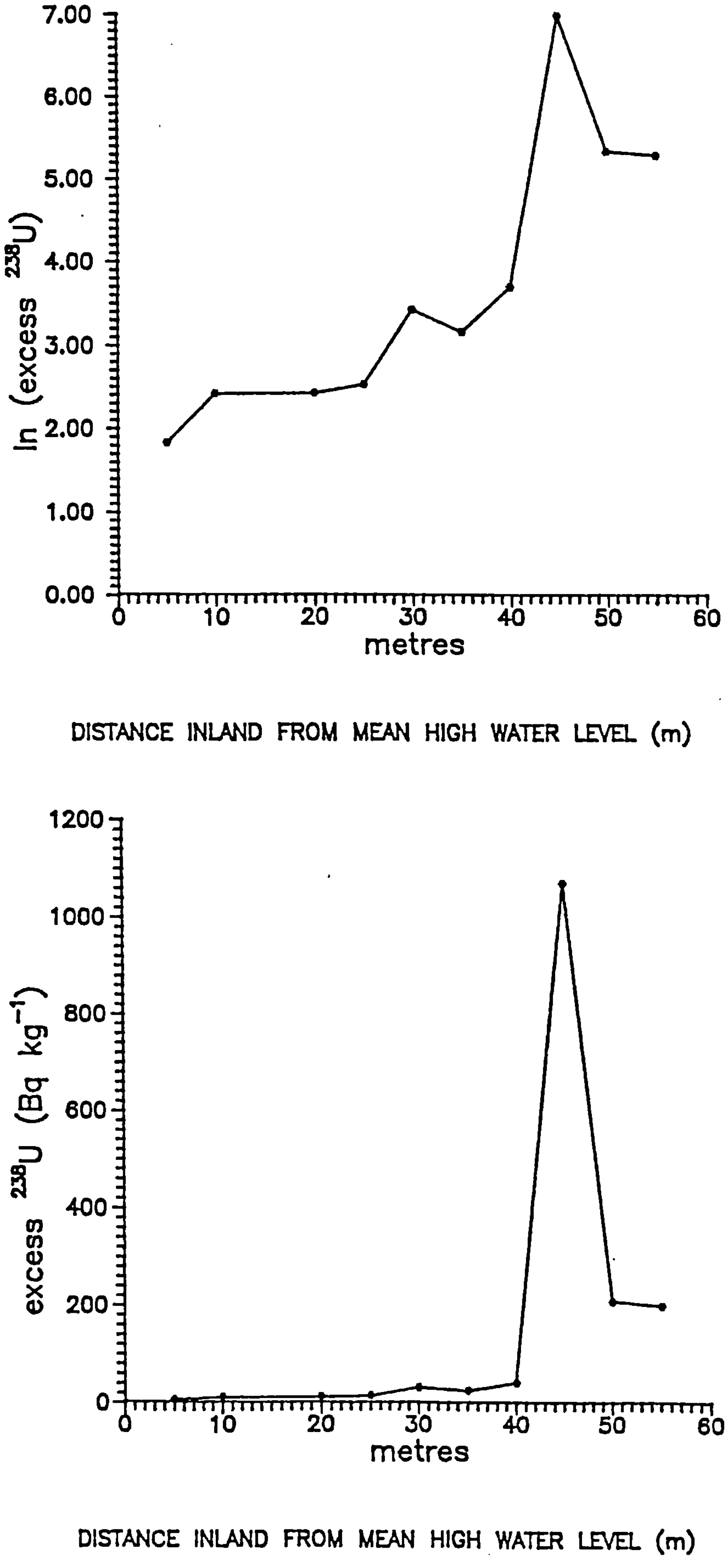


DISTANCE INLAND FROM MEAN HIGH WATER LEVEL (m)



DISTANCE INLAND FROM MEAN HIGH WATER LEVEL (m)

Figure 12 Excess ^{238}U concentrations and ln (excess ^{238}U) plots for samples from the surface transect (Figure 6) at the Needle's Eye natural analogue site



