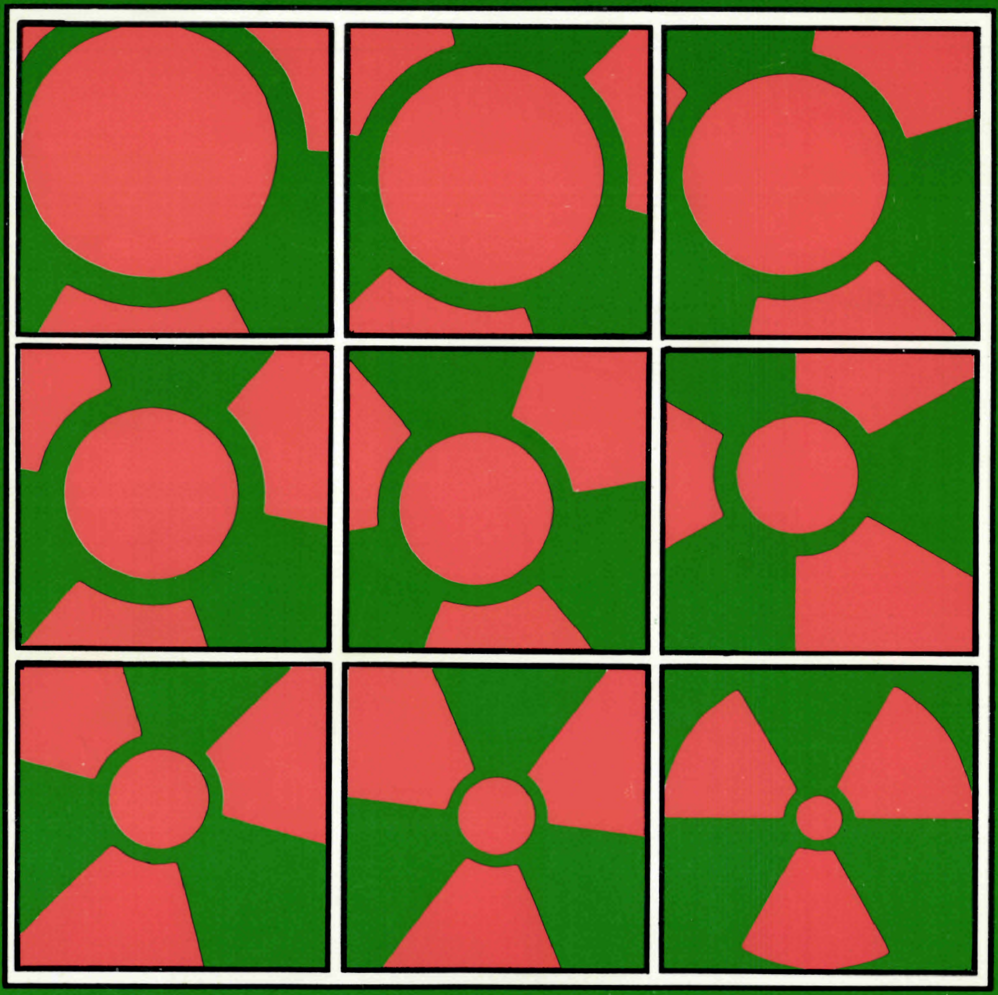
Commission of the European Communities

nuclear science and technology

NATURAL ANALOGUE WORKING GROUP

First Meeting, Brussels, November 5-7, 1985

FINAL MEETING REPORT



Report

EUR 10315 EN-FR

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FINAL MEETING REPORT

Edited by

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Programme on Radioactive Waste Management

Directorate-General Science, Research and Development

1986 EUR 10315 EN-FR

Published by the
COMMISSION OF THE EUROPEAN COMMUNITIES

Directorate-General
Information Market and Innovation

Bâtiment Jean Monnet
LUXEMBOURG

FOREWORD

A Natural Analogue Working Group was established by the Commission of the European Communities in 1985. The purpose of this group is to bring together modellers with earth scientists and others, so that maximum benefit can be obtained from natural analogue studies with a view to safe geological disposal of radioactive waste.

The first meeting of this group was held in Brussels from November 5 to 7, 1985. The discussions mainly concerned the identification of the modellers' needs and of the earth scientists' capacity to provide for them. Following the debates, a written statement was produced by the Group; this document forms the core of the present Report. Notes and outlines of many of the presentations made are grouped in the four appendixes. The valuable contribution of all those involved in the meeting is gratefully acknowledged.

The departments of the Commission of the European Communities act as Secretariat for this Group. In order to ensure coherence at international level, a core of correspondents was identified among the main bodies being active in the field of natural analogues. This Core Group comprises :

P.L. AIREY (AAEC, Australia)
N.A. CHAPMAN (BGS, UK)
B. CÔME (CEC, DG XII).
I. G. Mc KINLEY (EIR, Switzerland)
F.P. SARGENT (AECL, Canada)
M. E. SHEA (OCRD, U.S.A.)
J.A. SMELLIE (SGAB, Sweden)

As the situation evolves at international level, it may prove useful to modify the membership of this Core Group.

The next meeting of the Natural Analogue Working Group is planned to take place in June 1986. This meeting is timed to coincide with the initiation of several major national and international natural analogue projects.

An international conference on analogue studies will be organised by the CEC to take place in early 1987, which will allow presentation of preliminary results of these projects, along with other established studies, to a wider audience.

CONTENTS

FOREWORD III

PROGRAMME OF THE MEETING VII

LIST OF PARTICIPANTS IN THE MEETING IX

STATEMENT BY THE WORKING GROUP 1

APPENDIX 1 : The Modellers' Needs 13

APPENDIX 2 : Geochemical Model Needs 41

APPENDIX 3 : What the Earth Scientists Can Provide 91

APPENDIX 4 : Major International Programmes 165

Natural Analogue Working Group
First Meeting, Brussels, November 5-6-7, 1985

PROGRAMME

Tuesday, November 5

10.30 Welcoming Address : Pierre VENET (CEC)

10.45 Introduction : Neil CHAPMAN (BGS)

11.10-15.00 Session I : The Modellers'Needs
Animateur : Peter SARGENT (AECL)

11.10-11.30 : David HODGKINSON (UKAEA)
11.30-11.50 : Ivars NERETNIEKS (RIT)
11.50-12.10 : Abe VAN LUIK (BPNL)
12.10-12.30 : Ghislain de MARSILY (EMP)

12.30-14.00 : Lunch

14.00-15.00 : Session I continued : Discussion

15.00-17.30 Session II : Geochemical Model Needs
Animateur : Ed PATERA (US DOE)

15.00-15.20 : Bror SKYTTE-JENSEN (RISO)
15.20-15.40 : Peter AIREY (AAEC)
15.40-16.00 : Ian McKINLEY (EIR)
16.00-16.15 : Peter GLASBERGEN (RIVM)
16.15-16.30 : Break
16.30-17.30 : Discussion

17.30 Close

18.00 Cocktail Party

Wednesday, November 6

9.00-12.30 Session III : What the Earth Scientists can provide
Animateur : Ivars NERETNIEKS (RIT)

9.00- 9.15	: John SMELLIE (SGAB)
9.15- 9.30	: Jean-François SUREAU (BRGM)
9.30- 9.45	: Peter SARGENT (AECL)
9.45-10.00	: Aldo BRONDI (ENEA)
10.00-10.15	: Miro IVANOVICH (UKAEA)
10.15-10.30	: Marco d'ALESSANDRO (JRC)
10.30-10.45	: Break
10.45-11.00	: Neil CHAPMAN (BGS)
11.00-11.15	: Mike SHEA (OCRD)
11.15-12.30	: Discussion
12.30-14.00	: Lunch

14.00-17.30 Session IV : Major international programmes
Animateur : Ferruccio GERA (ISMES)

14.00-14.20	: CEC (Bernard CÔME)
14.20-15.10	: Pocos de Caldas, Brazil (John SMELLIE)
15.10-16.00	: Alligator Rivers, Australia (Peter AIREY)
16.00-16.15	: Athabasca Basin, Saskatchewan (Peter SARGENT)
16.15-16.30	: Break
16.30-17.30	: Discussion
17.30	: Close

Thursday, November 7

9.00-12.30 Session V : Preparation of a written statement

12.30-14.00 : Lunch

14.00-15.30 Session VI : Future activities
Animateurs : Neil CHAPMAN and Bernard COME

1. Form of final meeting report
2. Style of NAWG meetings and need for larger open meetings
3. Topics and venue for 1986 NAWG
4. Other business

15.30 : Close and disperse

****

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STATEMENT BY THE WORKING GROUP

1. INTRODUCTION

1.1 PERSPECTIVE

The purpose of a geological repository is to dispose of radioactive wastes in a manner which protects public health and safety. Long-lived radioactive wastes require isolation for such extremely long time periods that direct observation and experimental verification that a repository is working throughout its lifetime is not feasible. Therefore reasonable assurance of safety for a proposed repository will be judged by a consensus of opinion among the scientific community, regulatory agencies, and the public.

The long-term behaviour and evolution of the repository system, and of the individual repository components, will be affected by the interaction of numerous complex processes. Safety assessments of repository performance will be made using predictive models based upon our understanding of how such processes act over long times in the various geological settings proposed for disposal.

The study of natural analogues of a nuclear waste repository is one method for providing assurance that a proposed repository site and design will be safe. Results from natural analogue studies must be combined with laboratory experiments and field studies to provide as large a database for safety assessments of repository performance as is scientifically feasible. Multiple data sources will maximise confidence that a repository will actually behave as predicted.

A natural analogue can be defined as an occurrence of materials and/or processes which resemble those expected in a proposed geological waste repository. Natural analogues can include examples as diverse as the geothermal circulation of groundwater above a deep heat source in the earth's crust, the immobilization of uranium ores at redox interfaces in geological materials, or even iron nails which have survived burial in a near-surface environment since Roman times (an archaeological analogue).

1.2. FUNCTIONS OF NATURAL ANALOGUES

The predictive models which comprise a safety analysis are based on mathematical descriptions of processes which are known or are expected to take place. In many cases the processes involved are very complex and involve many separate mechanisms. Most of our experience and data have been obtained from experiments performed over timescales ranging from days to years and on size scales which are suitable to laboratory experimentation. However, the predictions drawn from these studies are expected to cover timescales which range from thousands to millions of years. To gain added confidence in these predictions, it is important to obtain observations on longer time and size scales. The study of naturally occuring phenomena where the processes of interest play a major role may provide the necessary information.

One of the primary uses of natural analogues is thus to validate the models used. This means that the processes which are described in the models must be observable in nature and behave as predicted. A further important use is to ascertain that no processes occur in the complex real environment over long time scales which were not anticipated in the modelled system. Analogues may also be used to obtain data on processes which are not obtainable in other ways (e.g. if no experimental technique is feasible).

There are, however, inherent difficulties in using natural analogues to obtain unambiguous quantitative data on processes. The initial and boundary conditions of Nature's own experiments cannot usually be fully reconstructed. In such cases the data extracted from the observations may have a considerable uncertainty. Often a single clear-cut mechanism has not dominated the process and the end result cannot be unambiguously interpreted. However, the overall observation may still be of considerable qualitative use, especially if it is consistent with other similar observations. This adds to the confidence that no essential, and as yet unknown processes occur.

The term 'natural analogus' can be used in a very broad sense and there are numerous potential examples, some key types being described in section 2. Table 1 lists some of the most important processes, mechanisms and properties which may be studied with the aid of natural analogues. The relative importance of each of the processes listed varies between disposal concept, but covers all those considered generically to be most significant in assessing repository performance.

2. APPLICATION OF ANALOGUES

2.1 USING ANALOGUES IN THE ASSESSMENT PROCESS

The main concern in performance assessment is the confident prediction of repository behaviour and its safety implications, particularly in the far future. Such predictions can never be without some uncertainties, which arise from choice of scenarios, models, and parameter values. Analogues can assist in understanding all three of these components in that estimates of scenario probability, the validity of models, and the range of parameter values can be assessed in the natural environment over long time periods.

In applying natural analogues, the question of confidence may need to be addressed at different levels of detail to different audiences, such as the researcher, the regulator/assessor, or the general public. For example the researcher may need confidence in some very specialised detail of a particular model , whereas there is more general reassurance in analogues such as those which may show that insignificant surface releases have occurred from large deeply buried uranium ore deposits.

A key element in applying natural analogues, is thus to define the ultimate objective and to recognise that this in turn will determine the level of detail or level of quantification which is needed. There is a continuum of possibilities and any analogue can potentially be used in a variety of ways, depending on how the data are obtained, and the quality of information available. However, it is useful to divide the means of application into 4 discrete groups.

Area of influence / Process or Mechanism	Leaching/ Mobilisation	Transport	Retardation/ Retention
Solubility limitation	X		X
Groundwater accessibility	X	X	X
Radiolysis	X		
Material thermal stability	X	X	X
Colloid formation	X	X	
Dispersion		X	
Channeling		X	
Short-Circuits Pathways	X		
Fracture Hydrology		X	
Diffusion:			
Matrix		X	X
Intra-crystalline	X		
Backfill	X	X	
Redox behaviour	X		X
Sorption:			
Fracture			X
Mineral			X

Table 1: The most important processes or mechanisms where analogue data are required, and their key areas of influence (Relative significance of individual processes will vary between different disposal concepts)

2.2. MEANS OF APPLICATION OF ANALOGUES.

There are essentially four ways of applying analogues in the modelling and assessment processes;-

1. As natural experiments which replicate a process, or a group of processes, which are being considered in a model. This is probably the most quantitative application of analogues, which allows confident constraints to be placed on, for example, extrapolations of laboratory experiments to larger time or space scales.

2. For determining the bounds of specific parameter values. This application would be most useful at the stage where a modeller needs limiting values on a parameter, but can obtain these from any or many geological systems. The origins of the data are not particularly important, and need not be linked to the process being modelled. Diverse sources may be used and a statistical approach adopted. An example of this is thermodynamic or kinetic data, which could be obtained from any system.

3. As simple 'signposts' indicating which phenomena can occur in the system being modelled by reference to a parallel natural system. This is a purely qualititative application which gives "yes-no" answers, or indicates the "direction" of long-term processes. It would be the first means of application used when carrying out scoping exercises.

4. In an empirical sense to integrate the results of many processes at one site, over long time periods. Not all of the processes involved may be evident, nor may the manner in which they have been linked. Only the end result is important, and in this sense this application is the most directly useful to a safety assessment (as distinguished from the individual models which comprise it). An example might be to determine whether there is any surface radiological manifestation of a deeply buried uranium ore body.

2.3 EXAMPLES OF THE FOUR MEANS OF APPLICATION.

The degree of characterisation of specific natural analogues will determine their ultimate range of application. Thus this section deals with different examples of natural analogues used in the past in order to illustrate the range of approaches in each of the four Groups of application.

2.3.1 Group 1 (NATURAL EXPERIMENTS)

The Loch Lomond analogue (Hooker, *et al*; 1985) is a good example of the first type of application. The route followed is outlined below.

a) Set objectives: - study of elemental migration in clays analogous to disposal host or backfills.

b) Site selection: - a prior knowledge or rational basis for expecting a geochemical anomaly in the late Quaternary deposits of Loch Lomond (the succession of terrestrial to marine sedimentation regime).

c) Sample collection: - reconnaissance sampling by piston coring.

d) Chemical analysis: - chemical analysis of clay samples confirmed the existence of geochemical partitioning of several elements between fresh water and marine sediments.

e) Additional quantification of migration processes:
   - time scale was established by radiometric and palynologic dates.
   - migration processes have been identified as diffusion and advection.
   - models of these processes have been constructed to account for the observed geochemical profile in terms of transport and retardation processes.
   - boundary conditions have been estimated using the chronological data and the mathematical description of the processes .
   - initial conditions could not be defined unambiguously but were later treated as a parameter in the model
   - value of required parameters were estimated (e.g. advective velocity due to compaction).

f) Result of experiment: - Maximum apparent diffusivity for one element (bromine) was calculated for a series of hypothetical initial concentrations in the marine sediment fluids and compared to anion diffusivities in consolidated clays such as Boom clays.

g) Future work
   Additional work is foreseen on tuning the model in order to reduce ambiguity concerning initial and boundary conditions. To achieve this end, further laboratory and analytical work should be carried out (e.g. diffusivity measurements, leaching rates) and deeper samples collected.

The above methodology follows in detail the five steps procedure for selection of natural analogues defined by Chapman et al (1984), namely:

- The process involved should be clear-cut. Other processes which may have been involved in the geochemical system should be identifiable and amenable to quantitative assessment as well, so that their effects can be 'subtracted'.
- The chemical analogy should be good. It is not always possible to study the behaviour of a mineral system, chemical element or isotope identical to that whose behaviour requires assessing. The limitations of this should be fully understood.
- The magnitude of the various physico-chemical parameters involved (P, T, pH, Eh, concentrations, etc) should be determinable, preferably by independant means and should not differ greatly from those envisaged in the disposal system.
- The boundaries of the system should be identifiable (whether it is open or closed, and consequently how much material has been involved in the process being studied).
- The timescale of the process must be measurable, since this factor is of the greatest significance (the raison d'etre) for a natural analogue.

2.3.2.Group 2. (BOUNDARY PARAMETER VALUES)

The determination of distribution coefficients for natural series radionuclides from diverse formations and groundwater systems is an example of such data collection (Krishnaswami et al., 1982)

a) Set objective: derive ranges or statistics for distribution coefficient of relevant nuclides.

b) Site selection: several sites with different hydrogeological characteristics, and where relevant, data were selected from published literature.

c) Collect data: concentrations of natural series nuclides were measured in well defined groundwater samples.

d) Define conceptual model: equilibrium conditions between water and rock were assumed.

e) Additional measurements: porosity and density of rocks.

f) Result of analysis: range of distribution coefficients for Ra, Th and Pb in a variety of hydrogeological systems. This range was found to be relatively narrow.

g) Future Work: Eh, pH, and co-solute data needs to be collected in order to explain some of the observed variability.

2.3.3. Group 3 (SIGNPOSTING)

This is essentially a sensitivity analysis where a site is selected in order to establish a hierarchy of processes in a qualitative way. This would enable modellers to decide which processes can be safely ignored to simplify models. Important processes would thus be highlighted and could then be further investigated in some detail leading to a Group 1 type analysis, but not necessarily at the same site.

An example is matrix diffusion, a process which is of great importance in dual porosity media and which might be a significant retardation mechanism in crystalline rock. A 'yes-no' answer on whether it can be observed in nature was needed, and studies by Smellie et al (this volume) have been designed to provide this in a qualitative sense in Swedish and Swiss granite.

2.3.4.Group 4 (EMPIRICAL, INTEGRATED ANALOGUES)

An example of this Group is the existence of a deep uranium deposit in Saskatchewan (Cigar Lake) which remained undetected by conventional prospecting techniques due to the lack of obvious surface manifestations, such as enhanced uranium and radium levels in local surface waters.

The implication is that nature can create hydrogeochemical conditions capable of retaining large quantities of uranium for very long periods of time. Obtaining a detailed understanding of the sub-components of such systems would then place such an analogue into Groups 1 or 3, as explained earlier.

3. MODEL REQUIREMENTS RELATED TO AVAILABLE ANALOGUES

On the most general, global scale (Group 4) of giving confidence in the results of repository safety assessments, the Oklo site is an important analogue, but many other ore bodies could also be considered in this regard. On a more specific, quantitative basis, analogues are selected to elucidate particular processes or mechanisms incorporated (or deliberately ignored) in safety assessment models. In this section are listed examples of relevant analogues of some of the key processes in modelling both the near-and far-fields identified earlier, and which have already been used, or could be considered for use in the future. The area of biosphere modelling and dose calculation is not specifically addressed although many relevant analogue studies have been performed, for example examining plant/animal concentration factors for radionuclides at Morro do Ferro, Brazil (Eisenbud, et al, 1984).

The relevant processes and equivalent analogues are briefly summarised in Table 2. It has already been pointed out that the individual processes and their relevant importance are very site-and repository concept -specific. As a particular example, for sites in which very saline waters are expected, this factor constrains analogue selection for most far-field and many near-field processes. Not specifically included in the list are analogues of process-coupling, which is very important and should be borne in mind during analogue selection; for example considering the influence of the backfill on leaching of the waste matrix. Also excluded are possible perturbing factors which could affect many of the processes listed (eg microbial activity), but again such may be amenable to analogue study or, at least, should be taken into account during analogue interpretation/-analysis. The number of gaps in the Table is notable, indicating in particular many items for which analogues may be available, but which have so far not been sought or investigated.

TABLE 2: AVAILABLE ANALOGUES

PART 1: NEAR FIELD.

Processes	Analogue (current)	Analogue(possible)
Chemical buffering/ barrier life time	archaeological sites. pore water in natural bentonite intrusives into clays e.g. Orciatico (Italy)	historical disposal sites
Radiolysis	Oklo	U ore bodies (Fe^2/Fe^3) in vicinity of e.g. pitchblende veins
Near field hydrology	geothermal systems (BRGM studies) intrusives e.g. Alamoso Stock	
Mobility in barriers (including dispersion)	advance of U secondary mineralisation (Koongarra) Loch Lomond	U deposits: Pocos de Caldas Cigar lake
Colloid formation and transport.		U Ore bodies
Gas formation and transport		natural gas fields methane lenses in clays
Synergistic effects (e.g. effect of clay on glass leaching rates)		volcanic glasses
Migration of fluid inclusions in salt	Gorleben - identified by drilling and chemical assay.	

2: FAR FIELD

Process	Analogue (current)	Analogue(possible)
Groundwater hydrology:		
- short circuits	Gorleben - migration through cap rock	He/Rn emanation
- constancy of hydraulic systems (palaeo-effects)	isotope hydrology (dating, stable isotope studies)	isotope hydrology of proposed repository sites.
- integrity of salt domes	hydrology of Quaternary aquifer systems (Holland and Germany	
Radionuclide transport:		
- Retardation (sorption)	U ore bodies (Alligator River)	U ore bodies e.g. Pocos de Caldas, Cigar Lake, etc. all geochemical prospecting sub-surface nuclear weapon tests
- Matrix diffusion	Swedish/Swiss U-series study Marysville U deposit unweathered ore - Alligator River ? granite blocks in contact with seawater (Cornwall)	U ore bodies (other) other mineralisation in joints and fractures
- Fission product/ transuranic element transport	U ore bodies - Alligator River	U ore body - Cigar Lake - Pocos de Caldas cosmogenic isotopes (^{129}I, ^{14}C) fall-out isotopes (^{137}Cs,Pu)
- Colloid transport	U ore bodies (Alligator River)	U ore bodies elsewhere proposed repository sites.

4. GENERAL CONCLUSIONS AND RECOMMENDATIONS

The investigation and use of natural analogues is contributing significantly to the overall goal of safe disposal of nuclear waste. The role of the analogue is multi-faceted. The primary scientific use is establishing and justifying the use of specific processes and data for environmental and safety assessments of waste disposal concepts, and ultimately for the licensing of specific sites.

The consensus generated at this and the previous meeting in Chicago in 1984 (KBS TR-84-18) is that no one analogue can perfectly mimic the overall performance of a complete disposal system. It was concluded that the most significant use of natural analogues is to support and justify the use of specific detailed research models and their simplification for incorporation into large assessment codes.

The need to have a very well defined system or process and a similarly tightly defined analogue was a recurrent theme. It is considered that any future research into analogues should be more critically evaluated in terms of how precisely it relates (directly or indirectly) to specific nuclear waste disposal concept.

The following specific recommendations emerged:-

a) There is a genuine need for an informal means of scientifically coordinating national and international research programmes into the use of natural analogues. This will take the form of information meetings to exchange results, and discuss interpretations and new studies, organised by the Natural Analogue Working Group (NAWG).

b) These meetings must be attended by both modellers and 'measurers' (earth scientists, archaeologists, etc). Such meetings are synergistic for those involved and produce useful positive and negative feedback to funding and regulatory agencies.

c) A small core-group of correspondents will be set up to organise meetings and exchange information.

d) Three projects were presented for possible international involvement (Australian, Brazilian and Canadian uranium deposits). The purpose of this meeting was not to discuss their organisation or funding, but to assess them technically as far as was practicable at present.

There was general consensus that all three had merit with respect to some aspects of particular modelling requirements, or specific disposal concepts. The proponents of the three major projects should present and exchange information on programme plans, techniques and the end uses of the data on a regular basis, using the NAWG as a forum. The next meeting will provide this opportunity, when these programmes are fully designed and just getting underway.

e) For all future analogue studies, at both national and international levels, it is regarded as essential that modellers be involved right from the outset, at the planning stage. This may sound obvious, but it has rarely occurred in past studies.

f) There should be a greater interaction between the NAWG (and individual project groups) and the licensing or regulatory agencies in all countries involved. This will primarily take place by very rapid dissemination of informal reports such as this, to enable the full value of the discussions to be utilised in decision making. Consideration should also be given to having observers attend certain meetings.

5. REFERENCES

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APPENDIX 1

The Modellers' Needs

1. Natural Analogues for radioactive waste burial : a modelling perspective (D. HODGKINSON and D. LEVER).

2. The need for geologic evidence for radionuclide migration in the geosphere (I. NERETNIEKS).

3. The use of natural analogues in the process of building confidence in performance assessment models (A. VAN LUIK).

4. A modeller's viewpoint on the possible use of analogues for flow and transport (G. de MARSILY).

AERE-R.12064
DOE/RW/85.195

Natural Analogues for Radioactive Waste Burial:
A Modelling Perspective

D.P. Hodgkinson and D.A. Lever*

Presented at the first meeting of the Natural Analogue Working Group, Brussels, 5-7 November, 1985.

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December 1985

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Executive Summary

Radionuclides will move very slowly from the deep geological repositories that have been proposed as a possible option for their long-term disposal. Laboratory and field experiments can be devised to investigate the important physical and chemical processes, however these only yield information on relatively short time-scales (up to 1 year). Natural geological systems have been developing over far longer time-scales, and so potentially they can provide important insight into the behaviour of radionuclides over times that are relevant to repository safety assessments.

This paper discusses some possible uses of analogues, from the point of view of those involved with the development and use of mathematical models. The characteristics of models used for performance assessment and for analysing experiments are outlined in order to address the question of to what extent natural analogues can be used to validate models. The safety case for burying cemented intermediate-level waste in deep geological formations is outlined and the most critical processes and parameters are identified. Natural analogues have the potential to provide useful information about some of these, especially long-term chemical processes and migration rates in the geosphere. There is likely to be considerable uncertainty and ambiguity associated with the interpretation of natural analogues and thus it is their general features which should be emphasised, and models with appropriate levels of sophistication should be used.