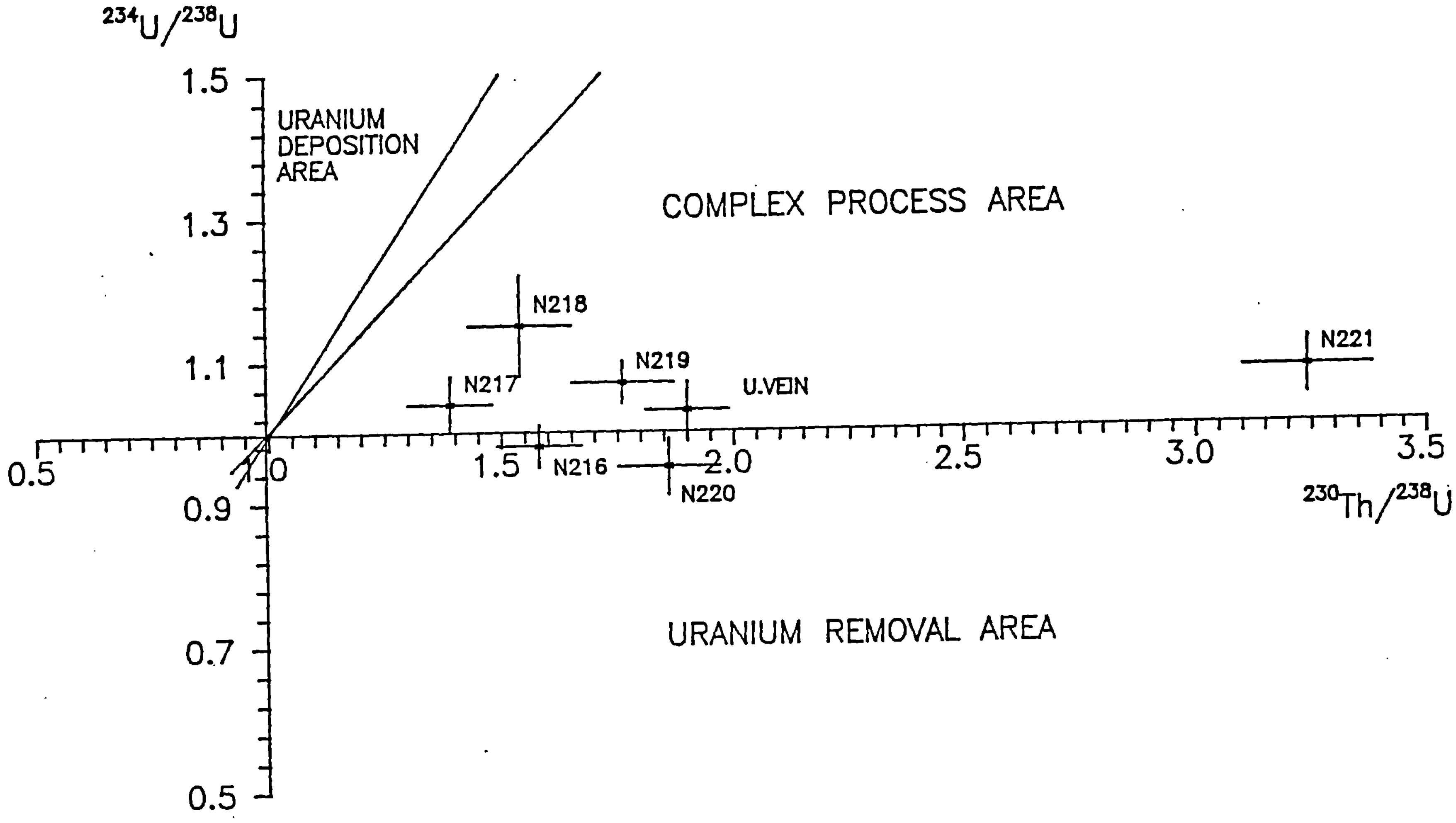


Figure 13 Plot of $^{234}U/^{238}U$ versus $^{230}Th/^{238}U$ activity ratios for samples from the 0cm profile in pit NEPH2 at the Needle's Eye natural analogue site.

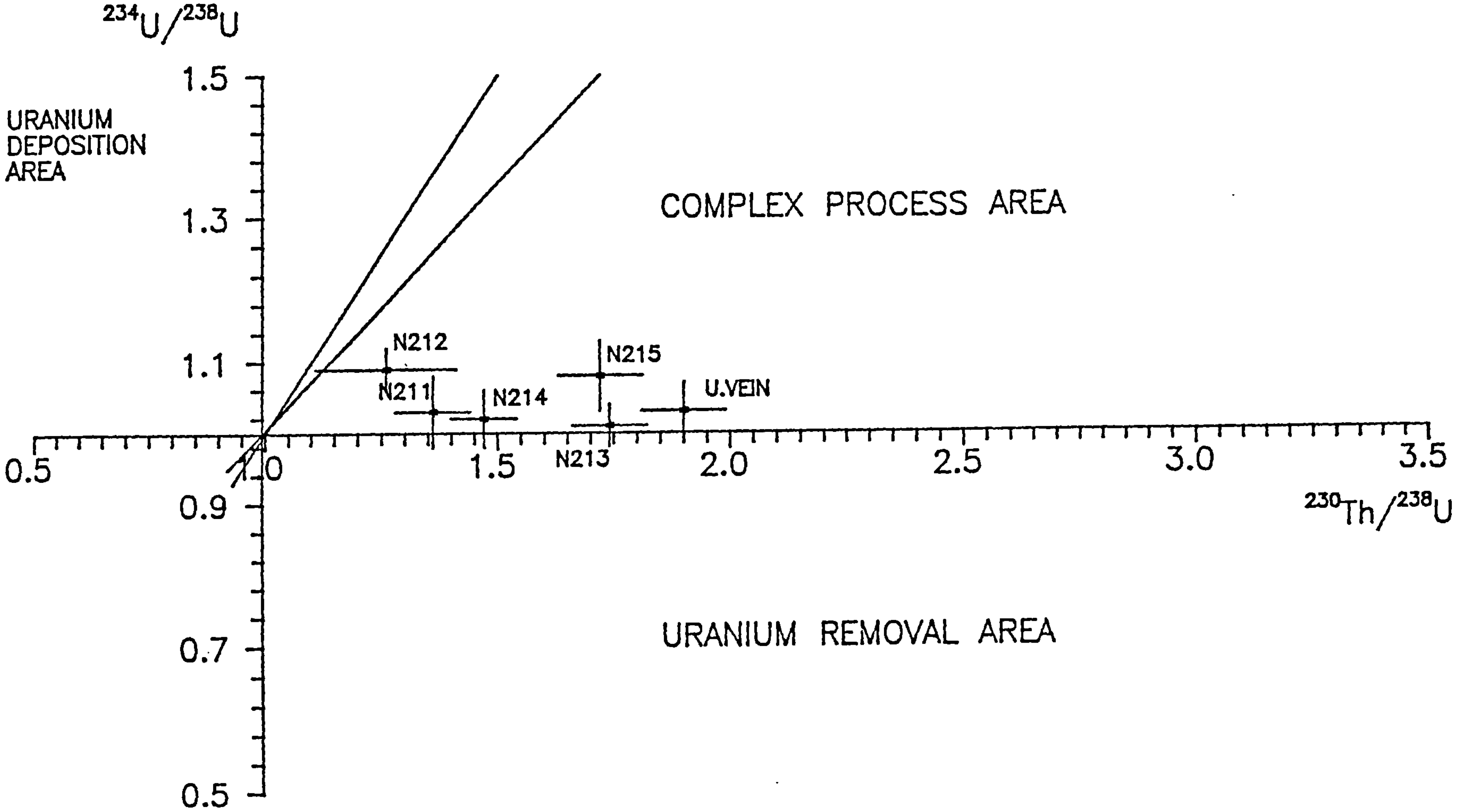


Figure 14 Plot of $^{234}U/^{238}U$ versus $^{230}Th/^{238}U$ activity ratios for samples from the -20cm profile in pie NEP2 at the Needle's Eye natural analogue site.