1. Introduction

This paper presents some ideas about the potential usefulness of natural analogues in assessing the safety of radioactive waste disposal. In particular it focuses on the specific case of intermediate-level waste (ILW) disposal in deep geological formations. It is based on recent experience with developing [1-3] and using [4,5] mathematical models for performing such safety assessments and for analysing laboratory [6] and field [7,8] migration experiments and natural analogues [9].

The plan of the paper is as follows. The characteristics of mathematical models used for performance assessment and data analysis are discussed in section 2. Section 3 gives an overview of the safety case for deep disposal of cemented ILW and identifies the critical processes. Then situations where natural analogues can play a useful role are discussed. In section 4, some of the questions that should be considered when modelling natural analogues are presented and some of the potential problems are identified. Finally, some conclusions are drawn together in section 5.

2. Mathematical Models

The above applications require a variety of different models depending on the level of detail required, the quality of the available information and the requirements for accuracy, flexibility, generality and computational efficiency. These models will range from simple ones with analytical solutions, through more complicated one-dimensional models to fully numerical multi-dimensional models that deal with a wide variety of phenomena, properties and geometries. The attributes of the models required for each application are outlined below, in order to address the question of the extent to which natural analogues can be used to validate models.

2.1 Performance Assessment

The most commonly discussed types of model are those used to assess the water-borne migration of radionuclides from a repository [10]. Such performance assessment models should only include mechanisms which are based on general scientific principles since it is difficult to make convincing safety arguments based on details of the system remaining invariant over thousands to millions of years. They may be deterministic, such as three-dimensional finite-element flow [11] and migration [12] models, or probabilistic such as system variability codes [13-15]. These two approaches clearly have differing requirements for input data, accuracy and flexibility.

In either case they should be used with a combination of pessimistic assumptions, sensitivity and uncertainty analysis [16] in order to investigate a range of possible time evolutions of the system. This is necessary because of the many uncertainties in our knowledge of present and future conditions. Fortunately, there is no requirement to predict the future with any certainty. The primary requirement is to show that the radiological consequences are below limits specified by regulatory authorities [17].

Performance assessment models are essentially tools which allow rational decisions to be taken about whether particular disposal options are acceptably safe. Their usefulness lies in the fact that they can integrate together a variety of different phenomena and their associated data.

2.2 Laboratory Experiments

In a laboratory it is possible to characterise the physical and chemical properties of a rock sample precisely, by using a range of techniques and by repeating experiments to ensure reliable results. Thus it is worthwhile to use detailed models to analyse such experiments. It is possible to validate the model by measuring its parameters using one set of experiments and then predicting the results of some different types of tests. However, it is sobering to realise that even when careful measurements of solute transport are made on a well characterised rock sample, the results are not always readily interpretable [18].

2.3 Field Experiments

The rock through which water and tracers pass during field experiments will inevitably be less well characterised than is the case for laboratory experiments. Thus less detailed models are generally required. The hope is that the analysis of such experiments should throw light on the important mechanisms operating on length scales of metres to tens of metres and time scales of days to years.

To date, even the most carefully performed and analysed field migration experiments have not yielded unambiguous interpretations [19]. For example, in fractured rock the results can be very significantly affected by the presence of poorly characterised channels in the plane of the fracture [20,21].

It is to be hoped that such ambiguities will be sorted out in future by performing a wider range of experiments at the field site, by making a number of associated laboratory measurements and by active participation of modellers. Also, the potential exists to validate models by calibration using one set of data and correctly predicting the results of some independent experiments.

2.4 Natural Analogues

The great advantage of natural geological migration systems is that they provide information relevant to the time and space scales required for repository safety assessments [22-24]. However, the corollary to this is that the hydrogeological conditions are likely to be poorly characterised. For example the initial extent and duration of a geochemical anomaly cannot be known with anything like the certainty of the source term in a field experiment. Also the speed and direction of the water flow may have changed many times.

Given these uncertainties, it is doubtful whether natural analogues can be used to validate models directly. This view is reinforced by the lack of independent data sets to calibrate and validate a model. However, models whose sophistication matches the quality of the available information will be required for analysis and interpretation of the experimental results.

Whilst it is unlikely that natural analogues can be used to validate models directly, they have a number of extremely important indirect uses, some of which are listed below.

1) They can provide general confirmation that under suitable circumstances radionuclides can move through rock masses on a geological time scale.

2) Even though the source and hydrogeological environment are likely to be poorly defined, it should be possible to obtain useful information about the relative migration of different species.

3) They can provide circumstantial evidence that the migration mechanisms included in models are important over relevant time scales.

4) They can give indications about important mechanisms which are not included in the models. A notable example of this is the apparent fixation of iodine in the marine sediments underlying Loch Lomond [25]. Laboratory and field experiments can then be used to provide quantitative information about the identified phenomena.

5) They may provide guidance as to whether long term changes in climatic and hydrogeological conditions can significantly affect migration, in which case they should be considered in repository safety assessments.

3. Safety Case

In order to decide which analogues should be studied, and the level of detail required, it is necessary to have an appreciation of the major aspects of the safety case. This is outlined below for the case of cemented ILW burial in a deep geological formation. It is followed by a discussion of the most critical processes and parameters.

3.1 Overview

The present discussion is limited to the disposal of cemented ILW into deep geological formations [4,5]. For the first few hundred years the radionuclides are expected to remain within the cement matrix material, surrounded by an intact metal canister. After some thousands of years the canister is expected to corrode and the cement matrix and concrete backfill will degrade and no longer provide physical containment. However, this containment period is long enough for short-lived fission products to decay to negligible levels.

Beyond a few thousand years the cementitious near-field environment will provide very significant chemical containment. The high pH and low Eh, provided in part by the corrosion of the metal canisters, severely limits the solubilities of actinides in the pore water of the cement and concrete. Moreover, the repository will be sited in a rock mass with a very low water flow rate. Thus there will be a very small flux of radionuclides into the geosphere.

In the geosphere the nuclides are affected by such processes as advection, dispersion, diffusion and retardation by sorption. The dispersive processes dilute the nuclide concentrations in the plume, while slow advection coupled with retardation processes ensures that some radionuclides decay to negligible levels before reaching the biosphere.

Flow rates of groundwater through deep impermeable rock masses are many orders of magnitude smaller than those occurring on the surface or in near-surface strata. Thus it is inevitable that contaminated water from a deep repository will become diluted in approximate proportion to their relative flow rates.

There are a number of ways in which radioactivity in such surface waters could have an effect on Man. The simplest pathway is by drinking contaminated water. Also, radioactivity could find its way into food, or conceivably give an external dose from land or water.

However, the very slow release from the repository, the dispersion and decay occurring in the rock mass, and the dilution in surface waters combine to reduce doses to negligible levels.

3.2 Critical Processes

For a variety of different waste types and geological scenarios, it appears that the highest dose rates arise from I-129, Tc-99 and Np-237. Thus these nuclides, or chemical analogues for them, should have the highest priority in natural analogue studies.

The processes which have the largest impact on the safety case outlined above can be placed in the following order of importance [5].

1) Low water flow rate through the repository. This limits the rate at which nuclides are released from the repository, and allows decay to take place in the geosphere.
2) Low near-field concentrations due to solubility limits in the high pH, low Eh environment, and sorption onto near-field materials.
3) Large dilution in surface waters.
4) Retardation in the geosphere.
5) Dispersion in the geosphere.

In fact it is possible that in normal evolution scenarios, the regulatory limits could be met by just making use of the first three processes. Thus the only use to be made of the properties of the rock mass would be the low flow rate through the repository, which is mainly determined by the local permeability. This would have the merit of not having to rely on retardation and dispersion in the geosphere, which are difficult to prove. However, since they are almost certain to occur, they would act as an independent barrier in the event that the slow near-field release and large biosphere dilution prove less reliable than expected.

3.3 Short Circuits

In addition to the normal evolution scenarios discussed above, the following processes could provide short circuits to the biosphere for some part of the radionuclide inventory. It is necessary to evaluate the probability of their occurrence and the potentially increased hazard with the aid of all available information, perhaps including natural analogue studies.

1) There could be undetected fast flow paths, such as faults, fracture zones or other inhomogeneities which could speed up the migration from some part of a repository.
2) While actinides are likely to be highly immobile in the near and far field, some fraction could be in a form which would migrate more rapidly. Possible examples of such mobile species are colloids or pseudo-colloids [26].
3) Organic ligands could form stable complexes with actinides and thereby increase their solubility and mobility.
4) Human intrusion into the repository could lead to enhanced dose rates to individuals who come into contact with the contaminated rock.

3.4 Discussion

It would be helpful to have information from natural analogues which relate to any of the five points listed in section 3.2 or the four points listed in section 3.3. However, it is likely that generic natural analogue studies will not be able to contribute to the points concerning groundwater flow, since they tend to be site specific. Also, geochemical environments with a pH approaching that of concrete ($\sim$10-12) are presumably not common and thus natural analogues may not be useful for assessing near-field concentrations. In addition, natural analogues are not relevant to the human intrusion problem.

Thus for the normal evolution scenario it seems that natural analogues will only be useful for the second rank phenomena of retardation and dispersion in the geosphere. In addition they might be able to throw some light on some of the chemical short circuits and put limits on the small fraction of the actinide content which might be in a mobile form. In summary, the major impact of natural analogues on the safety case for deep disposal of ILW is likely to be on the understanding of chemical aspects of radionuclide migration in the geosphere.

4. An Approach to Modelling Analogues

When modelling such analogues, the following questions should be asked:

1) Which phenomena need to be included in the model?
2) Which parameters can be measured in the field or in the laboratory, and how accurately are they known?
3) How much have these parameters varied over the time-scales of the analogue?
4) What were the initial conditions from which the analogue developed, and when did they occur?
5) What is the complexity of mathematical model appropriate to the data available?

The next stage is to fit the model to the data to estimate the unknown parameters and attempt to obtain a consistent picture. This provides a check on the parameters which are known with greatest certainty, and estimates the values of those not previously known. Frequently the number of unknowns which need to be estimated will be rather large. There is likely to be considerable scope for alternative explanations of the same data. This occurs in the analysis of field experiments [19] which are undoubtedly far better characterised than natural analogues.

One area where there could be substantial problems is in the estimation of the initial conditions. Quantifying the initial concentration and extent of the geochemical anomoly may be difficult. There may also be problems estimating when the species were first mobilized and started to migrate, and also the time-scale over which it took place. However, it would be desirable, if possible, to relate these processes to known geomorphological events.

Another problem with the unambiguous interpretation of a natural geochemical analogue is the difficulty in obtaining an accurate picture of the flow field. It is frequently inferred from a limited number of observations and so there is plenty of scope for error. Furthermore, it could have changed its magnitude and direction in an unknown way over the time-scale of interest. So there are considerable advantages with a simple one-dimensional flow field.

The modelling of chemical interactions could also pose some challenging questions. For example, in the analysis of migration through a weathered zone around a uranium ore body at Koongarra in the Alligator

Rivers Region in Australia [27] it seems that it is not adequate to model the solid as a single phase. As a minimum, two phases need to be considered, one which quickly comes into equilibrium with the water, and one with much slower kinetics. It is possible to get reasonable estimates of the distribution coefficients for each phase from laboratory experiments. It is much more difficult to estimate the rate constants for the second phase. Also, it should be pointed out that distribution coefficients can vary quite significantly with the geochemical conditions, such as pH, which may vary in time and space.

Finally, there could be phenomena which are important for the analogue but not for repository calculations. An example is recoil, where the energy from the decay transports the daughter to a different phase.

5. Conclusions

Natural analogues have the potential to provide important qualitative evidence about radionuclide migration over geological time-scales. While they cannot be used to validate performance assessment models directly, they have a number of indirect uses. These include general confirmation that radionuclides can migrate on geological time-scales, some information about migration speeds for various species, and circumstantial evidence about which mechanisms should be included in performance assessment models. Information about whether or not some fraction of the actinide inventory could be in a relatively mobile form, for example due to colloid formtion or organic complexation, would be pertinent to repository safety studies.

It is clear that there are likely to be many uncertainties involved in analysing natural analogues, and that many alternative interpretations are likely to explain the known facts. Thus it is their general rather than specific features which should be emphasised. In view of this natural analogues should be analysed with models whose sophistication is appropriate to the quality of the information available.

Acknowledgement

This work has been commissioned by the Department of the Environment under contract PECD 7/9/230-86/84, as part of its radioactive waste management research programme. The results will be used in the formulation of Government policy, but at this stage they do not necessarily represent Government policy.

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Summary of paper presented at the Natural analogues workshop, Brussels Nov. 5-7 1985

THE NEED FOR GEOLOGIC EVIDENCE FOR RADIONUCLIDE MIGRATION IN THE GEOSPHERE

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There are several processes which have been investigated in the laboratory or in the field, which would be better understood if it was possible to find evidence of them taking place in nature. Some important examples are: radiolysis around spent fuel, stability of spent fuel crystals in a water-saturated environment, matrix diffusion and migration of radionuclides in various rock types. The mentioned processes have been incorporated in several models in existence today. The data used to quantify the mechanisms are usually based on laboratory data and quite often experiments only give indirect evidence of the proposed phenomenon. Many of the phenomena cannot be expected to be possible to study in the laboratory because they are very slow and would not be visible in the time available. Other phenomena take place over such areas that it is impractical to design experiments to study them.

In such cases phenomena which take place or have taken place in nature might supply the information needed.

Radionuclides which are leached from some waste form and are transported with the water in some geologic medium will react with the minerals of the medium in various ways. The time scales involved are very large for many of the processes involved and it has not been possible to validate them in the laboratory.

For repositories in crystalline rock one of the most important retardation mechanisms is what is called matrix diffusion. Radionuclides will be transported with the water flowing in the fractures in the rock. The rock itself is porous, having a connected porosity of about a tenth of a percent to a few percent (Skagius and Neretnieks, 1984). The water in the pores is practically stagnant because the hydraulic conductivity of the rock matrix is very low. The pores form a connected network and have a considerable surface area with which the radionuclides can interact. The pore volume of the matrix is at least of the same order of magnitude as the volume of the mobile water in the fractures.

Radionuclides which move with the water in the fractures will diffuse into the porous matrix of the rock adjacent to the fractures. Those nuclides which sorb on the mineral surfaces will be retarded during their movement into the pore system. Some strongly sorbing species such as americium, plutonium, neptunium, thorium and other actinides can be expected to migrate a few centimeters up to a few tens of centimeters into the matrix during one million years. Other nuclides such as cesium which is less retarded will migrate further (on the order of a meter). Nonretarded species such as iodide and other negatively charged ions may migrate on the order of tens of meters in the same time period.

Matrix diffusion has been observed in the laboratory (Skagius and Neretnieks 1985) as well as in experiments in the field (Birgersson and Neretnieks 1983, Neretnieks et al 1985). There is also some preliminary evidence that the uranium decay series has been disequilibrated to a depth of several centimeters in samples adjacent to an open fracture (Smellie and Rosholt 1984).

Further evidence of matrix diffusion in rock which has occurred under natural conditions in deep lying rock would increase our confidence in this important retardation mechanism.

Radiolysis of the water wetting spent fuel may cause formation of oxygenating substances such as oxygen and hydrogen peroxide. Hydrogen, a reducing agent will also be formed. The hydrogen is probably more mobile and may diffuse away, leaving the oxidizing agents to react with the spent fuel or with the reducing minerals (ferrous iron) in the rock. In an oxidizing environment many of the radionuclides are more soluble than in the naturally prevailing reducing conditions in deep lying crystalline rock.

The oxidizing agents which react with the ferrous iron are neutralized. As the ferrous iron is located within the rock matrix, it must be accessed by diffusion. It is not known to what extent the ferrous iron mineral grains are accessible when they reside in the undisturbed rock matrix. Laboratory experiments are underway to investigate this process and field experiments have been proposed. Visual observations of colour changes in granites and gneisses show that there are sharp changes of colour from grey to brown or reddish in the rock adjacent to a fracture which has been invaded by oxygenated waters. The penetration depths vary. Often the penetration depth is not visible to the naked eye, but sometimes distances of millimeters or even centimeters can be seen. So far little effort has been directed towards quantifying these observations in terms of diffusivities in the matrix or accessibility of the ferrous iron minerals to oxidation. This is somewhat surprising because it probably is one of the most important mechanisms for reducing the naturally intruding waters in the bedrock and maintaining them reducing (Neretnieks 1984). From the point of view of a safety analysis which accounts for the retardation of actinides and technetium it is of utmost importance to know the redox state of the waters. In reducing waters many of the important species are retarded by many orders of magnitude more than in oxidizing waters. If redox disturbances cannot be neutralized by the rock, the retardation capacity of the rock might be severely impaired.

The extent of radiolysis by wetted spent fuel or reprocessed waste is influenced by many factors. Although the processes have been modelled (Christensen and Bjergbakke (1982) and investigated experimentally (Shoesmith et al 1985) there is still need to gather further evidence on long term effects in real environments. A successful analysis of the extent of radiolysis around one of the natural reactors in Oklo was recently published (Curtis and Gancarz 1983). They showed that about 10 % of the uranium in the reactor was mobilized and attributed this to the oxidation due to radiolysis. The same extent of reduction was found to have taken place as evidenced by the surplus of ferrous iron minerals in the reactor core itself. Similar evidence might be looked for around other concentrated bodies of uranium.

The release of radionuclides from the uranium oxide crystals of spent fuel may take place in several ways. Congruent dissolution will release all the constituents in the same proportion. Preferential leaching may take place if some of the species may diffuse faster than others in the crystals. Local recrystallization may take place and release some more soluble species which migrate away while the uranium oxide matrix and some of the actinides form new crystals in the same location where the original crystals were located. Several of the processes involved are very slow (solid diffusion, dissolution) and are difficult to study in the laboratory. Observations of conditions in naturally occurring mineral deposits may give additional information.

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The Use of Natural Analogues
In the Process of Building Confidence
In Performance Assessment Models

Notes of Remarks Made During the Discussion of Modellers' Needs,
Session I of the First Meeting of the
CEC's Natural Analogue Working Group

Brussels, Belgium
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The use of natural analogues in the process of building confidence in performance assessment models is difficult. At the October 1984 meeting on natural analogues in Chicago, Illinois, which was sponsored jointly by the U.S. Department of Energy (U.S. DOE) and the Swedish Nuclear Power Inspectorate, Dr. Norman Eisenberg of the U.S. DOE presented a list of these difficulties. In this list were included the lack of control that investigators have over the conditions under which these natural experiments took place, confounded by the likelihood that the events and conditions that produced the natural analogue may not be known. The first difficulty has to do with applying the knowledge gained from a natural analogue study to an appropriate problem, while the second difficulty addresses the uncertainty inherent in natural analogue studies that deal with processes that have taken place over geologic time. Other difficulties are relatable to natural analogues generally being complex and data poor, making their modelling complex and diminishing the prospects of using natural analogue study results in validating models.

Nevertheless, there needs to be an effort made that explores the potential usefulness of natural analogues, and this effort should include the following aspects:

- Complex, heterogeneous natural analogues of potential value need to be evaluated to see if there are simple processes identifiable within their complexity for which credible conceptual and quantitative descriptions may be obtainable.

- The transport behavior of stable elements in natural systems may be relevant to nuclear waste isolation systems in terms of providing confidence in ground water transport modelling.

- The aqueous chemistry of some stable elements or their compounds may aid the definition of the expected long term aqueous chemical behavior of analogous nuclear waste elements or compounds.

- The modeling of natural disruptive events, especially in terms of their geohydrological consequences, may help to establish the modelling of future, postulated event consequences for geologic repositories.

In order for a natural analogue study to be useful, in the process of building confidence in a model of a particular process, it must:

- Produce a credible conceptual description of a well defined process that can be modelled, and

- Provide quantitative information that can be used to determine the adequacy of the modelling effort.

It is difficult to separate the quantitative information that will be collected from the natural analogue investigation for the purpose of process model creation or calibration from the quantitative information that will be required to validate the same model. Experimental design thus becomes crucial to the confidence building effort.

COMMISSION OF THE EUROPEAN COMMUNITIRES

NATURAL ANALOG WORKING GROUP

BRUXELLES, NOVEMBER 5-7, 85

A Modeller's viewpoint on the possible use of analogs for flow and transport

1) Understanding of flow and transport systems.

The general principle of the modelling of flow and transport systems is to measure in situ the major rock properties (e.g. hydraulic conductivity, fracture proprerties...) and to estimate "average' behaviour. However, are our present techniques able to recognize possible "short circuits" ? This concern the connectivity of fractures, the channelling, the possible heterogeneities in sediments... all possible mechanism of dispersion in natural systems, leading to early arrival of poorly diluted solutions. Role of analogs : direct observation of short circuits, in a given site, and attempts to show that they could have been detected with proposed surveying technique.

2) Change with time of flow systems .

Role of the thermal phase of the waste on the modification of the flow field and rock properties; role of minor tectonic activity (e.g. isostatic rebound, residual stress field...) on the modification of the fracture system; clogging and sealing of fractures (and its influence on matrix diffusion, on channelling...)
Role of analog : thermal analogs (e.g. dykes...); evolution of natural flow systems leaving fossil evidences of changes.

3) Modelling speciation of elements and subsequent interaction with rock.

The current geochemical equilibrium codes need to be validated in intially very simple flow and chemistry problems; are the data bases and assumptions validated by field obsevations ? Role of kinetics ? Is there a fraction of elements which does not behave as predicted by speciation and sorption studies (e.g. evidence of colloidal transport, of complexation, of biological mechanisms modifying the predicted transport rates...). Are the field or laboratory measurements of geochemical properties coherent with observed transport rates ? As mass balance will be very difficult to calculate in natural anlogs, because of poor knowledge of the source term, the evidence that some elements have been retained is not a proof that some part of the same element has not migrated under a different form.
Role of analogs : validate speciation and sorption studies; research of other possible form of migration than predicted.

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APPENDIX 2

Geochemical Model Needs

1. Geochemical model needs (B. SKYTTE-JENSEN).

2. The role of natural analogues in modelling for field transport of radionuclides (P. AIREY).

3. Geochemical analogues of high-level radioactive waste repositories (P. AIREY and M. IVANOVICH).

4. Applications of analogues in near-field geochemistry (I. Mc KINLEY).

5. Special needs of modellers working in the field of geologic disposal in rock salt (P. GLASBERGEN).

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Geochemical Model Needs

Each day hundreds of chromatographic separations are made throughout the world proving that the one-dimensional migration equation is fundamentally correct and therefore need no additional validation.

To obtain the almost perfect gaussian elution curves, which theory predicts, a great effort has been done to eliminate disturbing influences. Packing materials have been made with minute monodisperse particles where adsorption occurs only on the surface, thereby eliminating the effect of diffusion into deep pores. The packing of columns is done carefully to avoid uneven flow due to channel formation etc. A careless experimenter neglecting these factors would obtain distorted elution curves, but even a skilled experimenter would get the same result if he/she is using plain soil as packing material in his columns.

It is obvious that field experiments will suffer from the above mentioned channelling and diffusion effect which gives rise to large skew dispersions, but other factors contribute to the creation of abnormal dispersion phenomena and slow adsorption kinetics or saturation effects may be equally important in this respect (Fig. 1). The deconvolution of elution curves into isolated phenomena is hardly possible even with laboratory data. Improved insight might be obtained by i.e. the determination of concentration distributions along the column or by systematical variation of elution conditions, but this is seldom done.

Irregularities in groundwater flow, slow adsorption kinetics, saturation phenomena etc. will all give rise to dilution effects which may be classified under the heading: dispersion.

It will probably never be possible to describe all dispersion phenomena occurring in nature adequately, but it may well be possible to identify critical path-ways like cracks or other highly permeable structures and concentrate field investigations on the consequences of their existence on the mobility of elements. Natural analogues may play an important role in such investigations.

Coming to the chemical reactions retarding or enhancing the migration of solutes through a geological formation we enter the field of geochemical modelling.

There is no doubt that the principles governing speciation calculations are fundamentally correct, but unfortunately the thermodynamic data which are needed for such calculations are not always good enough and furthermore some are still missing. For those working in the field it has become more and more clear that even minor amounts of organic acids in ground water may play a decisive role in its speciation chemistry. The often quoted supersaturation of calcite, $CaCO_3$, found for several natural waters is hardly believable for an experimental chemist and may easily be explained as due to the masking effect of complex-formation between Ca^{2+} and an organic component.

It is also realised that under the near neutral to slightly basic conditions found in ground waters most cations may dominantly be found as mixed hydroxy complexes with carbonate or organic acids. The thermodynamic data for these complexes are scarce wherefore geochemical speciation calculations on ground waters may deviate from actual composition because the formation of these complexes is neglected. Fortunately, new data are cropping up and there exists an obvious solution to the problem - namely the hard work of identifying and characterising these complexes with methods already available.

Speciation calculations are mathematically quite simple and the different computer programs doing this task, WATEQ, EQ-3, PHREQUE, WHATIF-AQ etc. differ mainly with regard to flexibility, userfriendliness, databases etc. and not in the fundamental approaches.

The assumption of thermodynamic equilibrium in the aqueous phase, which is inherited in all these programs is reasonable for solutions, although some disproportionation reactions of trace components may be so slow because of dilution effects, that they may never be in equilibrium.

The validity of the assumption of thermodynamic equilibrium in multiphase systems involving complicated silicates as solid phases is more dubious. For simple systems with calcite or similar simple crystalline components as solid phases the assumption of equilibrium may be acceptable, but realising the experimental difficulties encountered in synthesising complicated silicates one may easily imagine that in nature metastable phases grow up and disappear before the thermodynamically stable minerals are formed.

In the later years fundamental studies on dissolution mechanisms for different minerals are showing up in literature, but the difficulties of establishing a set of reliable rate-constants for use in geochemical calculations seem unsurmountable. The heterogeneous structure of geological formations, the effect of impurities on rate-constants, the particle-size distribution of components, etc. will effectively block the progress towards a geochemical modelling system able to handle all envisaged cases. At present the most fruitful approach is the mass-transfer or path-way calculations in which rudimentary rate variations may be built into the system thereby simulating supersaturation phenomena etc.

One may easily calculate the equilibrium assemblage of weathering products which should arise when water reacts with a mineral mixture, given time to establish the equilibrium. The calculation will naturally only be "true" insofar the thermodynamic data available are internally consistent and complete. In Figs. 2 and 3 is shown such a calculation made on Strath Ossian monzogranite and a mixture of microcline, albite and anorthite with a surplus of water. The calculations neglect the formation of solid solutions including ion-exchange on clay minerals as well as components in solution.