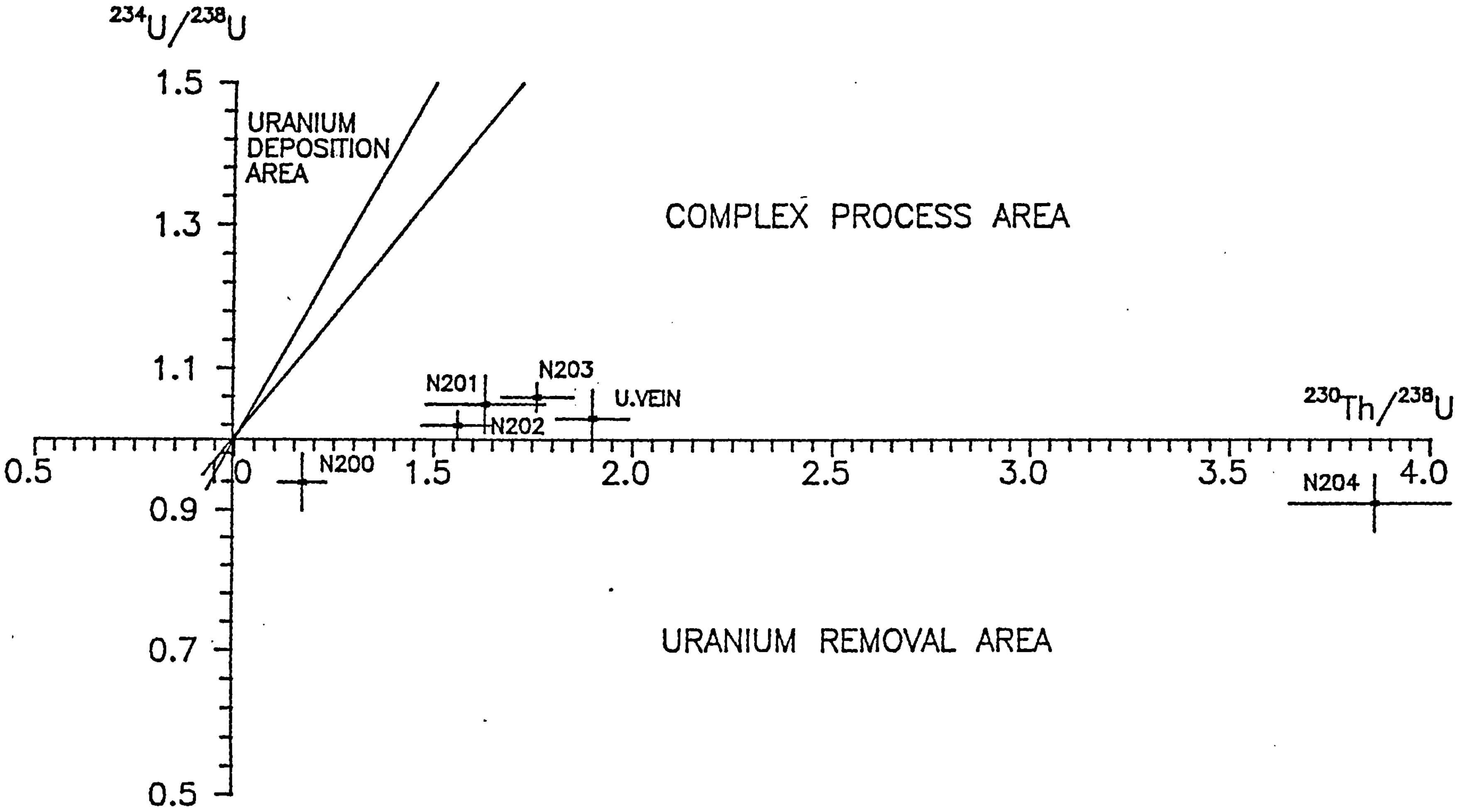


Figure 15 Plot of $^{234}U/^{238}U$ versus $^{230}Th/^{238}U$ activity ratios for samples from the -60cm profile in pit NEP2 at the Needle's Eye natural analogue site.

European Communities — Commission

EUR 13126 — Natural decay series radionuclide studies at the Needle's Eye natural analogue site

A. B. MacKenzie, R. D. Scott, C. M. Houston, P. J. Hooker

Luxembourg: Office for Official Publications of the European Communities

1991 — XII, 61 pp., num. tab., fig. — 21.0 × 29.7 cm

Nuclear science and technology series

ISBN 92-826-2347-5

Catalogue number: CD-NA-13126-EN-C

Price (excluding VAT) in Luxembourg: ECU 6.25

This report covers work on a natural radioactive geochemical system and has been carried out with the aim of improving confidence in using predictive models of radionuclide migration in the geosphere. It is one of a series being produced and is concerned with the U/Th decay series characterization of the hydrothermal mineral veins and the movement of these radionuclides into post-glacial flood plain deposits.

Venta y suscripciones • Salg og abonnement • Verkauf und Abonnement • Πωλήσεις και συνδρομές
Sales and subscriptions • Vente et abonnements • Vendita e abbonamenti
Verkoop en abonnementen • Venda e assinaturas

BELGIQUE / BELGIË

Moniteur belge /
Belgisch Staatsblad
Rue de Louvain 42 / Leuvenseweg 42
1000 Bruxelles / 1000 Brussel
Tél. (02) 512 00 26
Fax 511 01 84
CCP / Postrekening 000-2005502-27

Autres distributeurs /
Overige verkooppunten

Librairie européenne/
Europese Boekhandel
Avenue Albert Jonnart 50 /
Albert Jonnartlaan 50
1200 Bruxelles / 1200 Brussel
Tél. (02) 734 02 81
Fax 735 08 60

Jean De Lannoy
Avenue du Roi 202 /Koningslaan 202
1060 Bruxelles / 1060 Brussel
Tél. (02) 538 51 69
Télex 63220 UNBOOK B
Fax (02) 538 08 41

CREDOC
Rue de la Montagne 34 / Bergstraat 34
Bte 11 / Bus 11
1000 Bruxelles / 1000 Brussel

DANMARK

J. H. Schultz Information A/S
EF-Publikationer
Ottiliavej 18
2500 Valby
Tlf. 36 44 22 66
Fax 36 44 01 41
Girokonto 6 00 08 86

BR DEUTSCHLAND

Bundesanzeiger Verlag
Breite Straße
Postfach 10 80 06
5000 Köln 1
Tel. (02 21) 20 29-0
Fernschreiber:
ANZEIGER BONN 8 882 595
Fax 20 29 278

GREECE

G.C. Eleftheroudakis SA
International Bookstore
Nikis Street 4
10563 Athens
Tel. (01) 322 63 23
Telex 219410 ELEF
Fax 323 98 21

ESPAÑA

Boletín Oficial del Estado
Trafalgar, 27
28010 Madrid
Tel. (91) 44 82 135

Mundi-Prensa Libros, S.A.
Castelló, 37
28001 Madrid
Tel. (91) 431 33 99 (Libros)
431 32 22 (Suscripciones)
435 36 37 (Dirección)
Télex 49370-MPLI-E
Fax (91) 575 39 98

Sucursal:

Librería Internacional AEDOS
Consejo de Ciento, 391
08009 Barcelona
Tel. (93) 301 86 15
Fax (93) 317 01 41

Llibreria de la Generalitat
de Catalunya
Rambla dels Estudis , 118 (Palau Moja)
08002 Barcelona
Tel. (93) 302 68 35
302 64 62
Fax 302 12 99

FRANCE

Journal officiel
Service des publications
des Communautés européennes
26, rue Desaix
75727 Paris Cedex 15
Tél. (1) 40 58 75 00
Fax (1) 40 58 75 74

IRELAND

Government Publications
Sales Office
Sun Alliance House
Molesworth Street
Dublin 2
Tel. 71 03 09

or by post

Government Stationery Office
EEC Section
6th floor
Bishop Street
Dublin 8
Tel. 78 16 66
Fax 78 06 45

ITALIA

Licosa Spa
Via Benedetto Fortini, 120/10
Casella postale 552
50125 Firenze
Tel. (055) 64 54 15
Fax 64 12 57
Telex 570466 LICOSA I
CCP 343 509

Subagenti:

Libreria scientifica
Lucio de Biasio - AEIOU
Via Meravigli, 16
20123 Milano
Tel. (02) 80 76 79

Herder Editrice e Libreria
Piazza Montecitorio, 117-120
00186 Roma
Tel. (06) 679 46 28/679 53 04

Libreria giuridica
Via XII Ottobre, 172/R
16121 Genova
Tel. (010) 59 56 93

GRAND-DUCHÉ DE LUXEMBOURG

Abonnements seulement
Subscriptions only
Nur für Abonnements

Messageries Paul Kraus
11, rue Christophe Plantin
2339 Luxembourg
Tél. 499 88 88
Télex 2515
Fax 499 88 84 44
CCP 49242-63