In Figs. 2, 3, 4 and 5 are shown results of path-way calculations for the weathering reactions for the same mixture assuming that the dissolution rates for microcline, albite and anorthite are 1:1:1 or 1:3:10. For Ossian monzogranite the dissolution rate has been assumed proportional to the mineral composition of the granite.

In this calculation has been assumed that equilibrium is established between the secondary minerals and solution at any point during the progress of reaction. An interesting observation on the diagrams for total solubility is that after the precipitation of 5-6 weathering components, the system seems to exert a strong buffering effect keeping the water composition approximately constant rather close to compositions found in granitic ground waters (Fig. 5). The composition of actual ground waters could therefore be determined by equilibria with a set of intermediary weathering products among which the clay minerals seem to be an important group. In the present calculations - and in all other published in literature - the effect of the formation of solid solutions, including ion-exchange, has not been taken correctly into account. It can be shown, that if this is done, the buffering effect will be even more pronounced and the predictability of groundwater compositions seem within the reach of theoretical geochemical calculations.

The formation of solid solutions is rather simple theoretically, although many of the relevant parameters may not be known. Experimentally the experience may range from the ideal case with equilibrium throughout the whole system as encountered in ion-exchange to coprecipitation reactions following the Doerner-Hoskins law which assumed only surface equilibria, resulting in the build-up of concentration gradients in the solids. Each of these limiting cases may well be handled in path-way analyses as may be the simultaneous formation of a clay mineral and the ion-exchange processes on its surface.

Actual clay minerals are often described as solid solutions of several ideal end-member minerals into each other to account for their often very complicated analyses. If this hypothesis is true, and it probably is, it has consequences for some types of geochemical calculations. One important is that it will be impossible to describe the stability of a mixed clay by a solubility constant as has often been done, because solid solutions will never, except for improbable cases, be in equilibrium with their own solution. Equilibrium can only be established by transformation of the solid phase or its surface layers and the published solubility constants do therefore refer to unidentified species.

However, the formation of solid solutions, multielement ion-exchange and the mechanism of adsorption of trace elements onto minerals are phenomena which are becoming better understood in the present years and this new insight will no doubt soon enter into geochemical calculations.

The persons present today are probably all working in the field of radwaste disposal and concerned with its probable consequences. For psychological reasons one may wish to demonstrate the technical ability of making a disposal site and the safe handling of HLW-containers with proven technique. However, the long term behaviour of a storage facility is hard to demonstrate and it is here the study of natural analogues are important. From a primitive point of view only studies of actual waste seem relevant, but the more the fundamental processes which enhance or retard migration are understood, the analogues begin to comprise many other elements like uranium, chromium, copper, iron, tin etc. with well-known chemistries in solution. The earth sciences may identify zones enriched in some element by sedimentation or by other mechanisms and careful investigations of concentration distributions of the enriched element in the surroundings may demonstrate possible migration mechanisms and advanced geochemistry may pay back by identifying possible chemical mechanisms, which may play a role when radwaste is undergoing leaching and migration.

As I see it, the main difficulties in predicting migration phenomena lie in:

a) Insufficient knowledge of dispersion processes. Identification of critical path-ways and a study of the consequences of their existence seem to be a realistic alternative to fundamental studies on dispersion. A study of natural analogues no doubt will contribute significantly to a clarification of the problems.

b) Insufficient knowledge of the effects of organics on the migration.

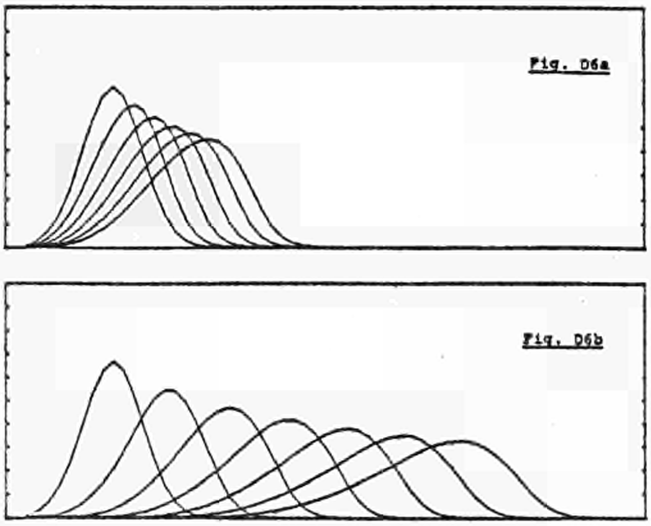
c) Lack of adequate thermodynamic data for elements under near neutral conditions. The characterisation of mixed hydroxy-complexes.

d) Insufficient knowledge of which factors govern the adsorption processes.

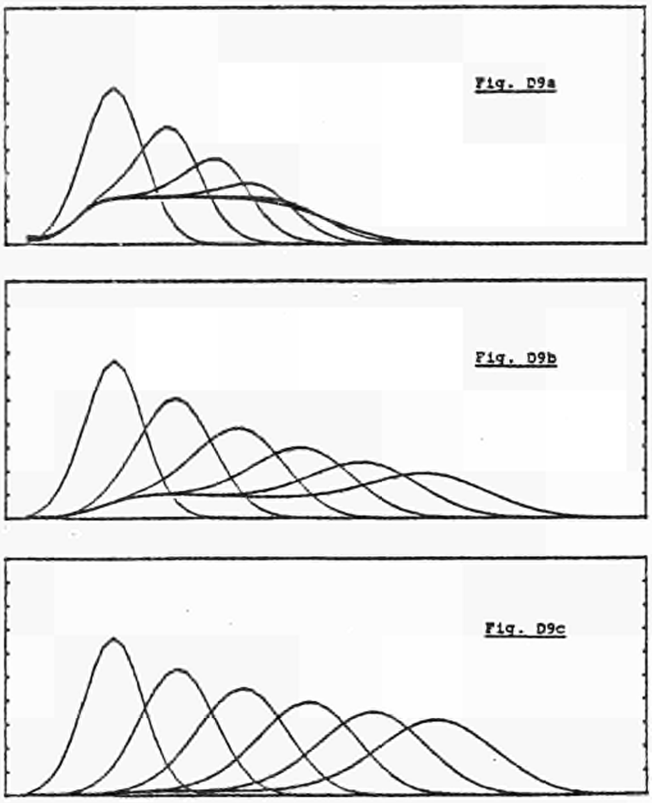
Although present day geochemistry may still be improved by investigations concerning fundamental chemical mechanisms, it seems as if the possibilities of geochemical calculations in its present form will soon have reached its credibility limits. We can get a computer to calculate fast and with high precision the interaction of thousands of equilibrium systems, but honestly we dare not pay too much attention to the final results because the assumption of equilibrium throughout the system may be false when applied to natural systems. I believe that earth scientists, to whom the contours of the earth seem to be delineated with brushes and not with pencils, share my doubt on the validity of the "advanced" geochemical calculations presented in reports today.

In the coming years it seems to be possible to build a bridge between the experience of the field workers and the laboratory investigators. The advance of new computers with fast access to a huge memory, with possibilities to handle exact as well as vague statements offer the possibility to combine the knowledge and experience of geologists and chemists in a united geochemical program which eventually may develop into a true learning system, built into its database the insight of late, existing and coming geochemists.

Fig. 1



Figs. D6a and D6b. Numerical calculation of concentration distribution for the migration of an initially gaussian distribution. Equilibrium adsorption according to a Langmuir adsorption isotherm is assumed. In Fig. a, the exchange capacity is four times the initial maximum concentration, and in Fig. b, four times smaller.
Dimensions arbitrary.



Figs. D9a, D9b, D9c. Calculated concentration distribution for migration of a solute in excess of the sorption capacity. From a to c, the rate of sorption-desorption decreases. The same equilibrium conditions will be found in each example.
Dimensions arbitrary.

Fig. 2

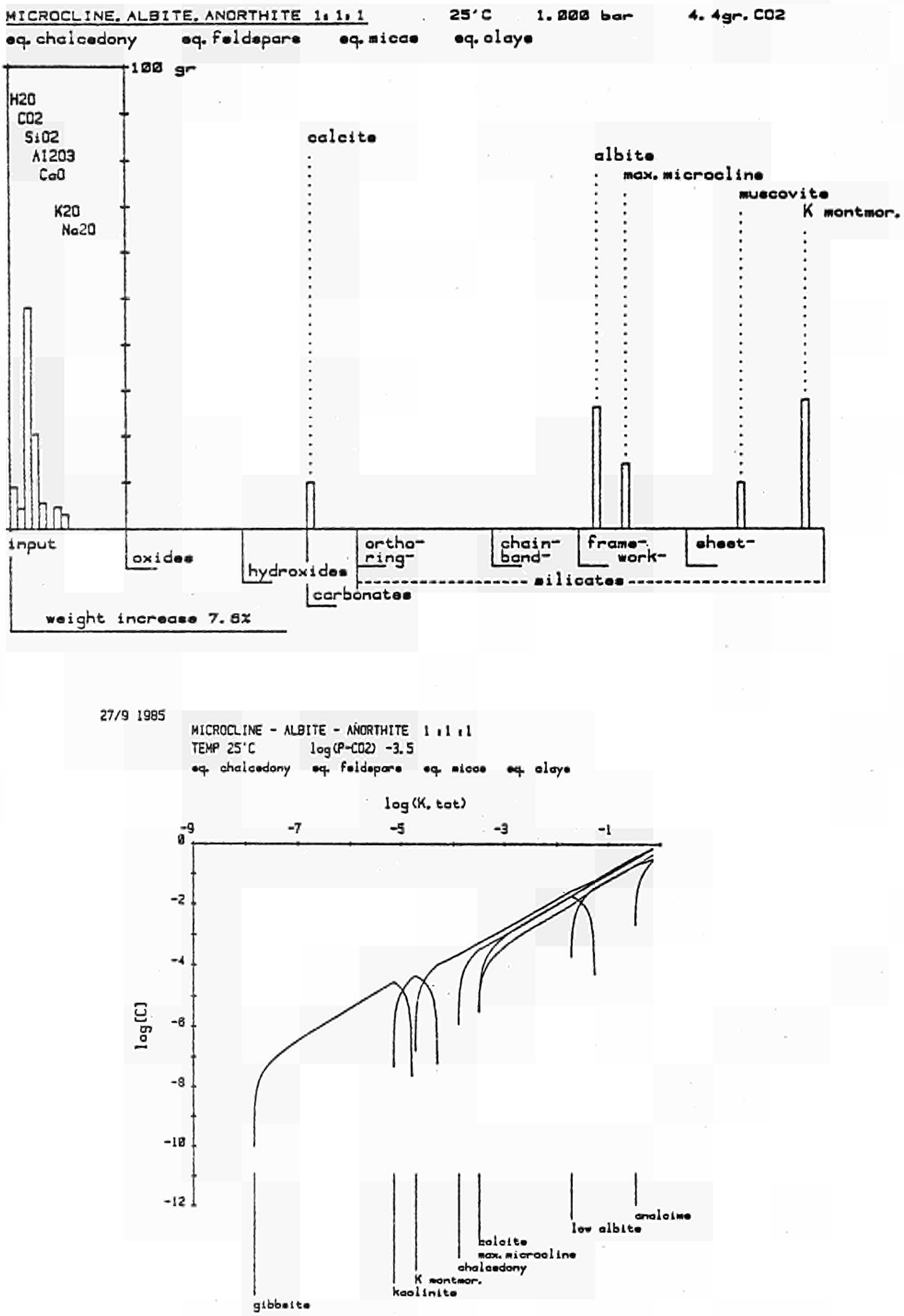

MICROCLINE, ALBITE, ANORTHITE 1: 1: 1
25'C
1.000 bar
4.4gr. CO2
eq. chalcedony
eq. feldspars
eq. micas
eq. clays
100 gr
H2O
CO2
SiO2
Al2O3
CaO
K2O
Na2O
calcite
albite
max. microcline
muscovite
K montmor.
input
oxides
hydroxides
carbonates
ortho-
ring-
chain-
band-
frame-
work-
sheet-
silicates
weight increase 7.8%
27/9 1985
MICROCLINE - ALBITE - ANORTHITE 1 : 1 : 1
TEMP 25'C
log(P-CO2) -3.5
eq. chalcedony
eq. feldspars
eq. micas
eq. clays
log(K, tot)
-9
-7
-5
-3
-1
0
-2
-4
-6
-8
-10
-12
log[C]
analcime
low albite
calcite
max. microcline
chalcedony
K montmor.
kaolinite
gibbsite

Fig. 3

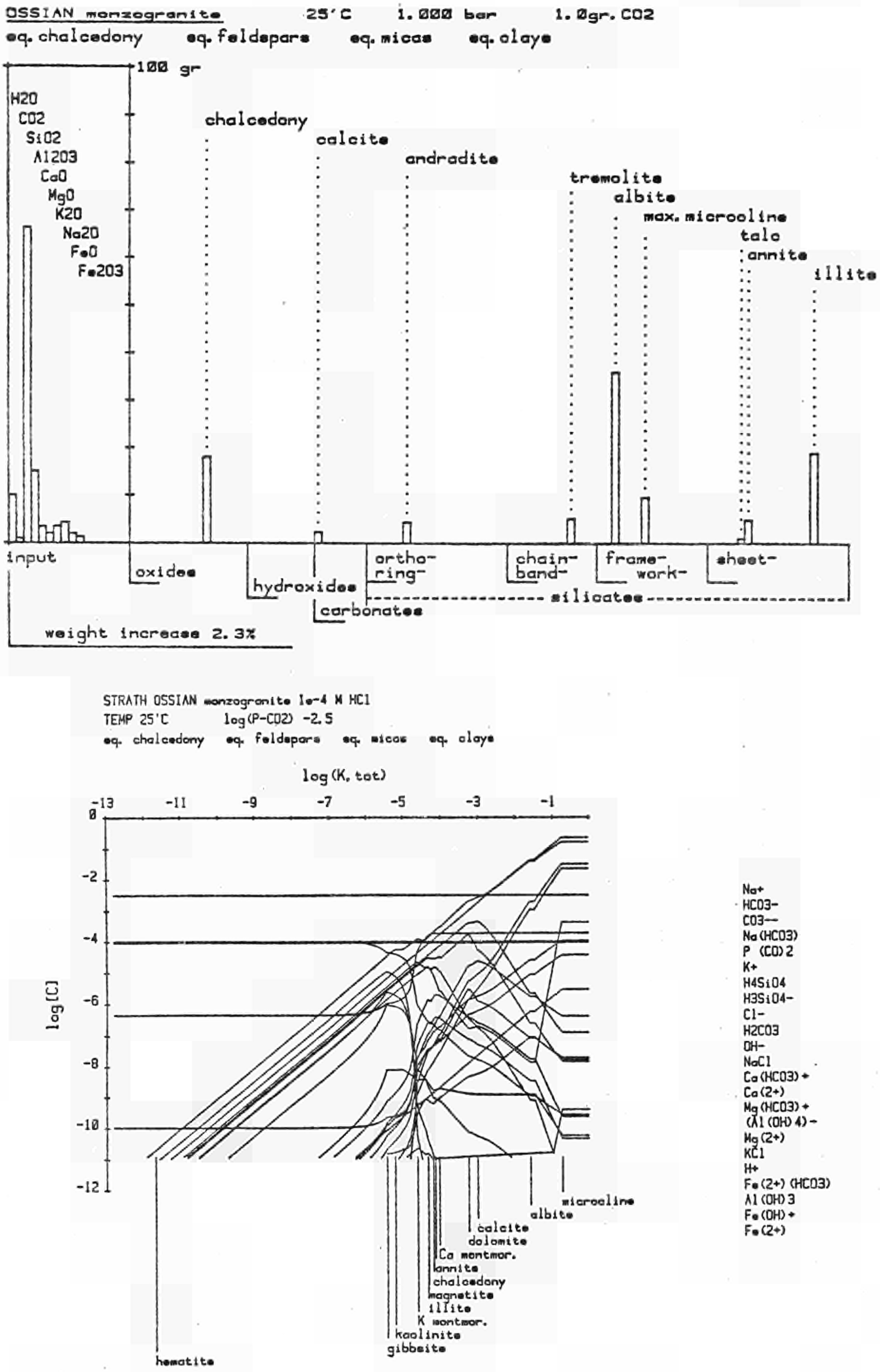
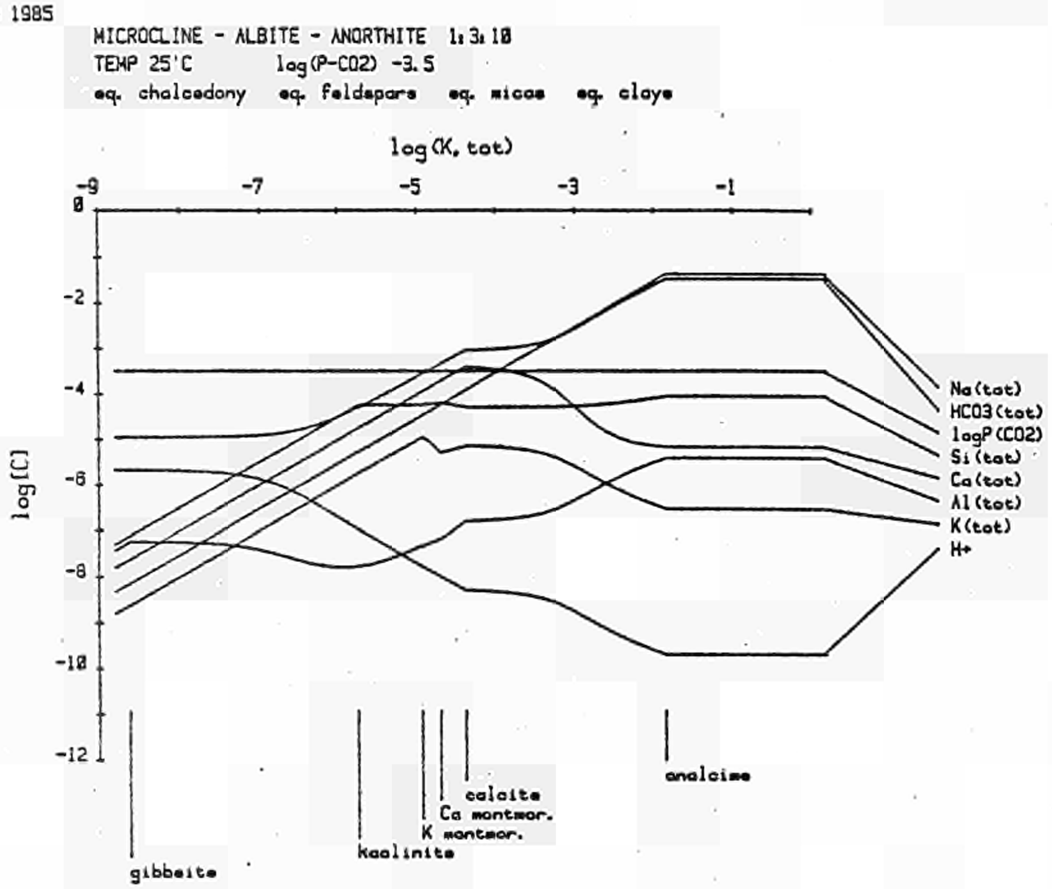
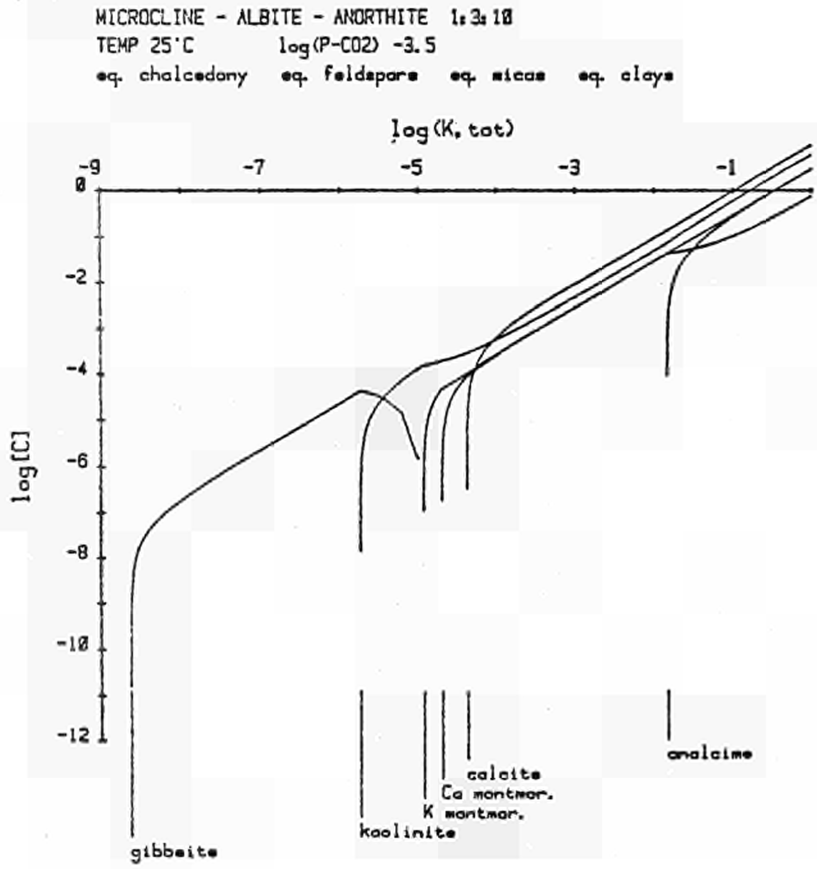

OSSIAN monzogranite 25'C 1.000 bar 1.0gr. CO2
eq. chalcedony eq. feldspars eq. micas eq. clays
100 gr
H20
CO2
SiO2
Al203
CaO
MgO
K2O
Na2O
FeO
Fe2O3
chalcedony
calcite
andradite
tremolite
albite
max. microcline
talc
annite
illite
input
oxides
hydroxides
carbonates
ortho-ring-
chain-band-
frame-work-
sheet-
silicates
weight increase 2.3%
STRATH OSSIAN monzogranite 1e-4 M HCl
TEMP 25'C log(P-CO2) -2.5
eq. chalcedony eq. feldspars eq. micas eq. clays
log(K, tot)
-13
-11
-9
-7
-5
-3
-1
0
-2
-4
-6
-8
-10
-12
log [C]
hematite
gibbsite
kaolinite
K montmor.
illite
magnetite
chalcedony
annite
Ca montmor.
dolomite
calcite
albite
microcline
Na+
HCO3-
CO3--
Na(HCO3)
P (CO)2
K+
H4SiO4
H3SiO4-
Cl-
H2CO3
OH-
NaCl
Ca(HCO3)+
Ca(2+)
Mg(HCO3)+
Al(OH)4)-
Mg(2+)
KCl
H+
Fe(2+)(HCO3)
Al(OH)3
Fe(OH)+
Fe(2+)

Fig. 4

27/9 1985

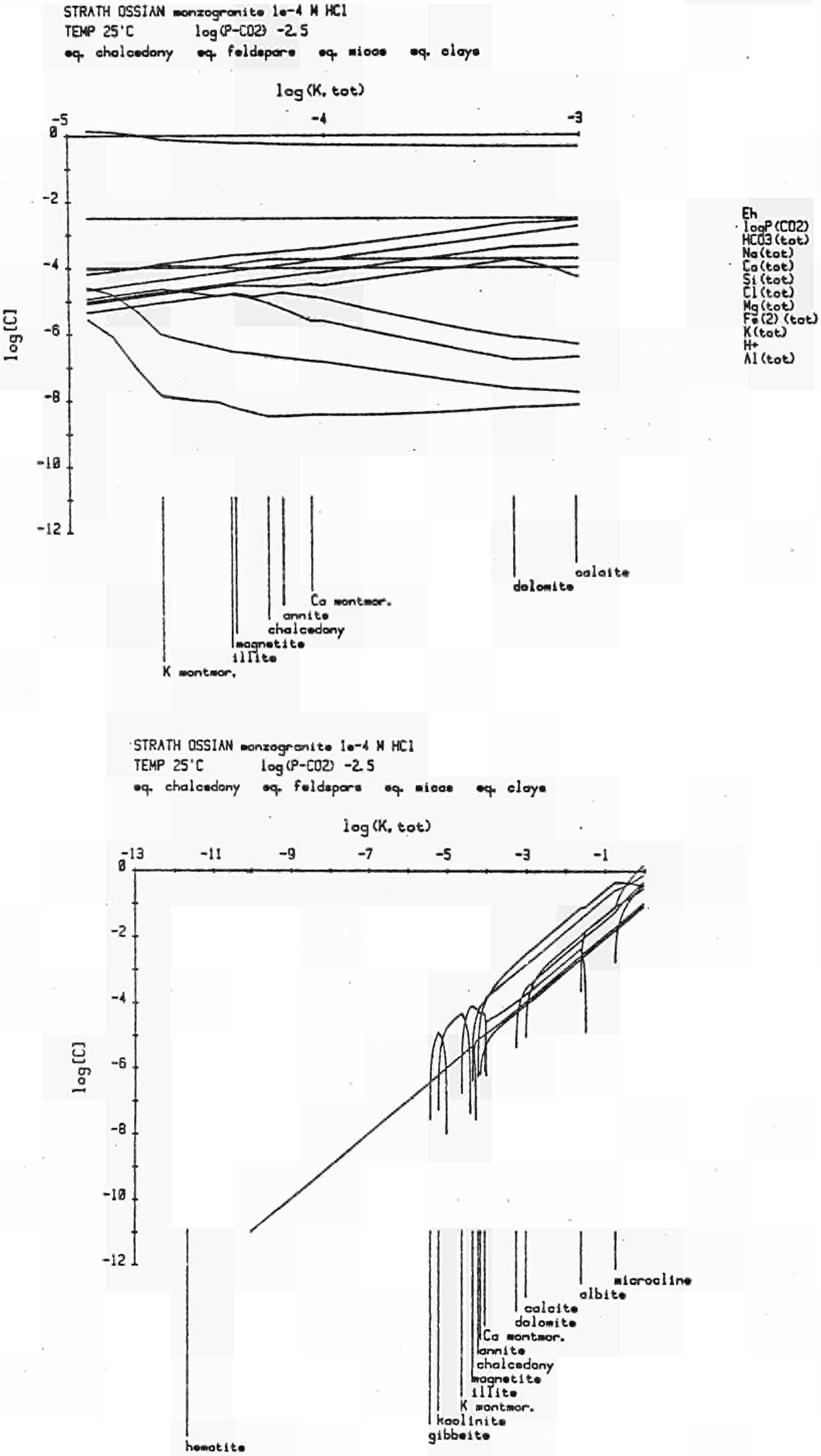


MICROCLINE - ALBITE - ANORTHITE 1:3:10
TEMP 25'C log(P-CO2) -3.5
eq. chalcedony eq. feldspars eq. micas eq. clays



MICROCLINE - ALBITE - ANORTHITE 1:3:10
TEMP 25'C log(P-CO2) -3.5
eq. chalcedony eq. feldspars eq. micas eq. clays

Fig. 5


STRATH OSSIAN monzogranite 1e-4 M HCl
TEMP 25'C log(P-CO2) -2.5
eq. chalcedony eq. feldspars eq. micas eq. clays
log(K, tot)
-5
-4
-3
0
-2
-4
-6
-8
-10
-12
log[C]
Eh
logP(CO2)
HCO3(tot)
Na(tot)
Ca(tot)
Si(tot)
Cl(tot)
Mg(tot)
Fe(2)(tot)
K(tot)
H+
Al(tot)
calcite
dolomite
Ca montmor.
annite
chalcedony
magnetite
illite
K montmor.
STRATH OSSIAN monzogranite 1e-4 M HCl
TEMP 25'C log(P-CO2) -2.5
eq. chalcedony eq. feldspars eq. micas eq. clays
log(K, tot)
-13
-11
-9
-7
-5
-3
-1
0
-2
-4
-6
-8
-10
-12
log[C]
microcline
albite
calcite
dolomite
Ca montmor.
annite
chalcedony
magnetite
illite
K montmor.
kaolinite
gibbsite
hematite

NATURAL ANALOGUE WORKING GROUP MEETING

Brussels, 5-7 November 1985

The Role of Natural Analogues in Modelling for Field Transport of Radionuclides

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Aim: The aim of modelling is to provide a basis for demonstrating compliance with regulations limiting the total dose commitment to future populations.