NEDERLAND

SDU Overheidsinformatie
Externe Fondsen
Postbus 20014
2500 EA 's-Gravenhage
Tel. (070) 37 89 911
Fax (070) 34 75 778

PORTUGAL

Imprensa Nacional
Casa da Moeda, EP
Rua D. Francisco Manuel de Melo, 5
P-1092 Lisboa Codex
Tel. (01) 69 34 14

Distribuidora de Livros
Bertrand, Ld.ª
Grupo Bertrand, SA
Rua das Terras dos Vales, 4-A
Apartado 37
P-2700 Amadora Codex
Tel. (01) 49 59 050
Telex 15798 BERDIS
Fax 49 60 255

UNITED KINGDOM

HMSO Books (PC 16)
HMSO Publications Centre
51 Nine Elms Lane
London SW8 5DR
Tel. (071) 873 9090
Fax GP3 873 8463
Telex 29 71 138

Sub-agent:

Alan Armstrong Ltd
2 Arkwright Road
Reading, Berks RG2 0SQ
Tel. (0734) 75 18 55
Telex 849937 AAALTD G
Fax (0734) 75 51 64

ÖSTERREICH

Manz'sche Verlags-
und Universitätsbuchhandlung
Kohlmarkt 16
1014 Wien
Tel. (0222) 531 61-0
Telex 11 25 00 BOX A
Fax (0222) 531 61-81

SVERIGE

BTJ
Box 200
22100 Lund
Tel. (046) 18 00 00
Fax (046) 18 01 25

SCHWEIZ / SUISSE / SVIZZERA

OSEC
Stampfenbachstraße 85
8035 Zürich
Tel. (01) 365 51 51
Fax (01) 365 54 11

MAGYARORSZÁG

Agroinform
Központ:
Budapest I., Attila út 93. H-1012

Levélcím:
Budapest, Pf.: 15 H-1253
Tel. 36 (1) 56 82 11
Telex (22) 4717 AGINF H-61

POLAND

Business Foundation
ul. Wspólna 1/3
PL-00-529 Warszawa
Tel. 48 (22) 21 99 93/21 84 20
Fax 48 (22) 28 05 49

YUGOSLAVIA

Privredni Vjesnik
Bulevar Lenjina 171/XIV
11070 - Beograd
Tel. 123 23 40

TÜRKIYE

Pres Dagitim Ticaret ve sanayi A.Ş.
Narlibahçe Sokak No. 15
Cağaloğlu
Istanbul
Tel. 512 01 90
Telex 23822 DSVO-TR

AUTRES PAYS
OTHER COUNTRIES
ANDERE LÄNDER

Office des publications officielles
des Communautés européennes
2, rue Mercier
L-2985 Luxembourg
Tél. 49 92 81
Télex PUBOF LU 1324 b
Fax 48 85 73
CC bancaire BIL 8-109/6003/700

CANADA

Renouf Publishing Co. Ltd
Mail orders — Head Office:
1294 Algoma Road
Ottawa, Ontario K1B 3W8
Tel. (613) 741 43 33
Fax (613) 741 54 39
Telex 0534783

Ottawa Store:
61 Sparks Street
Tel. (613) 238 89 85

Toronto Store:
211 Yonge Street
Tel. (416) 363 31 71

UNITED STATES OF AMERICA

UNIPUB
4611-F Assembly Drive
Lanham, MD 20706-4391
Tel. Toll Free (800) 274 4888
Fax (301) 459 0056

AUSTRALIA

Hunter Publications
58A Gipps Street
Collingwood
Victoria 3066

JAPAN

Kinokuniya Company Ltd
17-7 Shinjuku 3-Chome
Shinjuku-ku
Tokyo 160-91
Tel. (03) 3439-0121

Journal Department
PO Box 55 Chitose
Tokyo 156
Tel. (03) 3439-0124

1/91

15

CD-NA-13126-EN-C

NOTICE TO THE READER

All scientific and technical reports published by the Commission of the European Communities are announced in the monthly periodical **'euro abstracts'**. For subscription (1 year: ECU 92) please write to the address below.

Price (excluding VAT) in Luxembourg: ECU 6.25

OFFICE FOR OFFICIAL PUBLICATIONS
OF THE EUROPEAN COMMUNITIES

L-2985 Luxembourg

ISBN 92-826-2347-5

9 789282 623473