Approach to modelling: Two approaches are possible -

(i) to use transport codes to seek as accurate a description of radionuclide transport as possible,

(ii) to use mathematical and other arguments to define upper bounds of the migration rate of designated radionuclides (particularly transuranics and fission products).

In practice, a combination of both approaches is likely.

Limitations to the predictive capability of models; the role of natural analogues: The precision with which codes can predict the long-term radionuclide transport is limited in at least three ways -

- paucity of data particularly related to the host rock/solute interation for designated radionuclides under repository conditions,
- lack of understanding of the time dependence of model parameters,
- limitations to the validity of the generating equations (eg effects of colloidal transport).

Comments on how analogues can address these problems are made in the attached table. Modellers may react to the findings

either by modifying generating equations in response, for instance, to evidence for time dependent sorption coefficients,

or by using the natural analogue data to place upper bounds on parameters in the conventional generating equations.

Examples will be considered in the oral presentation.

ROLE OF NATURAL ANALOGUES IN REDUCING UNCERTAINTIES IN THE LONG-TERM PREDICTION OF FAR FIELD RADIONUCLIDE TRANSPORT

Source of Uncertainty	Analogue	Comments
Groundwater flow field; time dependence	Proposed repository site* - groundwater hydrology	Compare flow field calculated from a hydraulic model with that from systematic groundwater dating (eg ^{14}C) which reflects cumulative effect of transport over long time scales.
Sorption coefficients; time dependence	Uranium ore body and proposed repository site - groundwater/host rock interface	Procedure for assessing effect of residence time on Ra sorption coefficients demonstrated at Koongarra; may be applied widely.
Sorption coefficients; redistribution between mineral phases (α-recoil effects)	Uranium ore body and proposed repository site	By modelling the distribution of uranium series elements between selected iron and clay minerals, the effect of α-recoil may be calculated. The procedures are being developed on weathered ore samples, but may be widely applied.
Retardation factors; comparison of field estimates with those from sorption coefficients	Koongarra ore body - secondary mineralisation	Relative ^{234}U, ^{238}U and ^{230}Th retardation factors obtained from modelling evolution of uranium series fractionation at Koongarra secondary mineralisation.
Retardation factors; effect of colloid transport on estimates	Koongarra ore body - secondary mineralisation	Establish which models of the colloidal transport of thorium are consistent with the observed uranium series disequilibria in groundwater.
Retardation factors; validity of chemical analogues	Koongarra ore body	Direct measurements of ^{239}Pu in groundwater and drill core are being attempted.

* Repository site prior to emplacement of an HLW repository is considered to be an analogue of the area after closure, when considering radionuclide transport.

GEOCHEMICAL ANALOGUES OF HIGH LEVEL RADIOACTIVE WASTE REPOSITORIES

by

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ABSTRACT

In this review, an attempt has been made to broaden and systematise the concept of the geochemical analogue approach to the prediction over long time intervals of the behaviour of radionuclides leached from high level radioactive waste repositories. An analogue exhibits two essential properties, a spatial discontinuity across which the migration of indicator elements may be measured, and a basis for establishing a time-frame. Selected examples of published analogues are discussed. Such research is of value in assessing the siting of repositories for the following reasons:

(i) Analogues may determine the limits of migration of indicator elements under conditions which are frequently more rigorous than those met under operation conditions.

(ii) They can be used to establish a scientific basis for the long-term prediction of radionuclide migration rates.

(iii) The findings may be transferred from the site of the geochemical analogue to that of the waste repository.

(iv) The locality of the proposed repository site may be developed as an analogue of the distant field radionuclide transport regime under operating conditions.

1. INTRODUCTION

The engineering design and geological location of high level radioactive waste (HLRW) repositories are chosen to ensure that the total dose commitment to the population is less than a prescribed maximum. In the United States, these standards are set by the Environmental Protection Agency (EPA)(1). Responsibility for licensing rests with the Nuclear Regulatory Commission (NRC) which has defined a rule (10CFR60) for the disposal of high level wastes in geologic repositories(2). The criteria under which the NRC rule is consistent with the EPA requirements have recently been reviewed(3).

The EPA is proposing quantitative requirements for the cumulative release of waste to the accessible environment for 10 000 years after disposal. The standards are defined in terms of the maximum probability that releases for a range of radionuclides exceed tabulated values. These and other studies(4,5,6) have led to a short list of critical radionuclides which include amongst others ^{237}Np, ^{239}Pu, ^{241}Am, ^{226}Ra and ^{99}Tc. It is appreciated that guarantees of the future performance of a system cannot be had in the ordinary sense of the word. Instead EPA requires that there is a "reasonable expectation based on performance assessment" that compliance with regulations will be met.

Deep burial of HLRW in geological formations relies on the multiple barrier concept. The process of performance assessment involves the quantitative evaluation of component and system behaviour to support the development of a HLRW repository. A number of analyses indicate that the most important contribution to long-term environmental protection comes from the geological characteristics of the repository site(7,8,9). It follows that considerable effort must be expended in reducing uncertainties in the long-term prediction of the rate of migration of radionuclides through the far field to the accessible environment.

The migration rate of radionuclides depends on the groundwater velocity and the retardation factor which in turn depend on the distribution coefficients and the effective porosity. In principle, distribution coefficients can be measured in the laboratory. However, doubts may be expressed on the extent to which laboratory data reflect the natural environment for the following reasons:

(i) Distribution coefficients are dependent on such factors as Eh, pH, groundwater chemistry and the properties of accessible minerals which cannot be readily reproduced.

(ii) Groundwater colloids and organic complexes may play a significant role in the transport of some radionuclides.

(iii) Distribution coefficients may vary with time, due to the effects of diffusion and the slow alteration of accessible surfaces.

(iv) Under many conditions, the concentration of radionuclides in groundwater may be determined by the solubility product and not the adsorption properties.

A useful approach to the problem of long-term prediction is a study of the cumulative effects of transport over geological time of systems which are acceptable analogues of HLRW repositories. Although no single system can adequately reflect all the relevant properties down-gradient of a repository, well chosen analogues have features which can contribute to the basis of long-term prediction. The best known examples are the collection of fossil natural reactors at Oklo, Gabon. However, a number of other systems will also be discussed, including igneous intrusives, uranium ore bodies and Morro do Ferro thorium mineralization.

The aims of the paper are as follows:

(i) To define the essential characterisics of a geochemical analogue and to discuss the role of such systems in studying the scientific basis for the long-term prediction of radionuclide transport.

(ii) To discuss examples of the analogue approach

and

(iii) to assess methods of relating findings from the geochemical analogue to the proposed repository site.

2. THE GEOCHEMICAL ANALOGUE

A geochemical analogue may be defined as a geological entity, exhibiting -

(i) a spatial discontinuity - a well-defined boundary across which the transport of indicator elements may be measured;

(ii) a temporal discontinuity - a well-defined start to the process, or, in the case of a system which has reached a steady state, a basis by which a time frame may be established.

Spatial discontinuities clearly include a range of igneous intrusives and regions of mineral, particularly uranium accumulation. However, aquifer/aquiclude boundaries, the fracture walls in crystalline rocks and geothermal systems are also included. Some artificial systems such as tailings dams and low level burial sites(10) and cavities formed by underground nuclear explosions are also useful(11).

No geochemical analogue can model all aspects of radionuclide migration. The modern tendency is to select analogues of specific components or sub-systems of the HLRW repository. A comprehensive listing has recently been presented(9). It is instructive to classify analogues according to function.

Class 1 Analogues may be used to elucidate processes or assess mechanisms which affect retardation factors over long periods. Processes include:

- effect of radiolysis on the redox potential and hence the adsorption coefficient of multivalent nuclides
- effect of α-recoil on adsorption coefficients
- effect of accessible minerals, particularly iron minerals, on retardation.

In addition, analogues may be used to assess the validity of the matrix diffusion mechanism of radionuclide migration through crystalline rocks.

Class 2 Analogues may be used to define the limits of migration of indicator elements under conditions which are frequently more rigorous than those which would be met under operating conditions. The Oklo natural reactor, and many of the intrusives such as the Eldora Bryan stock and the Alamosa River monzonite which are associated with the circulation of hydrothermal fluids fall into this category.

Class 3 Natural analogues can in principle be used to examine the validity of proposed chemical analogues of ultra-low levels of transuranics and fission products. No work along this line has been reported. However, the level of plutonium in uranium ore bodies can be measured with modern mass spectrometers. It should therefore be possible to assess the value of Nd as an analogue of Pu^{3+}.

With passage of time, new requirements for analogues will evolve. A current interest is in their possible use for verifying computer transport codes. This application will be discussed in detail below.

3. EXAMPLES OF GEOCHEMICAL ANALOGUES

3.1 Oklo Uranium Deposits

Perhaps the best known example of a natural analogue which fits well the above definition is that of the Oklo uranium deposit in Gabon, Africa. About 2 x 10^9y ago thick lenses of uraninite were formed sufficiently compact and with the correct mixture of neutron moderating elements to start fission chain reactions. The reactors operated for about 2 x 10^5y leaving behind radionuclides with relative abundances not normally found in uranium ore deposits. Several features made the study of these fossil reactors significant. The nuclide migration or containment occurred over geological time (10^9y); the radionuclides present in the areas of fossil reactors were identical to those of modern reactor waste products; and average thermal loading within the reactor zones during operation was estimated to be several times greater than the thermal loadings proposed for high level radioactive waste repositories. The suggested studies(12) were expected to indicate which elements migrated, when the migrations occurred and what migration mechanisms were responsible. In addition, many of the reactor products being radioactive, including uranium itself provided radioactive clock facilities which have been used to determine rate of element migration. Detailed studies carried out by the team at Los Alamos National Laboratory(13,14) have revealed that radionuclide products of the natural reactor operation were contained in crystalline uraninite which remained unaltered mechanically for some 2×10^9y since the period of sustained nuclear reactions. Despite this stability, selected radionuclides have been released but the quantities removed were limited by the rate of diffusion from the crystalline host. This rate was dramatically accelerated by high temperatures and/or large radiation doses associated with the nuclear reactions. In this limited sense failure to contain occurred on a time-scale of less than 10^6y.

Thus, for example, after release from their host phase ruthenium and ^{99}Tc and neodynium were removed from the reactor zones and redistributed into the surrounding rocks. However, the retention properties of these sediments were quite effective as apparent rate of movement of these elements was of the order of 10^{-5}my^{-1} in the presence of fluids convecting at a much faster rate of 5 my^{-1}.

As a further example, U/Pb studies of Oklo uranium ore samples both from within and without the reactor zones have shown depletion in radiogenic lead when compared to amounts calculated from uranium decay(15,16). The average loss of about 50% was interpreted by Gancarz(17) to indicate a primary age of 2.05×10^9y with Pb loss from uraninite by continuous volume diffusion. Further, lead isotope data reported by Gancarz and Curtis(18) have identified lead isotope migration paths and have demonstrated the potential of the Oklo uranium deposit and natural fission reactors as a long time-scale analogue for the radioactive waste repositories.

3.2 Geological Intrusives

3.2.1 Eldora Bryan stock intrusive into the Idaho Springs Formation

The Bryan-Eldora stock(19) is a composite body of quartz monzonite, syenodiorite and granodiorite which intruded the meta-volcanic and meta-sedimentary rocks of the Idaho Springs Formation about 58 My BP (million years before present)(20). The temperature of the intruding magma was about 780°C. The magma, rich in volatiles could have had pronounced effects in producing hydrothermal fluids which might have penetrated the contact zone over the cooling period which is estimated to be between 10^4 and 10^6y. The heat from the intrusive was sufficient to affect mineral isotopic systematics up to 2000m from the contact. However, petrographic studies reveal that only in the 1 to 3m contact zone is there any evidence of new generation of minerals due to the infiltration of magma derived fluids or other possible hydrothermal fluids.

Systematic measurements of Na, K, Fe, Cs, Sc, Ta, Cr, Rb, Co, U, Th, La, Ce, Nd, Sm, Eu, Tb and Yb were measured in traverses across the contact zone. There is no evidence for migration beyond 3m of the contact zone. The authors conclude, that, based on this study, crystalline rocks may be suited as a host for HLRW repositories.

3.2.2 Alamosa River Monzonite intrusive into tuffaceous and andesitic rocks

The Alamosa River stock is a monzonite intrusion emplaced about 29.1 ± 1.2 million years before present (MYBP)(21). Based on oxygen isotope studies, Williams(22) has suggested that heat from these intrusives initiated extensive hydrothermal circulation. A later hydrothermal event at 22.8 MYBP was associated with the emplacement of the mountain quartz latite porphyry; temperatures were calculated by Williams to be within the range of 250 to 370°C.

A detailed study was made of the distribution of Th, U, Co, Sr, Be, Cs, Rb, Se, V and Fe at 10 metre intervals along a traverse across the contact zone.

Strong contrasts between the monzonite and tuff were evident, with higher concentrations of all elements except strontium and barium in the monzonite. On the scale of sampling used, there is evidence for gradients of Cs, Th and Co away from the contact zone but only within a few tens of metres. The authors acknowledge the need for more detailed sampling close to the contact zone. The distribution of other elements is apparently unaffected by the intrusion. It is concluded that the absence of widespread elemental migration between the monzonite and the tuff, even in a convective system, supports continued assessment of such rocks for HLRW repositories.

3.3 Thorium Deposits (Morro do Ferro)

Another example of geochemical analogues is that of Morro do Ferro thorium deposit situated on the Pocos de Caldas plateau in the state of Minas Gerais, Brazil. The Pocos de Caldas plateau is believed to be deeply eroded caldera and the Morro do Ferro deposit itself is near the centre of the plateau, rising some 140m above its immediate surroundings. The geology of the area has been described by many workers(23-27). The age determinations(25) show that body of alkalic igneous rocks was built by piece-meal additions over some 20 million years towards the end of the Cretaceous Period. The caldera must have formed later by collapse of the intruded rocks. The underlying rock has been subject to extensive alteration by both weathering and hydrothermal activity. The only outcrop rock is magnetite and it occurs as a set of subparallel dikes a few meters thick.

Thorium and rare earth elements (REE) are especially concentrated near some of the dike contacts but the thorium-rich material is not directly associated with magnetite and the abnormal thorium concentrations exist to depths of nearly 200m(24,28). The reasons for the thorium and REE accumulation in this site are not understood. However, recent mineralogical study (see ref. 28) has shown that most of the thorium (and presumably the REE) is present on the surface of clay and oxide minerals.

The Morro do Ferro deposit has been studied by Eisenbud and co-workers(28-30) with three objectives in mind: (1) to predict by analogy with the thorium deposit, the environmental implications of an ancient residue of plutonium in a radioactive waste repository which has been subject to erosion to the surface or groundwater intrusion; (2) to develop models for transport of uranium, thorium, ^{226}Ra, ^{228}Ra, REE etc.; and (3) to evaluate the dosimetric implications to humans living near the site. The rationale for the assumptions that thorium is a valid analogue of plutonium and that some REE such as neodynium and lanthanum are valid analogues for curium and americium has been discussed by Eisenbud et al in reference 30.

Eisenbud et al(28) have estimated the mobilisation rates of thorium and lanthanum at Morro do Ferro both due to surface erosion by rainfall action and solubilisation by groundwater (the more relevant to a geological repository). These have been found so low ($10^{-9}y^{-1}$) that in spite of the long half-lives of some of the actinides essentially complete in situ decay would take place if the analogues studies are valid. Thus, if it is assumed that the annual groundwater mobilisation rate of ^{239}Pu remained constant at the present measured rate for thorium, the mean life of the deposit would be $7 \times 10^{8}y$ compared to $3.4 \times 10^{4}y$ for ^{239}Pu. The results are all the more remarkable in view of the fact that the Morro do Ferro deposit meets none of the National Research Council selection criteria for geological repositores(31) i.e. that the repository be placed at great depth, in unweathered rock, under hydrological conditions that would assure long transit times for nuclides carried by groundwater. Nevertheless, the quoted thorium mobilisation rate is so low that if thorium/plutonium analogy is valid the deposit itself would meet the accepted radioactive waste discharge standards. Furthermore, even tetravalent neptunium which is not a close chemical analogue of thorium should also remain immobile as long as conditions remain reducing. Thus, the thorium migration data obtained at Morro do Ferro indicate clearly that none of the transuranic radionuclides would be mobilised appreciably by groundwater contact with the radioactive waste in a repository provided natural range of pH and Eh is preserved. The findings(28-30) that the transuranic actinide elements are so extraordinarily immobile is consistent with findings at Oklo described in section 3.1. So far only the first objective quoted for this project in reference 30 has been achieved and reported on. The completion of the other two objectives will provide the values of parameters required for modelling transuranic mobilisation and evaluating radiological impact of such mobilisation.

3.4 Uranium Deposits (Alligator Rivers Uranium Province, Northern Territory, Australia)

Geochemical analogues may be used to reduce the uncertainties in predicting the long-term transport of radionuclides. In this study the migration of members of the uranium series within and down-gradient of four ore bodies in the Alligator Rivers uranium province of the Northern Territory of Australia is described(32-34). A mathematical framework has been developed to permit calculation of the rate of leaching or deposition of uranium and radium between defined zones of the ore body, and the rate of loss of the nuclides due to groundwater transport and surface erosion.

A detailed study has been made of the distribution of uranium, thorium and radium isotopes within various minerals comprising the weathered ore assemblage. Uranium and thorium concentrate principally in the iron minerals and radium in the clay quartz phases. Substantial isotope fractionation is observed which is attributed to a combination of α-recoil and chemical effects. The system has been modelled mathematically.

The transport of uranium series nuclides in groundwater intersecting the deposit has been investigated. Down-gradient of the Ranger One deposit, the maximum retardation factor of uranium is 250. A new technique has been applied to the separation of colloids from up to several thousand litres of groundwater. A preliminary study has been made of the distribution of uranium and thorium isotopes between the solution and the colloids.

Systematic measurements have been attempted of the parent/daughter systems ^{232}Th/^{228}Ra, ^{230}Th/^{226}Ra; ^{228}Th/^{224}Ra and ^{227}Th/^{223}Ra to study the dependence of relative adsorption coefficients on the mean life-times of the radionuclides and their distribution on specific mineral phases within the ore assemblage. A method has been found to electroplate radium from aqueous solution onto stainless steel planchettes(35). The technique is being applied to a study of the effect of α-recoil on radium adsorption coefficients.

A conceptual framework has been developed for evaluating the matrix-diffusion mechanism of the transport of solute through crystalline rock over geological time. Attempts may be made to incorporate ^{239}Pu, and the fission products ^{99}Tc and ^{129}I into the analogue.

3.5 Host Rock/Groundwater Interface

Processes occurring at the host rock/groundwater interfaces are useful analogues of phenomena leading to the retardation in the far field of radionuclides leached from repositories. Provided uranium or thorium series disequilibria can be measured with sufficient precision, the systems incorporate the essential elements of a useful analogue, viz. a spatial discontinuity and a basis for establishing a time frame.

The principal reason for studying host rock/groundwater interfaces at the microscale level is to examine whether there are mechanisms of retardation which occur over the long-term which are not manifest over laboratory time-scales. Factors which might be involved include:

(i) the alteration of accessible minerals over long time intervals;

(ii) the effect of α-recoil on retardation factors;

(iii) the role of colloids in groundwater transport.

(i) The alteration of accessible minerals over geological time.

Selective phase extraction techniques are commonly used to study the distribution of heavy metals through alluvial material(32,36). Where comparison is possible, data from the Alligator Rivers study are consistent with those from other areas. The principal findings are:

(a) Uranium and thorium isotopes are associated principally with the iron minerals,

(b) radium adsorbs preferentially on the clay/quartz fraction,

(c) in contrast to the crystalline iron, the radionuclides adsorbed on the amorphous iron are accessible to the groundwater.

The open system uranium model, which was developed to understand gross features of the uranium redistribution in the upper sequences of the ore bodies in the Alligator Rivers region has been extended to the microscale groundwater/amorphous iron/crystalline iron/clay-quartz systems. The model has been formulated to facilitate estimates of:

(a) α-recoil induced transfer of daughter radionuclides between phases,

(b) exchange of radionuclides between the groundwater and the amorphous iron and clay quartz phase,

(c) the slow exchange between the amorphous iron and crystalline iron phases.

amorphous iron (adsorbed radionuclides, accessible to groundwater)	$\rightleftharpoons$	crystalline iron (incorporated radionuclides, inaccessible to groundwater)

Adsorption of uranium and thorium from the groundwater onto the amorphous iron and its subsequent incorporation by crystallisation into crystalline iron is a retardation mechanism which applies over geological, but not over laboratory, time-scales.

A promising method of studying these effects is based on the systematic measurement of related parent daughter couples, ^{232}Th/^{228}Ra, ^{230}Th/^{226}Ra and ^{228}Th/^{224}Ra.

Some pioneering studies have been reported$^{(37-38)}$. Detailed insights will only be possible if the isotopic fractionation both in the groundwater and on the host rock is recorded. For instance, it is commonly observed that ^{228}Th is in large excess of ^{232}Th. This is normally attributed to the parent ^{228}Ra which is formed by α-recoil. It is probably significant that radium tends to associate with the clay minerals, whereas thorium tends to adsorb on the iron components. The decay of ^{228}Ra to ^{228}Th would not lead to recoil-induced redistribution. Thus, observed differences in the ^{232}Th:^{230}Th:^{228}Th activity ratios may be primarily due to the differences in the location of the thorium isotopes on the minerals of the host rocks.

(2) α-Recoil. Experimental evidence for the effect of α-recoil on the radium distribution coefficients Rd between an aqueous phase (pH 4.25) and the sodium forms of montmorillinite, kaolinite and illite has recently been obtained. An enhancement of a factor of about two was found on illite$^{(34)}$. For a given porosity, the retardation factors are directly related to the Rd values. This effect is of particular importance for that component of the ^{226}Ra formed by decay of the parent ^{230}Th leached from the repository site.

(3) Colloid transport. There are two principal reasons for studying the distributions of the uranium series nuclides between the solution and the colloid phases.

(a) The sorption phenomena in soils and weathered rocks is largely due to fines, i.e. clay minerals, amorphous iron minerals, and fumic acids. The <2 μm fraction contributes 99% or more of the total surface area.

(b) Groundwater colloids are responsible for the migration of significant proportions of thorium isotopes and possibly of other relatively insoluble radionuclides.

The role of colloids in the transport of heavy metals in river systems is well recognised. However, relatively few investigations of groundwater colloids have been undertaken. Techniques are now available. for the concentration of colloids in predetermined size ranges from hundreds of litres of water without air contamination. In this investigation 5 nm to 1 μm colloids were initially concentrated by a factor of about 100. The activities of ^{234}U, ^{238}U, ^{228}Th, ^{230}Th and ^{232}Th were measured. The principal findings were as follows:

(i) Between 0.03 and 1.7 per cent of the uranium, and between <0.1 and 20 per cent of the thorium was associated with the colloid.

(ii) In neither case was there evidence of isotopic equilibrium between the solution and the colloids.

(iii) The isotopic composition of the colloid was more similar to the solution than to the drill core.

(iv) The relative colloidal transport can only be quantitatively assessed with knowledge of the relative rates of colloid and groundwater migration.

Aquifer-host rock analogues of the distant field down-gradient of a proposed repository site are of use if the levels of indicator elements are higher than those normally found and facilitate detailed study of properties of the system determining radionuclide retardation over long periods. Study regions in the vicinity of uranium deposits are of clear interest. Firstly the fractionation of elements in the thorium and uranium series can be measured precisely. More importantly, however, it may prove possible to measure directly the levels of certain transuranic elements (e.g. ^{239}Pu) and fission products (^{229}I and ^{99}Tc). In most geological settings, the levels of these indicator elements would be below the detectable limit.

4. APPLICATION OF THE FINDINGS FROM GEOCHEMICAL ANALOGUES TO PROPOSED REPOSITORY SITES

There are at least four general ways in which research into geochemical analogues of repositories is of potential value to both the proponents of proposed installations and licensing authorities.

(1) They may determine the limits of migration of indicator elements under conditions which are frequently more rigorous than those which would be met under operating conditions and over timescales much longer than those of interest

For instance the Oklo natural reactor remained critical for between 10^5 and 5×10^5y during which the heat dissipation within the reactor zone was about 50W m^{-2}, which is at least twice that determined for reference waste repositories. Evidence of circulating hydrothermal fluids of temperatures between 450°C and 600°C and pressures of about 1 kbar was found up to 30m from the zones of criticality. Despite the extreme conditions, the apparent rate of migration of ruthenium, ^{99}Tc and neodynium was of the order of 10^{-5}m y^{-1} in the presence of fluids which were convecting as fast as 5m y^{-1}(31).

Again the emplacement of the Alamosa River, Wightman and Jasper Creek intrusives occurred at 29.1 ± 1.2 MyBP and was associated with extensive hydrothermal circulation. Temperatures of a later event at 22.8 MyBP were calculated to be in the range 250-370°C. There is evidence of gradients of only three elements (Cs, Th and Co) of the ten studied within a few tens of metres of the contact zone.

(2) They can be used to establish a scientific basis for the long-term prediction of the rate of transport of radionuclides

Phenomena can sometimes be identified which affect retardation rates over long time intervals, but which are not necessarily manifest over laboratory timescales using conventional procedures. Examples which were discussed in section 3.4 include the effect of the alteration of accessible minerals on retardation, the role of colloids in sub-surface transport, the effect of radiochemical history (particularly α-recoil) and mean residence time on distribution coefficients.

(3) In many circumstances the findings may be transferred from the setting of the geochemical analogue to that of the waste repository

Two distinct steps are required:

(a) A correlation must be established between the hydrogeochemistry of the significant radionuclides and that of the indicator elements in the analogue. In a groundwater environment, uranium, neptunium and plutonium may exist in several oxidation states. While the chemical properties of different oxidation states of the same actinide vary greatly, different actinides in the same oxidation state behave similarly(39). Thus, acceptable predictions of the transport of Pu^{3+}, Am^{3+} and Cm^{3+} can be drawn from studies of the lanthanide elements, e.g. Ce^{3+}, Nd^{3+} and Eu^{3+}. Again, Np^{4+} and Pu^{4+} would behave in a similar manner to U^{4+}. Particular attention must be paid to the tendency of actinides to form strong complexes with oxygen ligands such as phosphates, sulphates, and organic acids. Detailed comparisons can be drawn on the basis of Eh/pH diagrams adapted to groundwater conditions.

(b) The second step in relating the findings from the geochemical analogue to the repository site involves the host rock. In some analogues such as Oklo and the igneous intrusives it is possible only to compare the petrology at the appropriate time. However, frequently laboratory tests can be used to compare the radionuclide adsorption properties of material from the two sites. The very serious question then arises of the relationship between the observed adsorption and leaching behaviour and the retardation factors valid over extended time intervals. Non-classical factors such as discussed in section 3.4 need to be considered. An approach applicable to the uranium ore body analogue has been discussed.

(4) Because of the ubiquitous nature of uranium and thorium, the general locality of the proposed repository site may be used as an analogue of the distant field radionuclide transport regime under operating conditions

Experimental techniques and principles of interpretation developed in the uranium and thorium ore body analogues could be used. Even though the actual repository site is being investigated, the approach is still that of an analogue. Uranium or thorium series nuclides, or other indicator elements were either present for extremely long periods within the host rock or were formed by radiogenic decay. Under operating conditions, all elements of interest, with the possible exception of ^{226}Ra would have migrated from the leached repository up-gradient, i.e. they would be allogenic. Attempts would be made to use information on the distribution of uranium and thorium series nuclides which has evolved over geological time, together with laboratory sorption and leaching studies to predict retardation factors over the next 10 000 years.

As indicated in section 1 the EPA has defined quantitative criteria for the release of radionuclides from repository sites over the period of 10 000 years following closure. Further, many analyses conclude that the most important contribution to long-term environmental protection comes from the geological characteristics of the repository site. It follows that a great deal of attention must be paid to the mathematical modelling of radionuclide transport in the far field. At least 20 transport codes have been developed.

A major international nuclide transport code intercomparison INTRACOIN study has been coordinated by the Swedish Nuclear Power Inspectorate SKI in cooperation with the Swiss organisation NAGRA. Important issues of the numerical accuracy of the codes, and their capability to describe in situ measurements are considered. However, serious questions concerning the accuracy of long-term prediction remain because of the inevitable simplifications in the governing transport for fluid flow and solute transport.

The significance of many of the additional processes affecting transport over long periods (colloid transport, α-recoil effects, surface mineral alteration) have been identified using natural analogues. An extension of this approach is to use analogues to attempt to investigate the capacity for codes to describe radionuclide transport over these time-scales. If successful this will provide an improved basis for assessing whether proposed repository sites comply with the licensing authorities' requirements for long-term containment.

5. ACKNOWLEDGEMENTS

The support of the United States Nuclear Regulatory Commission is acknowledged with gratitude.

Applications of analogues in near-field geochemistry

Ian G. McKinley

Introduction

The near-field consists of the waste itself, the engineered barriers (canister, backfill etc.) and any region of surrounding host rock which is significantly altered by the presence of the repository. Due to the range of materials present, this is a region of great chemical complexity which may be further complicated by the presence of temporally and spacially variable heat and radiation fields.

Experimental studies of the near-field generally fall into 2 classes: -

a) detailed examination of single processes with limited consideration (or none at all) of coupling with other processes

b) "integral" experiments examining the performance of several components of the near-field simultaneously under as realistic conditions as possible.

The data from such experiments can be used to develop geochemical models of the near-field. It is often found, however, that single process experiments are performed under inappropriate conditions while data from integral experiments are notoriously difficult to interpret. Near-field models thus tend to be relatively simple particularly with respect to: -

a) extrapolation from laboratory to expected chemical conditions

b) extrapolation from laboratory to geological timescales

c) coupling of synergistic/competative processes.

Analogue studies may provide important support for such models and may, indeed, be the only approach towards validation of temporal extrapolations. In particular, for the current level of safety analysis, analogues may at least demonstrate the conservatism of the models used.

Description of the Near-field

A comprehensive model of the near-field would include the following components: -

a) evaluation of engineered barrier longevity

b) description of chemical evolution of the near-field

c) quantification of radionuclide releases into the far-field

d) examination of possible perturbing processes e.g. colloids, radiolysis etc.

The model is complicated by the fact that these components are inextricably linked in a complex manner.

The composition of the near-field, significant processes involved and modelling approach varies considerably between various disposal concepts. For the purposes of this paper, four different near-field models will be compared to indicate both the complexity of this region and the variation in analogue needs for alternative disposal options. The examples selected are: -

a) the KBS-3 repository for spent fuel (KBS, 1983)

b) the Nagra repository for vitrified HLW (Nagra, 1985)

c) the Nagra repository for L/ILW (Nagra, 1985)

d) the UK near surface repository for ILW as described by the NRPB (Pinner et al., 1984)

The main characteristics of the near-field in each of these examples are summarised in Table 1. It should be emphasised that the near-field models in the references cited above are mainly for safety analysis and development of a comprehensive geochemical model has only been attempted (with a limited degree of success) for the Nagra HLW case (McKinley, 1985). The Nagra HLW analysis is also constructed on a "realistic", site specific basis while the others are either very conservative (KBS-3, Nagra L/ILW) or generic (UK, ILW).

Identification of analogue requirements

To identify analogue requirements, the four components of a general near-field model are considered seperately.

The longevity of particular near-field barriers - matrix, canister and backfill - assumed in the various models is summarised in Table 2. It can be noted that both L/ILW cases conservatively take little (or no) credit for matrix or canister stability while very long lives are predicted for all high level waste barriers. A major justification for the latter is the important constraint on hydrothermal reaction placed by the very low water flow in these

Table 1: Near-Field Characteristics

	KBS-3 HLW	NAGRA HLW	NAGRA L/ILW	UK ILW
Matrix	UO_2	Glass	Cement	Cement
Canister	Copper	Steel	Steel	Steel
Backfill	Bentonite	Bentonite	Concrete	Concrete
Host Rock	Granite	Granite	Clay	Clay
Depth (m)	$\sim$500	$\sim$1200	$\gtrsim$600	<20

Table 2: Model Barrier Lifetimes (in years)

	KBS-3 HLW	NAGRA HLW	NAGRA L/ILW	UK ILW
Matrix	7×10^6	1.5×10^5	-	10^2
Canister	10^5-10^6	10^3	-	10
Backfill	$>10^6$	$>10^6$	500*)	50*)
			10^4**)	500**)

*) Time for first degradation of physical properties

**) Time for total barrier destruction.

repositories. Barrier longevity is an obvious area for analogue study by consideration of both geological and archeological systems. It should be noted, however, that the sensitivity of the release of radionuclides to the far-field to barrier life varies in these different cases. Simplistically, two ranges could be considered for each barrier - one in which analogue demonstration of stability indicates significant overconservatism and one which shows model values to be optimistic and indicates significant under-prediction of releases. Some estimates of these timescales are listed in Table 3. Taking the Nagra HLW case as an example, the rate of breakdown of the matrix directly affects release rates of relatively few key nuclides and would have to be about a couple of orders of magnitude more or less than the model value to significantly affect overall releases. The canister integrity here plays very little direct role and even immediate failure would have little effect as long as the backfill performs as expected. Similarly, however, the canister lifetime would have to be extremely long to affect releases of the key nuclides identified in this study. Very long backfill life has little direct effect on releases but the essential role of this barrier as a colloid trap requires a lifetime $\gtrsim 10^6$ years.

The second component of a near-field model is evaluation of pore water chemistry in the region. Such chemistry will evolve with time as barrier materials are hydrothermally altered but very general characteristics of each of the reference near-fields are given in Table 4. Such general characteristics are essential background data for selection of the previously discussed barrier lifetime analogues while the timescales in Tables 2 and 3 give an indication of those required for chemical buffer performance. Analogues would be aimed at verifying efficiencies and ranges of the pH and redox buffers considered and their evolution over relevant timescales. Of particular interest also are reactions at barrier interfaces (e.g. steel/bentonite, bentonite/concrete, concrete/steel) which are very difficult to model at present.

The third, and most important, component of a near-field model is the quantification of nuclide release rates as a function of time. Different repository concepts and modelling approaches result in differing sensitivity of releases to various parameters, some of which are shown in Table 5. Here, in the Nagra HLW case, degradation rate of the waste matrix and nuclide solubility form the main constraints on near-field releases while taking account of the heterogeneity of far-field flow has been shown to greatly decrease releases into the far-field.

In comparison to KBS-3, radiolysis and canister lifetime have negligible effect on Nagra HLW releases. In the latter, sorption in the backfill was considered only to simplify far-field transport calculations and, as much, has little direct effect on releases of key nuclides while, in the former, the backfill "reservoir" provides important dilution of "prompt" released I-129 and Cs-135. For the L/ILW repositories solubility is not considered in the Nagra model while backfill sorption is not included in the NRPB model of UK ILW

Table 3: Relevant time ranges (in years) for barrier longevity analogues

	KBS-3 HLW	NAGRA HLW	NAGRA L/ILW	UK ILW
Matrix	$>10^8$	$>10^7$	$>10^3$	$>10^3$
	$<10^6$	$<10^4$	-	<10
Canister	$>10^7$	$>10^5$	$>10^3$	$>10^2$
	$<10^5$	-	-	<10
Backfill	-	-	$>10^4$	$>10^3$
	$<10^6$	$<10^6$	$<10^2$	<20

nb upper value allows significantly more conservative models to be justified
lower value indicates insufficient conservatism in present models

Table 4: Model Near-Field Chemistry

		KBS-3 HLW	NAGRA HLW	NAGRA L/ILW	UK ILW
pH	range	near neutral	mildly alkaline	very alkaline	? very alkaline
	buffer	host rock	bentonite/ canister	cement	? cement
Redox	range	oxidising	reducing	reducing	?
	buffer	radiolytic oxidants	canister	canister/ host rock	?

Table 5: Factors greatly affecting model radionuclide releases

	KBS-3 HLW	NAGRA HLW	NAGRA L/ILW	UK ILW
Waste Matrix solubility	x	x	-	-
Radiolysis	x	-	-	-
Nuclide solubility	x	x	?x	x
Canister life	x	-	-	-
Sorption in backfill	x	-	x	?x
Heterogeneous water flow in the host rock	x	x	-	-

disposal, but both these factors could be potentially very important. Of the release constraints listed, the one most likely to be suitable for analogue study which has not been previously considered is backfill sorption. For analogue selection, the chemistry and timescales previously described must be taken into account along with the key nuclides identified in each safety analysis (cf. Table 6). Analogues providing data on the solubility of relevant elements in appropriate chemical environments would be very welcome but would probably be very difficult to find.

The final component to be considered is analysis of potential perturbing processes which would not be included in a standard "base case" model, some of which are listed in Table 7. Colloids are potantially very important in the near-field if either they are mobile in the backfill or they are formed at the boundary between near- and far-fields at strong redox (e.g. KBS-3) or pH (e.g. L/ILW options) fronts. Any possible analogue investigation of this topic would be extremely valuable. Radiolysis is identified as a key factor only for the KBS-3 case considered, where analogues could examine either the reactions occuring in groundwater in a high alpha-flux or the mechanisms buffering any oxidising front formed in either near-field barriers or the host rock. Gas production, mainly from corrosion of steel, is a potential problem in all but the KBS system and of interest is both the rate of H_2 production from corrosion in relevant environments and the diffusivity of such H_2 in backfill materials. Finally, microbial activity may be important when suitable energy and nutrient sources are available in the repository. This is likely to be of greatest significance in L/ILW repositories, particularly for near-surface emplacement and key data requirements are the extent of microbial activity in relevant environments and their consequences, particularly in terms of formation of organic by-products which are efficient complexing agents.

Conclusions

The preceding section is obviously simplistic, intended more to illustrate the range of information required rather than to focus on particular processes. Nevertheless, it hopefully shows that in order to choose even rather simple analogues, some idea of the near-field context is required to ensure that the system selected is relevant (e.g. in terms of timescale or chemical environments). Obvious areas for analogue study include barrier longevity and nuclide sorption (retardation) in backfill materials, but, of greater importance might be examination of chemical buffering or nuclide solubilities in the near-field, although finding appropriate analogues for these may be much more difficult.

Table 6: Key radionuclides

	KBS-3 HLW	NAGRA HLW	NAGRA L/ILW	UK ILW
Np-237 chain	x	x	x	x
U-238 chain	x	x	x	x
U-235 chain	x	x	x	-
Cs-135, Tc-99	x	x	x	-
I-129	x	-	x	-
Se-79, Sn-126	-	x	x	-
Cl-36	-	-	x	-
C-14	-	-	-	x

Table 7: Possible perturbing processes

	KBS-3 HLW	NAGRA HLW	NAGRA L/ILW	UK ILW
Colloids	x	x	x	x
Radiolysis	x	-	-	-
Gas production	-	x	x	x
Microbes	-	x	x	x

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rivm rijksinstituut voor volksgezondheid en milieuhygiëne LBG 86-42
1986-02-12

Special needs of modellers working in the field of geological disposal in rock-salt

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In safety assessment studies for geological disposal in rock-salt, the impermeability of rock- salt is a starting point. In order to enable the release of radionuclides into the geosphere, either the salt formation itself must loose its integrity, or inhomogeneities inside the salt must become permeable due to stress differences near a mined repository.

The loss of integrity of a salt formation can be achieved by subsurface dissolution of rock salt. From field observations in deep wells it is known that in aquifers belonging to the same stratigraphical unit water with extremely high salt concentrations is present as well as water with low salinities. The observed differences are explained by the presence of bedded salt and salt dome penetrations of the aquifer.
Natural isotopes seem to provide a useful tool to differentiate between groundwater of marine origin and water containing dissolved rock-salt (Glasbergen, 1985). It is known that caprock is a residue of dissolution of salt. Direct estimation of the age of caprock, however, is impossible. Observations of groundwater quality, natural isotopes and knowledge of the flow system might support a model approach to this problem.
A first attempt has been made to calculate the rate of subrosion (Glasbergen, Jansen and Hamstra, 1985). A validation of the results has not been carried out yet. Since this process has been going on for probably millions of years, extrapolation into the future might be based on the use

of a natural analogue. Preliminary model studies are very useful in giving direction to the set-up of a programme of field reconnaissance. In this case the natural analogue consists of the process of dissolution at the surface of a rock-salt formation and the presence of dissolved salt in the surrounding groundwater system. Problems may rise in the description of the groundwater flow system, as direct measurements of very small pressure differences at large depths are difficult. Indirect methods such as dating with isotopes can be helpful, although the results are sometimes contradictory.

Inhomogeneities inside the rock-salt, such as anhydrite layers, could provide a release path for radionuclides (PSE, 1985). This pathway of several hundreds of meters is an important part of the total pathway to the biosphere (fig.1). Since anhydrite itself has a very low permeability, but might contain secondary porosity, laboratory experiments on small samples provide inadequate information on e.g. permeability and sorption. If a natural analogue can be found, consisting of deep-lying anhydrite in a saline environment and e.g. uranium containing water is transported across this layer, this would provide important information for the validation of a model for
release from a rock-salt host-rock.

The geosphere transport from the host-rock, the salt, to the biosphere forms a third domain in which analogue studies can be useful for the validation of models. Large differences in lithology occur in this domain (fig.2), while the salt concentration decreases from saturation to fresh water. Radionuclides which follow pathways to the biosphere by convection or diffusion will pass different physical and geochemical zones. Temperature and pressure decrease and the composition and form of the porous media change drastically. Regarding the very low water velocities, which can be expected at depths of several hundreds of meters, it is practical impossible to carry out laboratory experiments under realistic conditions. Laboratory work confirms that salt concentration effects the adsorption of radionuclides, although the results for different species do not give the same relationship (Prins, Pennders and Frissel, 1986). Any analogue in sedimentary aquifers with nuclides moving in groundwater of high salinity may attribute to improving the quality of a geosphere model, predicting the migration towards the biosphere.

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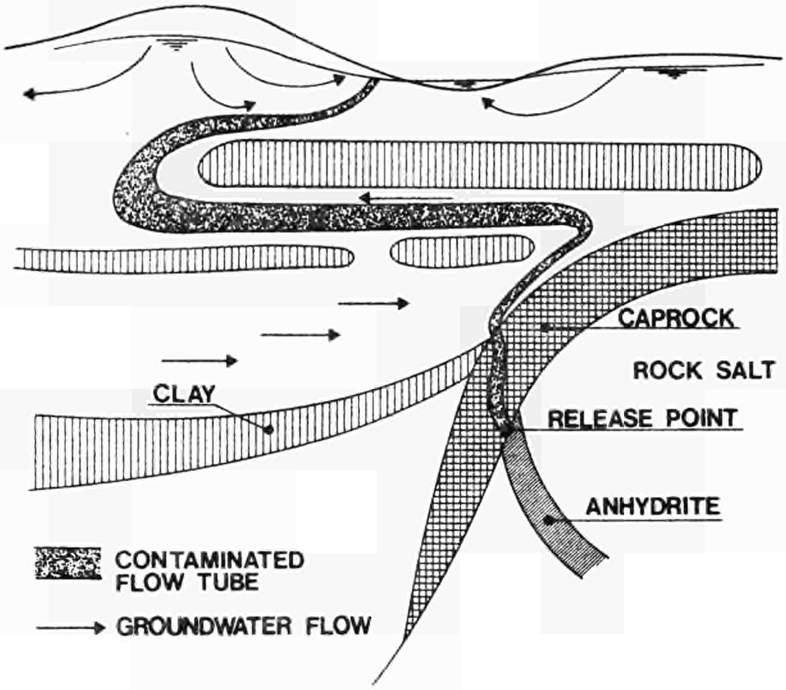

Figure 1

Potential pathway to the biosphere after release through a permeable anhydrite layer from a repository in rock-salt

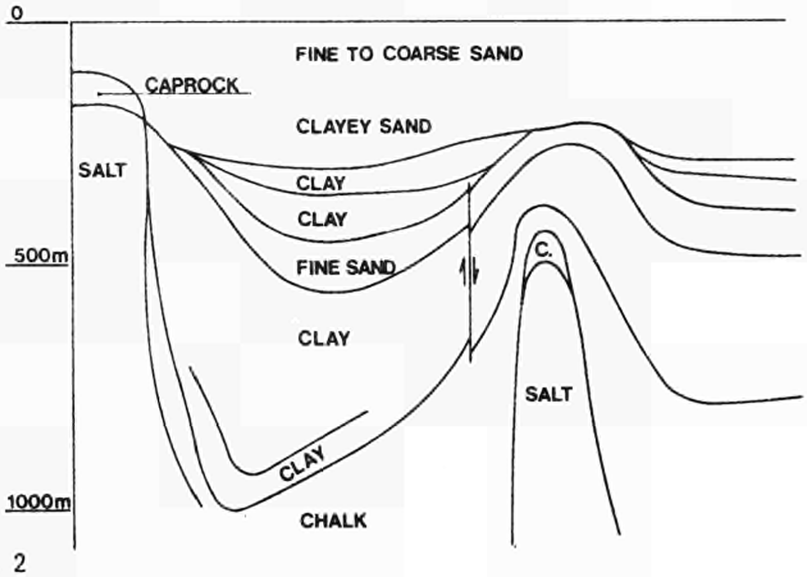

Figure 2

Example of lithological differences around salt-domes in The Netherlands

APPENDIX 3

What the Earth Scientists Can Provide

1. An analogue validation study of natural radionuclide migration in crystalline rocks using U-series disequilibrium studies (J. SMELLIE et al.).

2. Les gîtes minéraux : conditions limites de l'évolution des stockages de déchets radioactifs en milieu granitique ? (J.F. SUREAU).

3. What can the earth scientists provide (F.P. SARGENT).

4. Italian activity in the field of natural analogues and natural evidence (A. BRONDI).

5. Evidence for field measurements of retardation factors for U/Th/Ra radionuclides (M. IVANOVICH).

6. About the permeability of faults and fractures in clay formations (M. d'ALESSANDRO et al.).

7. Analogue of elemental diffusion over 5000 years in sediments; close but not close enough? (N. CHAPMAN).

8. Performance assessment input : Marysvale natural analog study (M. SHEA).

AN ANALOGUE VALIDATION STUDY OF NATURAL RADIONUCLIDE MIGRATION IN CRYSTALLINE ROCKS USING URANIUM-SERIES DISEQUILIBRIUM STUDIES.

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ABSTRACT

Concentrations and isotope ratios of natural decay series radionuclides have been studied in three contrasting crystalline rock drillcore sections intersecting water-conducting fractures deep in the bedrock. Radioactive disequilibria resulting from rock-water interactions were observed in two of the cores. These indicated uranium migration along distances of 40 cm or more on a timescale of 10^6 years in conjunction with thorium immobility under the same conditions. Fracture surface minerals showed a high affinity for radionuclide retardation and a limit of about 3 cm is suggested for the migration of radionuclides from fracture fluids into the saturated rock. This limit may correspond to enhanced matrix porosities resulting from earlier hydrothermal activity along the same channels.

INTRODUCTION

Assuming a "worst case" situation in which progressive corrosion of the near-field engineered barriers would result in the slow release of radioactive waste into meteoric waters circulating within the host bedrock, far-field retardation processes would qualitatively become the most important factors in controlling the release of radionuclides to the biosphere. During transport along hydraulically connected fractures in the host bedrock, radionuclides in solution will be subject to retardation processes such as sorption and migration into the water saturated rock matrix.

To date, much of the work and model derivation relating to radionuclide migration has been based upon short-term laboratory experiments. An obvious means of validating such work is to study the migration of natural radionuclides during geological timescales within crystalline bedrock, and the nuclides of the natural uranium decay series present a useful range of physical and chemical properties for this purpose. In particular, the various parent/daughter equilibria can be used to provide information on rock-water interactions. Since the initial work on this topic [1] such methods have become well established and have been applied in studies of a wide range of geological environments [2, 3, 4].

As part of a jointly-funded programme of research between the Swedish Nuclear Fuel and Waste Management Co. (SKB) and the Swiss Nationale Genossenschaft für die Lagerung radioaktiver Abfälle (NAGRA), drillcore lengths intersecting suitable water-conducting fracture zones were chosen from three contrasting hydrogeological environments; two in Switzerland (Böttstein and Grimsel) and one in Sweden (Kråkemåla), all located in granite bedrock. The samples analysed represented profiles from the intersected fracture face into the bedrock.

SAMPLING AND ANALYSIS

Drillcore lengths of 40 - 55 cm were chosen from the respective areas; these varied in diameter from 56 mm (Swedish sample) to 76 mm (Swiss sample). A thin rock slice was removed along the drillcore length for mineralogical and related studies. A portion of the core was retained for reference and the remainder was sectioned into 1 cm slices for analysis. The mineral coatings scraped from the inside surface of the fracture zone constituted another sample. The individual slices were powdered and subdivided for natural decay series analysis, INAA and Fe^{2+} determinations. Natural decay series measurements and INAA analysis were carried out using proven techniques [5, 6].

GEOLOGICAL SETTING AND MINERALOGY OF THE DRILLCORES

Kråkemåla Drillcore (Kl: 317.85-318.40 metres)

The Kråkemåla specimen was selected at a depth of approximately 318 m from one of three test holes drilled in the Götemar granite, located along the south-eastern coast of Sweden [7, 8]. The chosen core is traversed by a single, open fracture zone at 45° to the vertical drillcore length; from geophysical logging investigations the fracture zone is considered water-bearing. This is partly supported by fracture plane coatings of hematite and FeOOH-oxides. In addition, the feldspathic content marginal to the fracture zone shows evidence of alteration extending to 2-3 cm from the fracture plane.

The drillcore is representative of the Götemar coarse-grained granite and is macroscopically homogeneous. At greater resolution the rock is mineralogically variable consisting primarily of quartz (15-45 vol. %), plagioclase (30-42 vol. %) and potassium feldspar (30-50 vol. %) with subordinate biotite, muscovite and chlorite. Accessory minerals include interstitial amounts of magnetite, apatite, zircon, fluorite, sphene and monazite. Throughout the length of the drillcore sample the granite is weakly but uniformly hydrothermally altered; this is generally typical to the depths of maximum drilling in the massif [8].

The fractured area occupies a width of about 1 cm and is composed of a series of parallel to sub-parallel micro-fissures easily distinguished by FeOOH-oxide coatings. The central and largest fracture (max. 1.5 mm wide) is also partly infilled with hematite and subordinate chlorite. Macroscopically the influence of the fracture zone extends up to 2 cm into the host granite. This is apparent as FeOOH-oxide dustings present both interstitially within the rock matrix and included within altered to partly altered potassium feldspar phases; biotite and magnetite are also more markedly altered to chlorite and hematite respectively.

Böttstein Drillcore (BOE: 618.34-618.70 metres)

The Böttstein area is located in central northern Switzerland about 30 km north-west of Zurich and 5 km from the German border. Drilling in the area [9] encountered crystalline basement at a depth of approximately 300 metres. This consists of the Böttstein granite which extends down to at least 1500 m, the maximum depth of the drillhole. This granite is typically coarse-grained, rich in biotite, and porphyritic in texture accompanied by large phenocrysts of potassium feldspar. The chosen drillcore section was selected at a depth of approximately 618 m from a fracture intersection which was suspected as being water-conducting. The fracture was located near the contact between the granite and thin intruded horizons of pegmatite (up to 40 cm wide) and aplite (up to 1.5 m wide); the fracture occurs in the pegmatite only a few centimetres from the granite contact.

The selected drillcore length investigated consists of about 7 cm of pegmatite in contact with 13 cm of biotite-rich granite which is representative of the Böttstein porphyritic granite variety. In terms of average modal content (vol. %), the granite comprises 27% quartz, 26% plagioclase, 38% potassium feldspar and 8% biotite. Apatite and zircon are the most frequent accessories present.

The pegmatite containing the fracture zone is fresh, coarse-grained, and consists of quartz, potassium feldspar and albite, together with muscovite and tourmaline. Regarding the fracture faces, the dominant mineral phases are calcite, fine-grained quartz and clays (mostly interlayerings of illite and smectite) and sporadic apatite. Hydrothermal alteration of the granite extends for some 8 cm from the pegmatite contact. This is characterized by strong argillisation with illite/smectite as the dominant alteration phases; some calcite is contained in potassium feldspar and finely dispersed FeOOH-oxides give the rock a reddish tinge. A sealed fissure (0.5 - 2.0 mm wide) containing some calcite and clay minerals occurs at 8 cm and thereafter the granite is less altered (although the feldspars are still pigmented with iron-oxide) and the biotite content is higher.

Grimsel Drillcore (FLG: 94.12-94.52 metres)

The Grimsel area is located near the Grimsel Pass situated in central south Switzerland some 15-20 km from the Italian border. The site, which now constitutes the NAGRA underground test laboratory [10], was initially developed as an underground hydroelectric power scheme. The drillcore sample investigated was selected from a near-horizontal exploration borehole (SB 80.001:94.12-94.52 m) drilled into the bedrock from the access tunnel to the power station: the altitude of the borehole level is 1730 metres.

The granite is typically grey-coloured, fresh, mineralogically homogeneous in hand specimen, and medium- to coarse-grained in texture; the granite is also characteristically gneissose. The chosen fracture is fresh and intersects the core axis at 40°; no alteration on a macro scale was observed and no evidence of any fracture filling minerals. Its water-conducting properties are suspected on the basis of a large release of groundwater encountered while penetrating the fracture zone during drilling. The age of these fractures is uncertain, at least late Alpine to recent; the area is still considered tectonically unstable and the continuous formation of new fractures/joints cannot be excluded.

The average modal content of the granite core (expressed in vol. %) is 33% quartz, 34% potassium feldspar, 21% plagioclase, 7% biotite/chlorite, 1-2% muscovite, 1% hornblende and 2% epidote. The associated accessory phases are sphene, orthite, apatite, zircon, calcite and opaques. The feldspars have undergone some alteration to sericite, and the biotite to chlorite; magnetite is partly oxidized.

RESULTS

The following section summarizes the main observations relating to the natural decay series measurements. These results, together with the INAA data, particle track analysis and more detailed mineralogy, will be presented in full upon completion of this study.

Kråkemåla Drillcore

The drillcore contents and distributions of thorium and uranium and its daughter decay products are shown in Figure 1. The average uranium contents of uranium (15.67 ppm) and thorium (65.3 ppm) are anomalously high when compared with the average contents for world-wide granites. The average Th/U ratio of 4.4 indicates a general depletion of uranium which is consistent with previous work on the Götemar granite [8]. Most of the uranium is associated with zircon and monazite with subordinate amounts contained in sphene, magnetite, hematite, and ilmenorutile-type phases. Small amounts are also associated with sericite, epidote and FeOOH-oxide dispersions.

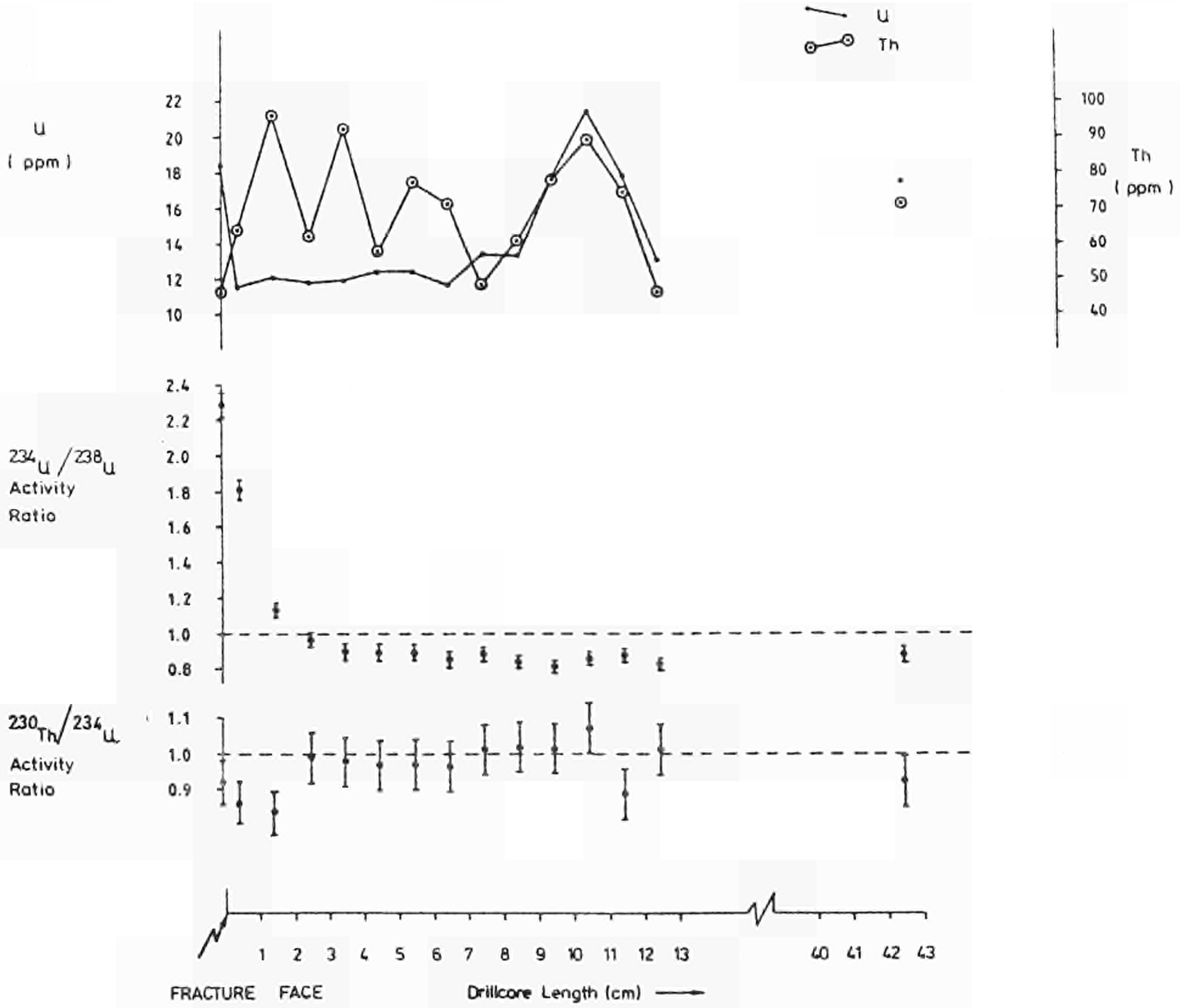

Figure 1: Contents and distributions of thorium and uranium and its daughter decay products (Kråkemåla Drillcore).

The distribution of uranium and thorium along the drillcore from the fracture zone shows that apart from the fracture face, which indicates an increase, the uranium content is fairly uniform for a distance of some 8 cm into the granite until a broad peak occurs over a length of 4 cm. In comparison, thorium indicates an antipathetic decrease at the fracture face, and then shows an extremely irregular fluctuation until it too forms a broad peak sympathetic to that observed for uranium. The similarity of the Th profile with those of the rare-earth elements (unpublished data) suggests that thorium has remained relatively immobile throughout the history of the granite, and its irregular distribution thus reflects the irregular distribution of the dominant Th-bearing mineral phase, monazite, which is of primary origin. With regards to uranium, which in comparison is easily mobilized and leached from granite provided the system has been open to fluid movement, Figure 1 shows some interesting features. There is a sympathetic increase in uranium and thorium from approximately 8 to 13 cm along the drillcore which shows that this part of the rock has probably retained its original uranium and thorium signature, although the intergranular labile uranium has almost certainly been removed. In contrast, the absence of any sympathetic uranium/thorium relationship within the initial 8 cm of the drillcore indicates that uranium has at some stage been leached from even the more resistate radioactive mineral phases possibly during some hydrothermal event, a process supported mineralogically by the partial alteration of monazite along this part of the core. However, uranium removal is not indicated from the fracture surface sample which instead shows a marked increase. This suggests that the groundwater/fracture uranium accumulation rather than the leaching is taking place.

Isotopically the ^{234}U/^{238}U ratio along the major length of the drillcore is less than unity indicating uranium leaching. In strong contrast, the granite marginal to the fracture zone is characterized by a systematic increase in the ^{234}U/^{238}U ratio to a value of 2.29 at the fracture face which indicates an accumulation of uranium. The ^{230}Th/^{234}U ratio is unity throughout most the core with a possible decrease being apparent close to the fracture.

The source of uranium giving rise to the enhanced concentrations and ^{234}U/^{238}U ratio values close to the fracture could be either uranium leached from the granite (as indicated by the ^{234}U/^{238}U ratios for the rest of the core), or from uranium transported in solution within the fracture migrating into the water-saturated rock. If the former process is responsible, then uranium migration over at least 40 cm is occurring whereas a constraint of about 3 cm can be applied if the latter process is taking place. The two processes are not mutually exclusive.

The ^{230}Th/^{234}U equilibrium and ^{234}U/^{238}U disequilibrium suggest that the process involved is either continuous or else indicates a time-scale long enough to allow re-equilibration of ^{230}Th with ^{234}U but short enough to maintain ^{234}U disequilibrium with ^{238}U, i.e. a time-scale of about 10^6 years.

The mechanism giving rise to uranium deposition at and near the fracture could be due to any or all of: a) precipitation at a boundary between differing physico-chemical conditions, b)sorption on the fracture filling minerals, and c) solution to solid recoil transfer.

Böttstein Drillcore

The drillcore contents and distributions of thorium and uranium and its daughter decay products are shown in Figure 2. Although not presented, higher amounts of Na and lower amounts of K and Rb support the mineralogical observations and help to distinguish the pematite from the granite. The pegmatite uranium contents range from 2.42 - 4.43 ppm and the thorium from 0.95 - 7.12 ppm (mean Th/U ratio of 1.06). In the adjacent granite the corresponding ranges are 3.37 - 5.73 ppmU and 21.69 - 33.49 ppmTh respectively (mean Th/U ratio of 6.35). The sampled core section indicates a significant depletion of uranium; thorium appears to have been immobile. Most of the uranium and thorium is believed to be associated with the accessory mineral contents which include zircon and apatite. Minor amounts of uranium and thorium may be accomodated by the mafic constituents such as biotite/chlorite, or as matrix sorptions associated with finely dispersed iron-oxides.

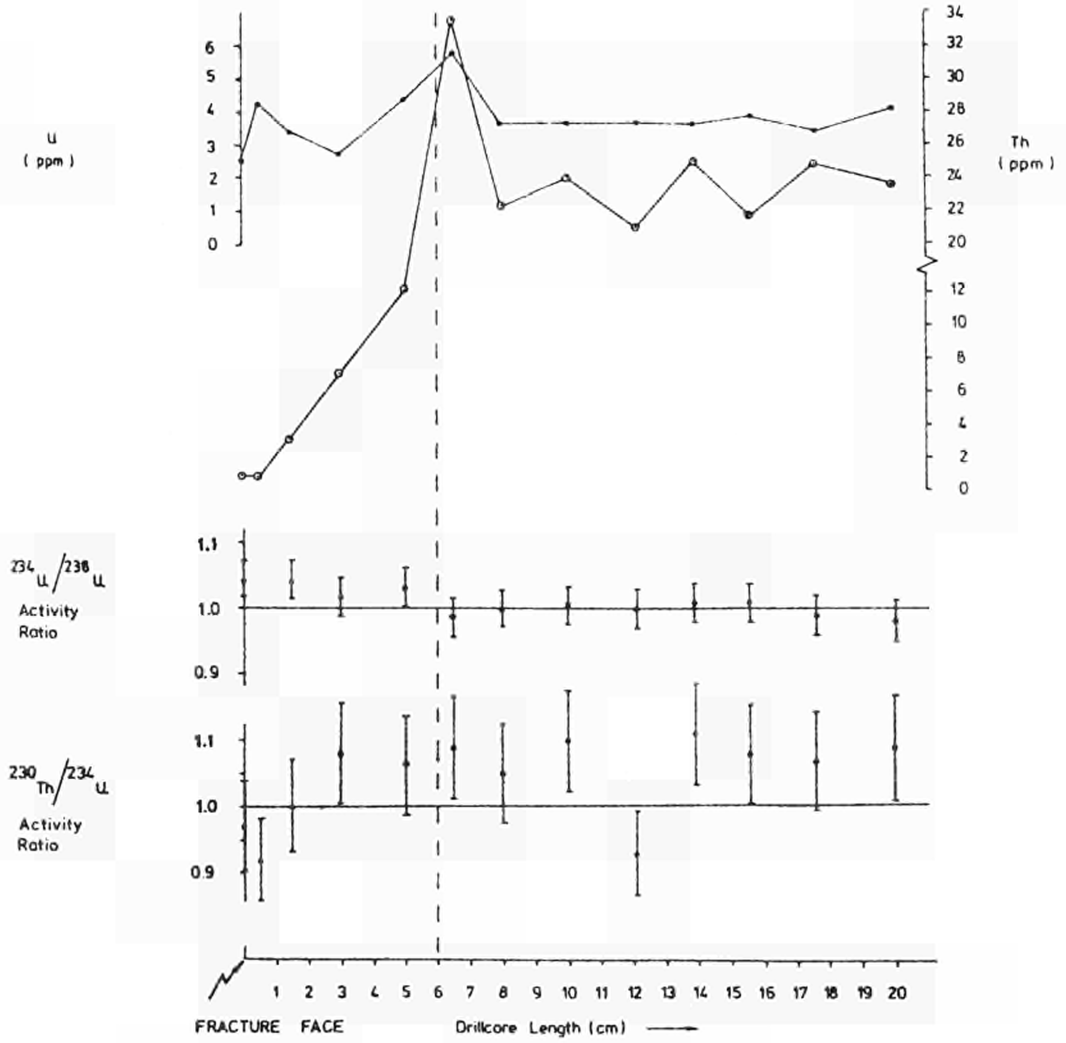

Figure 2: Contents and distributions of thorium and uranium and its daughter decay products (Böttstein Drillcore).

Within the granite portion of the drillcore the uranium content is uniformly distributed until the pegmatite is approached whereupon a small increase is observed. In the pegmatite the uranium decreases only to increase again some 3 cm from the fracture surface: a small decrease occurs at the fracture surface. The thorium is essentially sympathetic to that of uranium except that in the pegmatite a continuous decrease is observed.

As inferred by the mineralogy, the granite represented by this part of the drillcore has been subjected to hydrothermal temperatures in association with the emplacement of the adjacent pegmatite and aplite horizons. This appears to have remobilized and removed part of the available uranium in the rock resulting in low but uniform levels within both the granite and pegmatite. The observed increase of uranium and thorium at the granite/pegmatite contact may be due to limited remobilisation and concentration of both elements marginal to the pegmatite.

The $^{234}U/^{238}U$ ratio is unity for most of the core length although a slight increase is observed close to the fracture face. The above discussion of the Kråkemåla $^{234}U/^{238}U$ ratio distribution can again be applied in this case but the degree of uranium mobilisation involved is obviously less. The $^{230}Th/^{234}U$ results for Böttstein exhibit a value sligthly greater than unity except close to the fracture. This presents an obvious contrast to the Kråkemåla core and suggests solution to rock transfer of ^{230}Th produced by the decay of ^{234}U in solution. The difference between the Kråkemåla and Böttstein $^{230}Th/^{234}U$ results could be partly explained by a much more rapid fluid transport through the Kråkemåla core than in the Böttstein core.

Grimsel Drillcore

The uranium distribution along the drillcore length varies irregularly between about 5 and 9 ppm and this is even more accentuated by the thorium which ranges from 18 to 26 ppm. This variation is not affected by the fracture and can be explained by mineralogical inhomogeneities. There is no obvious relationship between the uranium and thorium, which suggests that the uranium and thorium contents are controlled by radioactive minerals which are distinctly uranium or thorium-bearing. Alternatively, it may reflect a redistribution of uranium within the rock; small additions of uranium are suggested by a mean Th/U ratio of 2.96. In contrast thorium has probably been immobile and has retained its original signature.

The consistent isotope values around unity indicate little or no isotopic mobilisation and thus an absence of rock/water interaction within the interval of the last 2 Ma. In all probability this fracture is young, having occurred at any stage from Alpine to recent times. A fairly recent joint may not have had time to react sufficiently with the groundwater which is now characterized by a chemical and isotopic signature obtained from other parts of the granite bedrock.

CONCLUSIONS

Although the data are incomplete, the most important conclusions resulting from this study are:

1. Two out of three of the investigated samples indicate that naturally-occurring uranium radionuclides have been remobilised by rock/water interaction processes within normal compact granite marginal to a water-conducting fracture zone at repository depths. Thorium does not exhibit mobilisation under the same conditions.

2. Rock/water interaction has taken place under predominately reducing conditions within measureable geological time, i.e. within the last 0.5 Ma as determined by the ^{238}U - ^{234}U - ^{230}Th decay series and may still be active at the present time.

3. Isotopic movement has been mostly from the granite to the fracture zone through distances of at least 40 cm.

4. Some radionuclide movement has also taken place from the fracture zone (via the groundwater) into the granite; the extent of penetration has been from 1-3 cm and this measure could therefore act as an upper limit in migration models. However, it may be an important prerequisite for penetration that the fracture system has been previously subject to hydrothermal processes resulting in a zone of enhanced porosity around the fracture. Furthermore, the mineralogical alteration products would make the rock more conducive to radionuclide sorption/retardation mechanisms.

5. Sorption and isotopic fractionation has occurred at the fracture/groundwater interface in association with fracture zone minerals such as hematite, chlorite, clay minerals and FeOOH-oxides. The major source of these radionuclides is believed to be the groundwaters.

6. It is not known at the moment the mechanism of the radionuclide migration, i.e. by fracture-flow or by matrix diffusion processes. Some indication may be obtained when the data are complete.

ACKNOWLEDGEMENTS

This project was jointly funded by the Swedish Nuclear Fuel Supply Company (SKB) and the Swiss Nationale Genossenschaft für die Lagerung Radioaktiver Abfälle (NAGRA), whose support at all stages of the study is gratefully acknowledged. With regards to the Swiss samples and for constructive comments on the manuscript, the considerable help of Dr. Urs Frick (NAGRA) is also acknowledged.

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DOCUMENT DE TRAVAIL

31 Octobre 1985

GROUPE DE TRAVAIL SUR LES ANALOGUES NATURELS

Première réunion les 5, 6 et 7 novembre 1985

LES GITES MINERAUX :
CONDITIONS LIMITES DE L'EVOLUTION DES STOCKAGES DE DECHETS RADIOACTIFS EN MILIEU GRANITIQUE ?

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LES GITES MINERAUX : CONDITIONS LIMITES DE L'EVOLUTION DES STOCKAGES DE DECHETS RADIOACTIFS EN MILIEU GRANITIQUE ?

J.F. SUREAU

L'un des principaux problèmes posés par les stockages de déchets radioactifs de longue vie dans des formations géologiques est d'évaluer leur comportement à long terme vis-à-vis du milieu dans le cas de libération des radioéléments.

Une façon de prendre en compte de longues périodes de temps ainsi que d'importants volumes de roches est de considérer des objets géologiques naturels (systèmes hydrothermaux, gisements minéraux) qui, par leur mise en place ou leur altération peuvent constituer des analogues de scénarios possibles de migration d'éléments chimiques dans l'environnement d'un stockage (champ proche et lointain).

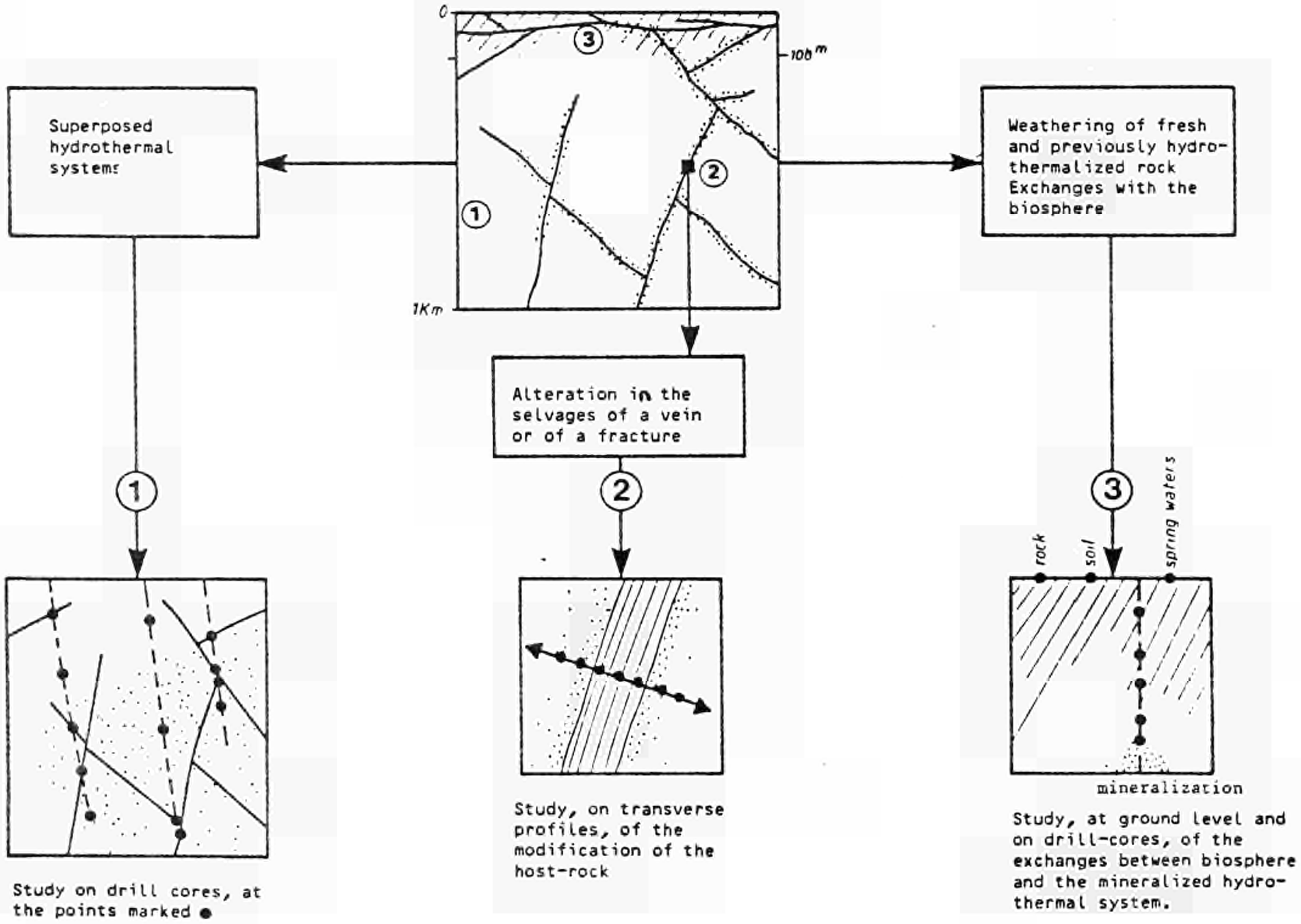
Certains gîtes minéraux présentent dans cette optique de nombreux caractères qui les rapproches des sites de stockages : nature de l'encaissant (principalement pour le granite), taille, morphologie, caractères géochimiques des éléments présents, durée des phénomènes d'évolution. Par contre des différences sont irréductibles, par exemple la nature minéralogique et chimique de la "source" qui oblige à réaliser une double analogie à la fois sur les mécanismes mis en jeu et sur les éléments chimiques impliqués lorsqu'ils ne sont pas naturellement présents (Transuraniens). Il n'existe donc pas de modèle analogue naturel complet. Il est nécessaire de réaliser une sélection dans les scénarios pour adapter son choix au meilleur site naturel de migration. L'analogie peut alors s'établir par le contexte géologique choisi (milieu granitique fracturé) par les mécanismes physico-chimiques mis en jeu (altérations, hydrothermales et météoriques) et par les éléments chimiques impliqués (terres-rares, U, Th, Cs, Co ...) (cf. figure). A ce stade de l'étude deux approches peuvent être proposées :

- Une approche statique qui consiste à dresser le constat de la migration des éléments à la suite du déséquilibre chimique entre le gîte minéral et l'encaissant. Les paramètres majeurs alors le volume de roche et/ou le temps d'évolution. Cette approche permet sur de grands volumes (km^3) et de longues périodes de temps (100 000 ans - 1 MA) d'approcher une valeur résultante de processus élémentaires dont l'inventaire est quasi impossible sans diminuer considérablement le volume d'investigation.

- Une approche dynamique qui consiste a isoler des processus géochimiques responsables de la mise en place des minéralisations ou de leur altération, afin d'en mesurer les conséquences sur la migration des éléments. Cette approche permet d'isoler et de quantifier les paramètres physico-chimiques réglant la dissémination. Cette démarche d'identification des phénomènes, d'analyse et sélection des paramètres doit permettre d'approcher le comportement dynamique des éléments chimiques analogues soumis aux aléas d'un contexte géologique. Le choix d'un gîte minéral permet, en accentuant les constrastes géologique entre encaissant et minéralisation, de recueillir des données analytiques sur des éléments rares dans un environnement géologique banal (TR, Zr, Nb, ...).

ALTERATION SYSTEM	SCALE OF STUDY	TEMPERATURE RANGE	HYDRODYNAMICS		CHEMICAL EQUILIBRIUM CONDITIONS	TYPE OF NATURAL ANALOGUE
			flow rate	volume of fluids		
Pervasive hydrothermalism 1	10^3 m	100 - 200°C	slow	large	slight disequilibrium	retention by a fractured granitic formation (near-and far-field)
Fracture-controlled hydrothermalism 2	m	100-200°C	fast	moderate	strong disequilibrium	migration of elements at the selvages of fractures (near-field)
Low-temperature alteration 3	10^2 m	< 100°C	slow	large	physicochemical fronts-controlled variable aquilibria	dispersion of elements (far-field)

Systems of alteration in a fractured granite



Study on drill cores, at the points marked ●

Study, on transverse profiles, of the modification of the host-rock

Study, at ground level and on drill-cores, of the exchanges between biosphere and the mineralized hydro-thermal system.

Dans les deux approches considérées la recherche entreprise se doit de réunir des données quantifiées rapportées à un volume (roche ou minéral réactant).

L'étude des gîtes minéraux comme analogues naturels de stockages de déchets radioactifs de haute activité n'a pas pour vocation de reproduire fidèlement un scénario de migration, mais elle se doit de fournir des données qui seront considérées comme des limites quantifiées de l'évolution d'un système à une échelle de temps et de volume choisie.

La réduction à l'essentiel des phénomènes rencontrés au cours d'une histoire complexe doit permettre une transposition des paramètres moteurs des transformations dans des modèles de sureté.

L'une des contributions importantes de l'étude des gîtes minéraux comme analogues naturels, et peut être la plus immédiate, réside dans la comparaison des paramètres mesurés avec les données obtenues par des codes de calculs dans le but de tester le pouvoir prédictif des simulations numériques.

C'est dans ce sens que les processus engendrés par les gîtes minéraux peuvent être considérés comme une bonne approche des conditions limites d'un système à évolution lente tel qu'un stockage de déchets rédioactifs en formation géologique.

WHAT CAN THE EARTH SCIENCES PROVIDE

(Notes for Analog W/S Brussels November 1985)

by

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Introduction

I have widened the scope of my presentation from only analogs to the inclusion of large scale experiments for model validation since this was included in one of the questions posed of the modellers. The Canadian Underground Research Laboratory (URL) is described as an example. Others are reviewed in the paper by Mather and Sargent (1985) presented at the Royal Society (London) discussion meeting on "The Disposal of Long Lived and Highly Radioactive Wastes.

My presentation on the use of analogs will be formulated after I have heard the presentations from the modellers on the first day of the workshop. I have been requested by the organizers to make this a controversial talk! An element I intend to emphasize is that the use of analogs is often a "double edged sword" i.e. there are often conflicting analogs that can be cited to support or undermine an assessment model for the behavior of a nuclear fuel waste disposal vault. I believe this theme will introduce the right degree of controversy needed to stimulate discussion amongst us all. It also will lead to a clearer understanding of what is needed to fully describe both the analog and the disposal concept, thereby ensuring they are sufficiently similar to justify their use to support the models and time extrapolations needed.

The Canadian Underground Research Laboratory (URL)

The URL facility, including a vertical access shaft, a ventilation raise bore, and a main horizontal experimental level, has been excavated to a depth of 254m, approximately 245m below the water table in a previously undisturbed rock mass. One of the unique features of the URL project, compared with similar experimental facilities in other countries, is the hydrogeologists are monitoring the hydrogeological conditions within a large volume of rock surrounding the URL excavation site prior to, during, and after the excavation of the shaft and underground workings. The information obtained from investigations carried out prior to any excavation has been incorporated into various numerical computer models that describe the hydrogeology of the study area. These models have been used to predict the three-dimensional piezometric drawdown that will occur in the rock mass during and after excavation of the underground facility. When these predictions are compared with the results of the continuous hydrogeological monitoring being carried out during and after excavation, researchers will be able to assess how well the models have actually represented the three-dimensional hydrogeological conditions of the rock mass surrounding the URL excavation site. This validation exercise is a major step towards the development of reliable models with which to predict solute transport through large volumes of plutonic rocks.

Detailed investigations have been underway since 1980 to determine the three-dimensional physical and chemical hydrogeological characteristics to depths of 500m within a study area 4.8km^2 in size encompassing the URL excavation site (Davison, 1984). Over 130 boreholes, including 25 to depths ranging from 160m to 1090m, have been drilled, logged, tested and instrumented to accomplish this.

Assimilation of the fracture information obtained from the entire network of boreholes revealed that three major extensive sub-horizontal fracture zones were present within the rock mass. It has been found that these zones largely control the movement of groundwater at the study area. Except for these distinct extensive fracture zones, the rock mass is relatively unfractured, with fracturing being slightly more pronounced near the ground surface. The URL shaft has been excavated through the upper fracture zone, which was encountered between 110m and 113m in the shaft, but stops above the second zone of intense fracturing. The hydrogeology of these two fracture zones has been studied in considerable detail, using a wide variety of borehole-testing techniques, including single-borehole straddle-packer test and large-scale multiple-borehole hydraulic pressure interference test (Davison, 1984). The results of this work have revealed that a complex pattern of permeability exists within each of the two fracture zones, and that these permeability distributions control the patterns of hydraulic head and groundwater chemistry.

Comparison between the recorded inflow rates to the shaft and the calculated values indicates that the model overestimates the inflow rates by approximately a factor of three (Davison and Guvanasen, 1985). Also, the model indicates that the inflow rates will reach a maximum when the uppermost fracture zone is intersected by the shaft. Subsequently the model predicts that the inflow rates will gradually decline to a constant value. This overall trend appears to agree well with the recorded data. A comparison between predicted drawdowns and field measurements was conducted for boreholes within a 400m radium from the shaft. In most boreholes, the drawdown rate, the magnitude of the drawdown, and the temporal variation of the drawdown are fairly accurately predicted by the model (Figure 1). At any given time, discrepancies between the model's predictions and field measurements, in general, appear to be proportional to the radial distance from the shaft; the further away from the shaft, the smaller the discrepancy.

During shaft sinking, four instrument arrays, at depths of 15m, 62m, 185m and 218m, were used to monitor excavation-induced displacements, excavation-induced stress changes and rock temperature (Chan, Lang and Thompson, 1985). These depths were chosen on the basis of borehole geological information. The major objectives of this monitoring were (1) to evaluate and improve the ability of numerical models to predict the mechanical response of the rock-mass, (2) to assess the validity of the concept of a rock mass deformation modulus and, if possible, to back-calculate this modulus as a function of depth, and (3) to evalute the quality of the geomechanical instrumentation in order to determine further instrumentation needs for future field experiments. It can be concluded that in the rock mass at the URL, where the fracture spacing is comparable with the excavation dimensions, the concept of a single rock-mass deformation modulus may not be valid and some of the discrete fractures should be modelled using, perhaps, a discontinuum approach. More accurate extensometers are essential for geomechanical measurements in future URL experiments.

Thus the URL shaft sinking has tested the models used and in the case of the hydrogeologic model shown it to be conservative.

Analogs

This section will be prepared following the first day's presentations by the modellers.

Although most national nuclear waste disposal programs emphasize the disposal of vitrified waste from reprocessing, in recent years there has been a move in some countries towards considering direct disposal of used fuel. In the latter case the thermal transients are very long, in excess of 10^4 years. Therefore, for vaults in granite it will be necessary to consider the setting up of hydrothermal convective cells and the extent of kaolinisation.

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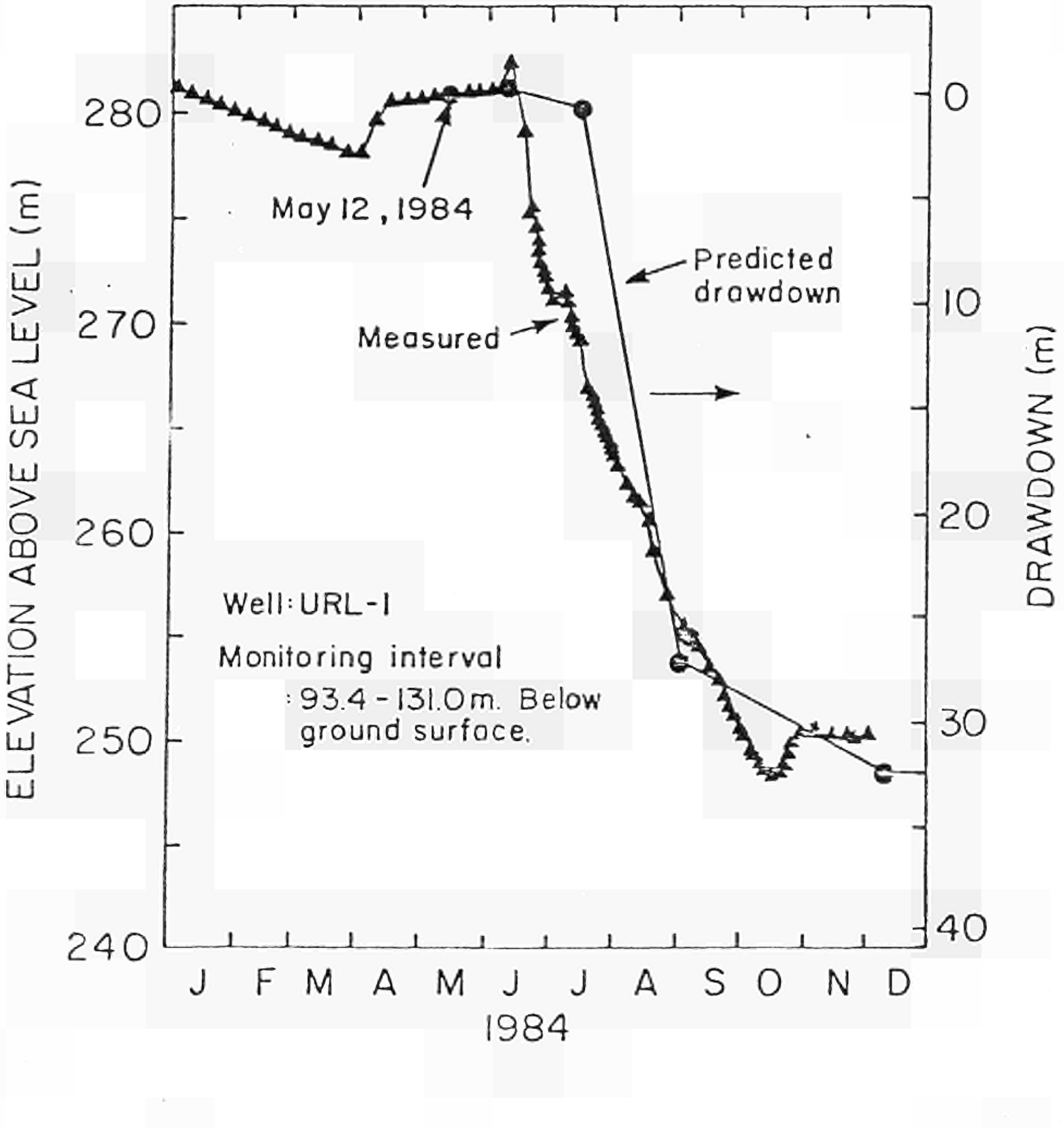

280
270
260
250
240
0
10
20
30
40
ELEVATION ABOVE SEA LEVEL (m)
DRAWDOWN (m)
May 12, 1984
Predicted drawdown
Measured
Well: URL-1
Monitoring interval
: 93.4 - 131.0m. Below ground surface.
J F M A M J J A S O N D
1984

FIGURE 1

ITALIAN ACTIVITY IN THE FIELD OF NATURAL ANALOGUES AND NATURAL EVIDENCE

A. BRONDI, F. BENVEGNU and C. POLIZZANO
ENEA, Italy

I. ORCIATICO SUBVOLCANIC BODY IN CLAY

Emplaced within clay (fig. 1);
Dimension : 1 x 0.5 km;
Depth : some hundreds meters;
Original temperature : about 800°C
Cooling time : many thousands years.

Effects on surrounding clay :

- Physical transformations :
  Re-crystallization, sharp loss of plasticity and very strong hardening of the first 0.5 - 1.5 m of clay with consequent micro-cracking and increased permeability.

- Chemical transformations :
  Important migration of highly mobile elements for distances up to 15 m because of hydrothermal circulation.
  Mobilized elements : Na > K = Rb and Ca > Ba > Sr (fig. 2 and 3).

- Mineralogical transformations :
  The mostly illitic original clay is turned into a K-feldspar-plagioclase-pyroxene-biotite assemblage in the first 0.5-1.5 m and into smectite and feldspars farther out up to 15 m from contact (fig. 4). Farther out original clay is intact and evidence of circulation (induced) is totally lacking.

Orciato may be used to demonstrate a worst case with regards to a radioactive waste repository.

II. IMPERMEABILITY OF CLAY DEMONSTRATED IN GEOTHERMAL FIELD (CENTRAL ITALY)

Trench clay basins in central Italy overlie geothermal fields (fig. 5).

The uprising of very hot (150 - 250°C) and high pressurized (20 - 60 atm) fluids is hindered by homogeneous clay in the center of the basin.

These fluids can cross the series in the marginal parts of the basin where the homogeneity of clay is affected by the progressively dominant sandy components.

Evidence of the outcoming of geothermal fluids at the borders of the basins are :

- outcomings of gases;
- occurrence of Hg mineralization;
- occurrence of chemical $CaCO_3$ deposits.

Alluvial distribution of cinnabar in the lateral part of the basin out of the axial part evidence that the outcoming of thermal fluids is accomplished there where clay becomes less homogeneous (fig. 6).

Clay demonstrates to be impermeable towards geothermal fluids. What about the situation of waste repository ?

III. FRACTURE PERMEABILITY OF CLAYS : OBSERVATIONS IN DEEP TUNNELS

Fracturing may induce a secundary permeability in clay. Direct observations of this condition may be done in tunnels excavated in clay. An investigation has been conducted in Italy interviewing people experienced in tunnel excavation.

Clays have been described as affected by secundary permeability in some cases. Water inflows into the gallery were noted in particular situations such as those corresponding to tectonic contacts, or intense tectonic crushing, or proximity to permeable levels.

Some cases, positive or negative are here illustrated :

- Carrito tunnel (fig. 7)
  Prepliocenic clay of the flysch formation.

  The clay is overthrusted by a water-bearing marly limestone. The whole area is interested by tectonic dislocution, which did not cause any recognizable difference in water percolation.

  Until the contact clay-limestone (overburden 300 m) the gallery resulted to be completely dry.

- Gran Sasso tunnel (fig. 8)
  Prepliocenic flysch clay overthrusted by Mesozoic limestone.

  Tunnel over 10 km long : 3 of them are made by marly clay. Maximum overburden is 1000 m.

  Water column is more than 600 m (> 60 atm). No difficulty during building; water inflow was limited to localized seepages.

- Hydraulic gallery of Disueri (Sicily) (fig. 9)
  Autochtonous prepilocenic (Tortonian) marls and clays passing to diatomitic marl and limestone on the upper part.

  Excavation completely dry until limestone was entered.

- Plio-pleistocenic clays

Some tunnels have been excavated. Fractures may be frequent. In spite of fractures the tunnels may have resulted dry as in the case of the Castiglione in Teverina gallery, 7.5 km long. In other cases seepage or water inflow have been observed. They can be ascribed to the occurrence of permeable beds or to the proximity to the topographical surface. In some case drilling put fractured clays or permeable beds in communication with overlying waters.

IV. PERMEABILITY OF FAULTS AND FRACTURES IN CLAY AS RESULTING FROM OBSERVATIONS IN OUTCROPPING CONDITIONS (fig. 10)

Fracturing in clay is easily and frequently observable at the surface because of the yellow colour bordering the fracture planes. This colour is due to the oxidation by percolating surficial water. It is developed downwards up to a depth of some tens of meters (1 - 4). Farther down no induced colour affects the gray clay. The limit of diffusion of the yellow colour probably coincides with the limit of secundary permeability of clay.

As far as the mechanism of oxidation is concerned field observations evidence : erosion causes unloading of clay affected by latent or closed fractures. Unloading makes latent fractures to be opened near the surface. Surficial water percolates into the fractures.

Very few faults in clay have been observed in field. They never showed yellow coloration. They are presumably impermeable.

V. RESISTANCE OF CLAY TO THE DESTABILIZING FACTOR OF ITS REDUCING CHARACTER. THE ORTE EXAMPLE

The reducing character is the principle advantage of clay as a geochemical barrier.

In the Orte series (fig. 11 and 12) clay levels are interbedded with sandy layers. These latter are oxided by penetrating oxigenated water from the surface. Clay levels, on the contrary mantain their original reducing character as :

- they are gray in colour as the underlying main clay body;
- they show the same content of trace elements as the underlying main clay body;
- U in the sandy layers is on the contrary presumably depleted with regards to the original content.

VI. MICRO-ORGANISMS IN CLAY

Micro-organisms give a major contribution in building and maintaining the reducing characters of clay, which assure the fixation of many radionuclides.

Micro-organisms have been found in :

- clay of Monterotondo quarry;
- clay of Orte quarry;
- clay of sediments of deep ocean (GME and SNAP sites).

E' STATO ACCERTATO CHE UNA MASSA MAGMATICA AD ALTA TEMPERATURA INTRUSA IN UNA FORMAZIONE ARGILLOSA HA PRODOTTO IN QUESTA SENSIBILI VARIAZIONI SOLO PER UNO SPESSORE MINIMO.

FIG. 1

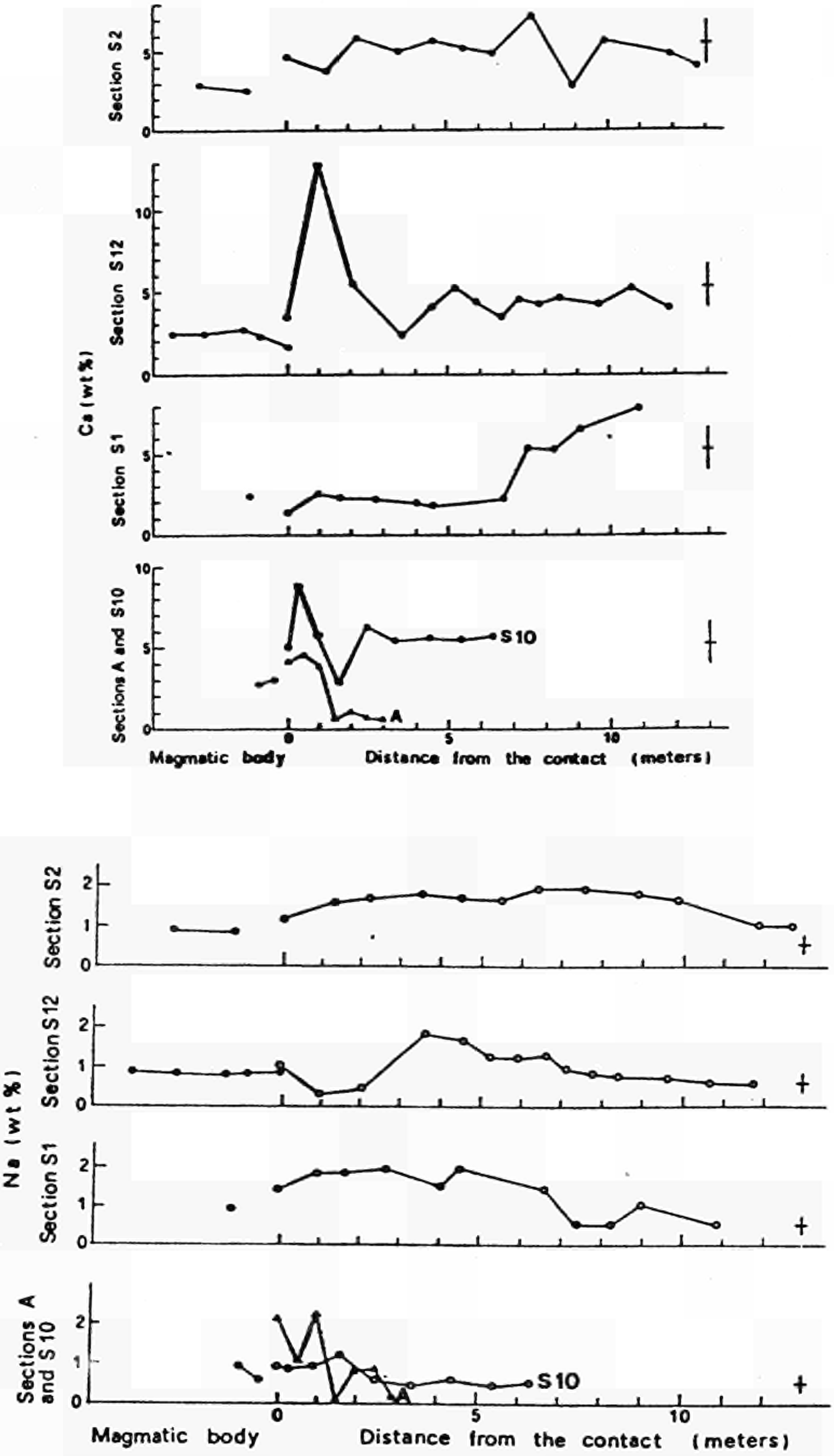

Ca (wt %)
Section S2
Section S12
Section S1
Sections A and S10
S10
A
0
5
10
Magmatic body
Distance from the contact (meters)
Na (wt %)
Section S2
Section S12
Section S1
Sections A and S10
S10
A
0
1
2
0
5
10
Magmatic body
Distance from the contact (meters)

FIG. 2

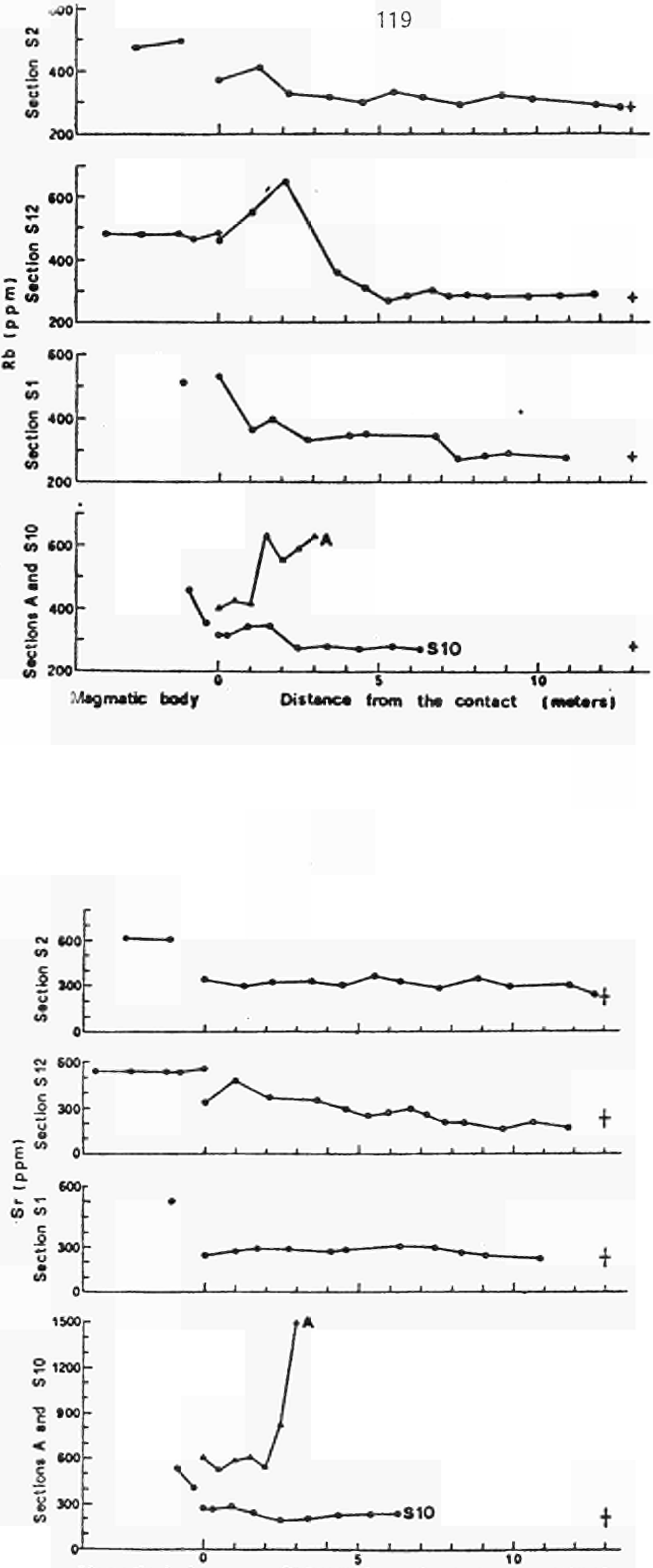

Rb (ppm)
Section S2
Section S12
Section S1
Sections A and S10
A
S10
Sr (ppm)
200
400
600
0
300
900
1200
1500
0
5
10
Magmatic body
Distance from the contact (meters)

FIG. 3

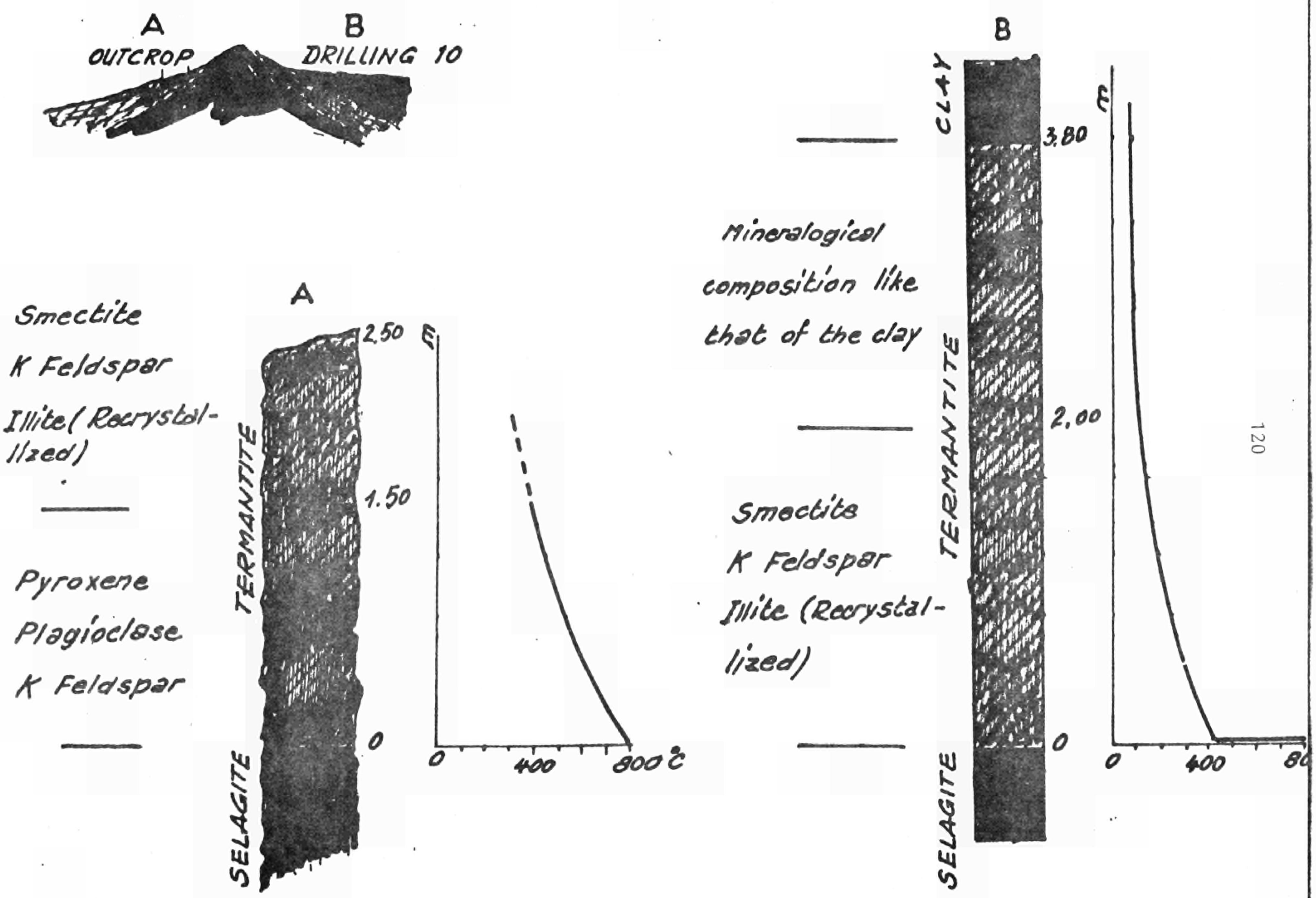

A
B
OUTCROP
DRILLING 10
Smectite
K Feldspar
Illite (Recrystal-
lized)
Pyroxene
Plagioclase
K Feldspar
A
TERMANTITE
SELAGITE
2,50
1.50
0
m
0
400
800 °C
Mineralogical
composition like
that of the clay
Smectite
K Feldspar
Illite (Recrystal-
lized)
B
CLAY
TERMANTITE
SELAGITE
3,80
2,00
0
m
0
400
80

FIG. 4

ROLE OF CLAY AS AN IMPERMEABLE OBSTACLE TO GEOTHERMAL FLUIDS UPRISING TO THE SURFACE

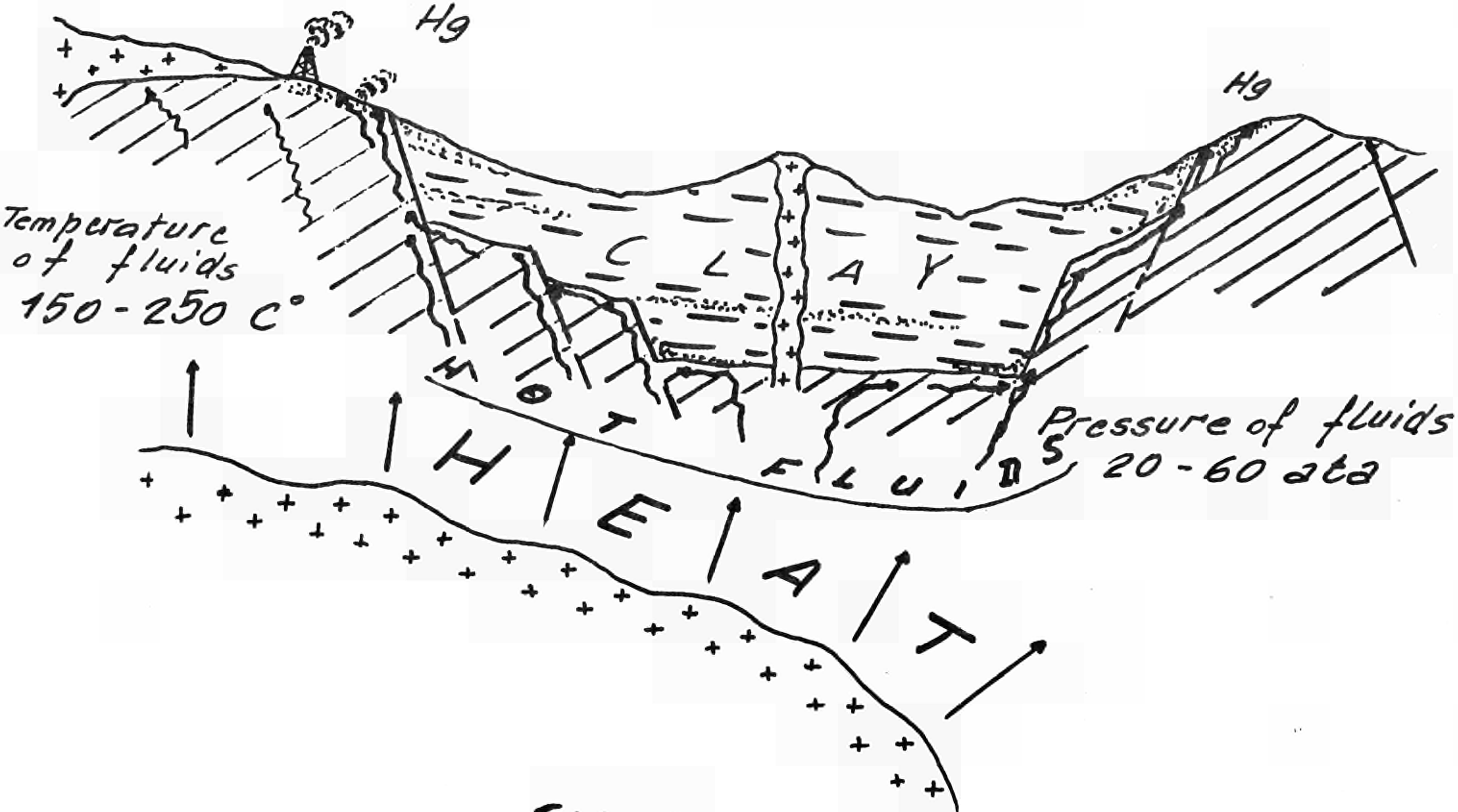


FIG. 5

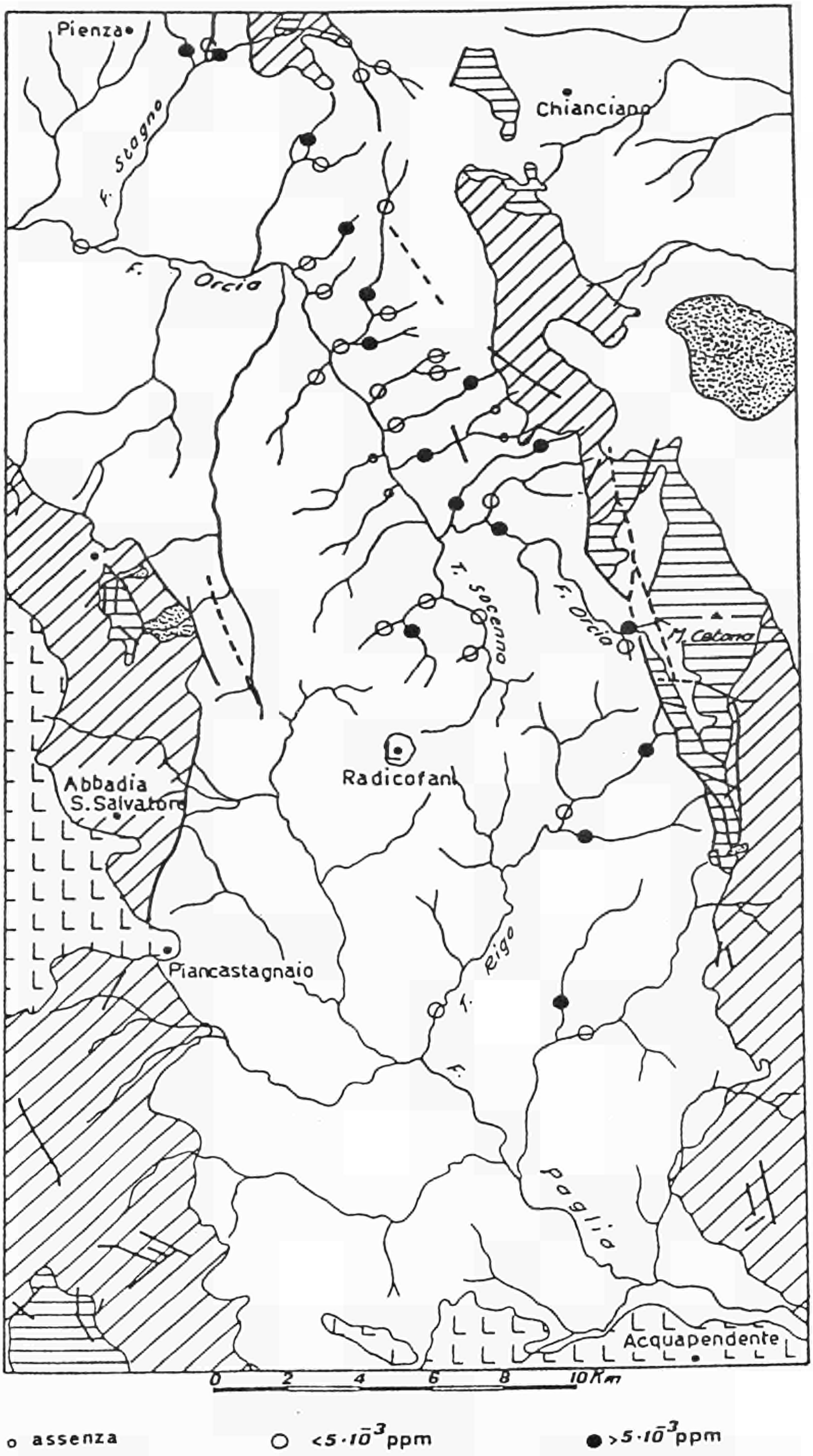


Fig. 6 - Concentrazioni di cinabro nei sedimenti fluviali del F.Orcia e del F.Paglia

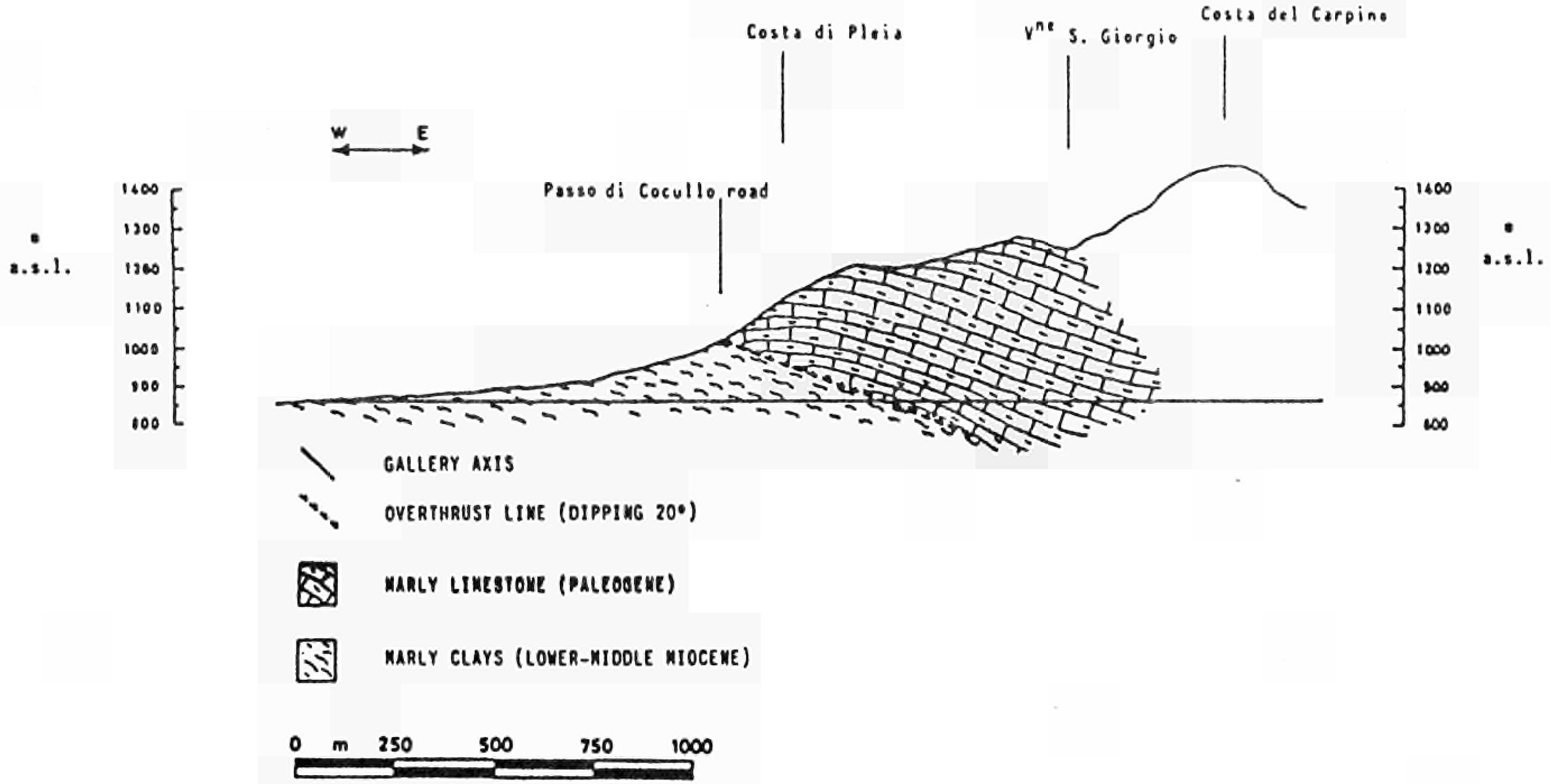


FIGURE 7 : CARRITO TUNNEL

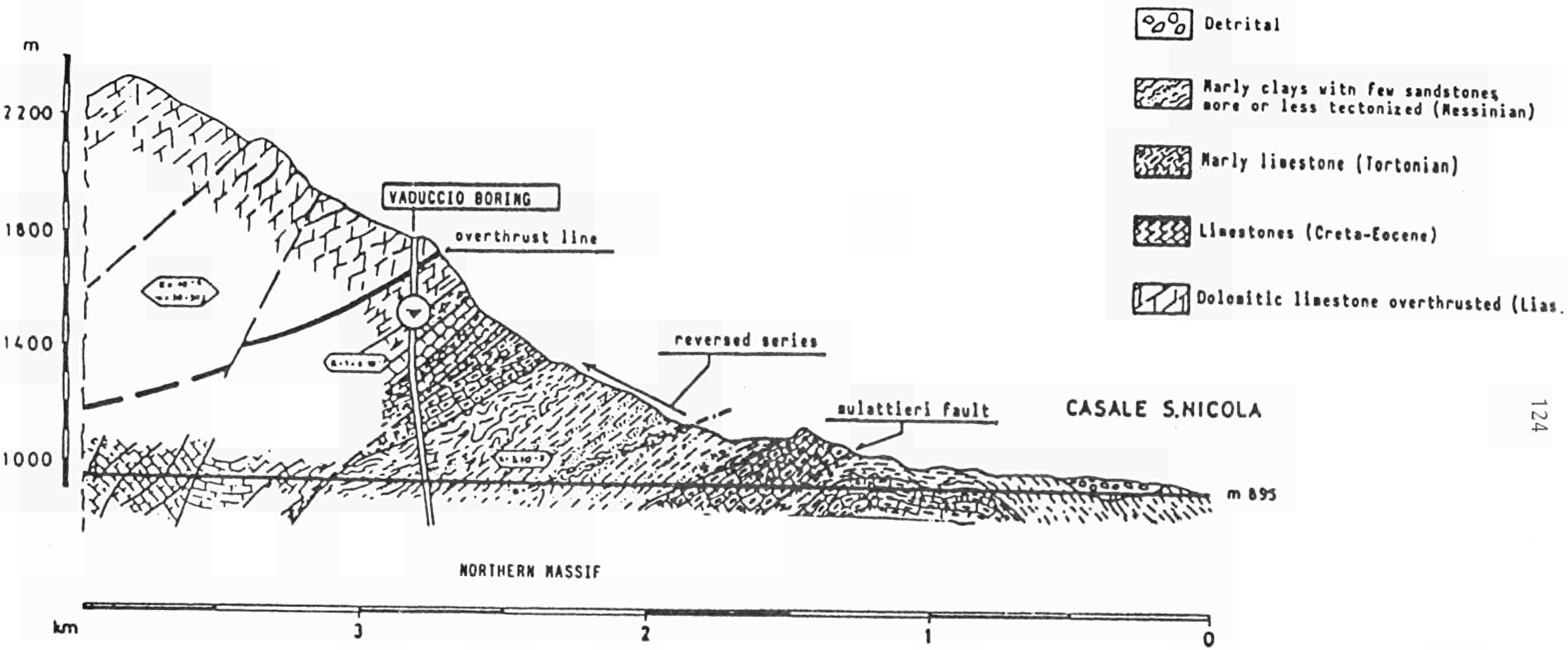


FIGURE 8 : NORTHERN STRETCH OF THE GRAN SASSO TUNNEL - GEOLOGICAL SIMPLIFIED SCKETCH

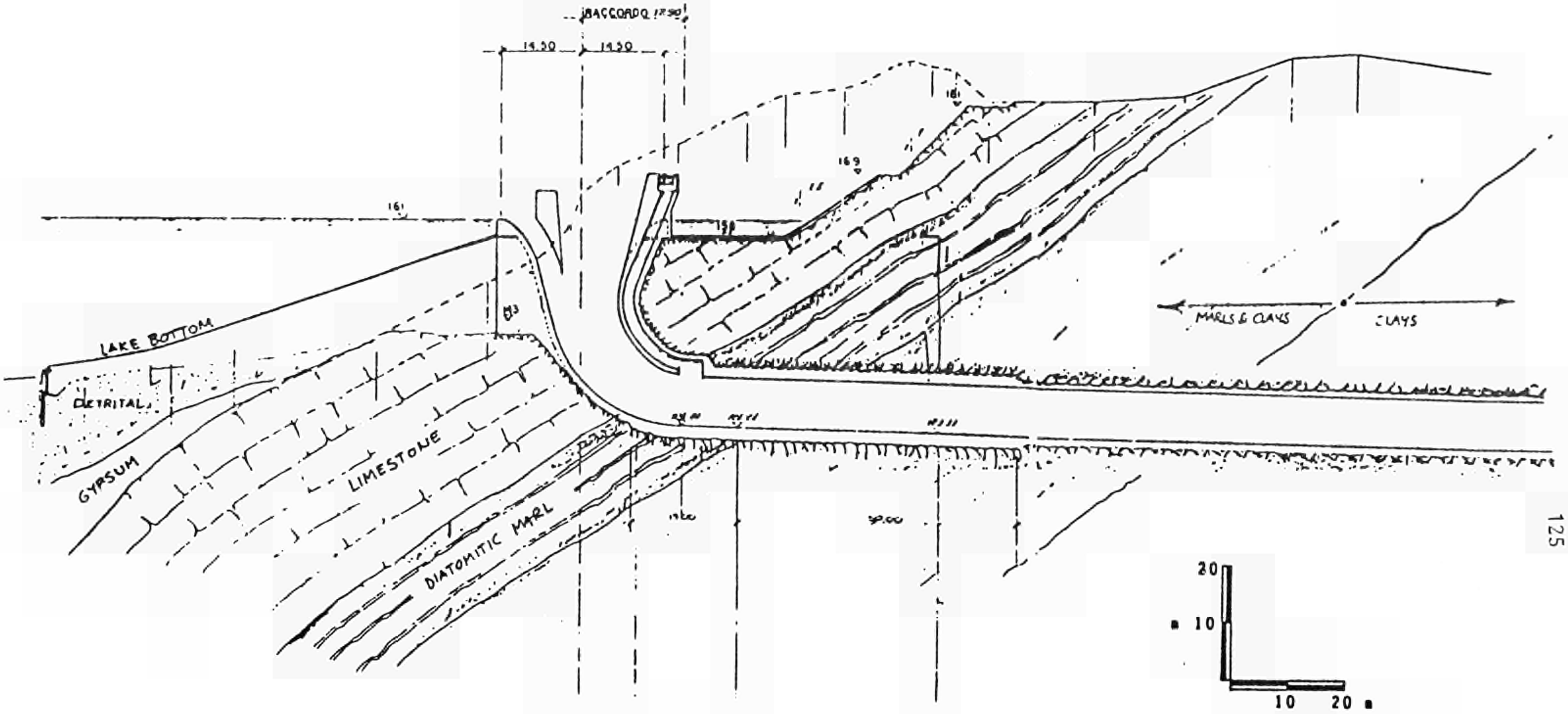
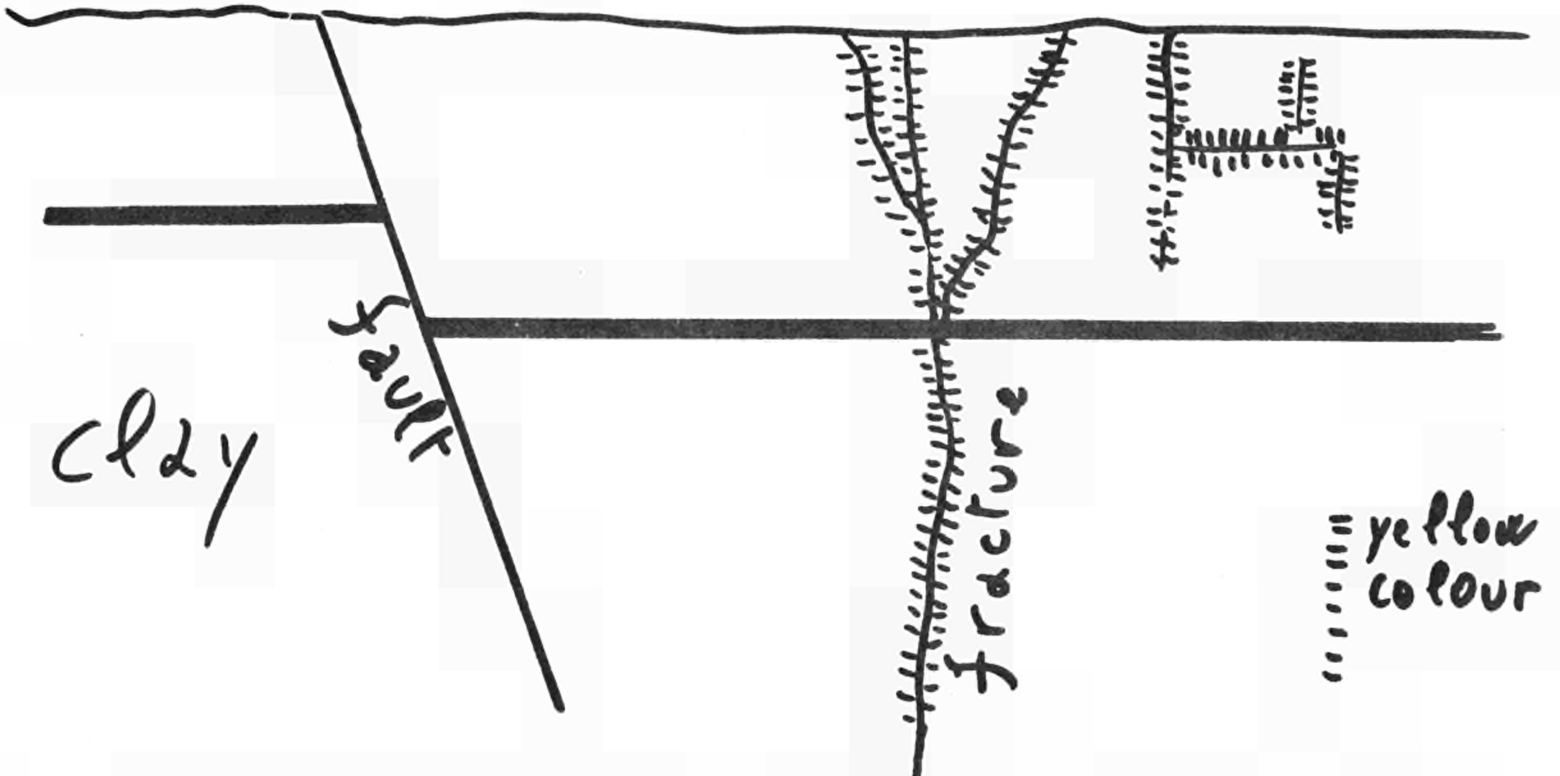
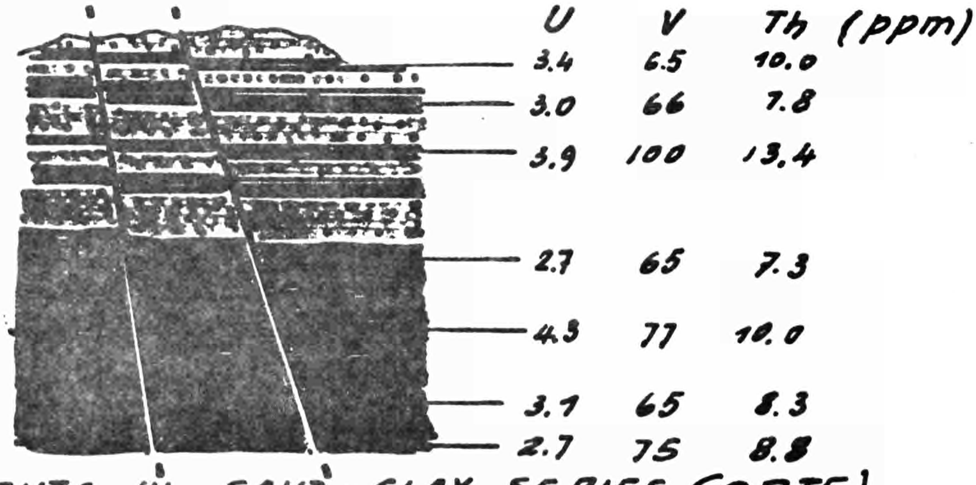


FIGURE 9 : DISUERI TUNNEL

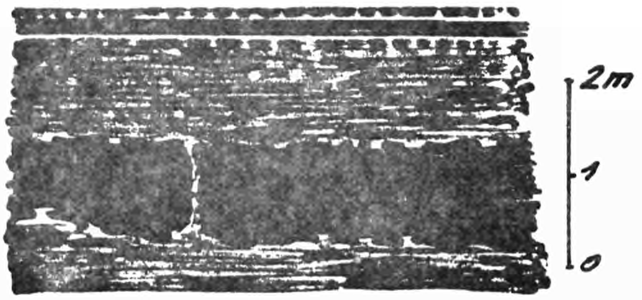


Oxidation in surficial fractures
Non oxidation in faults
FIG. 10

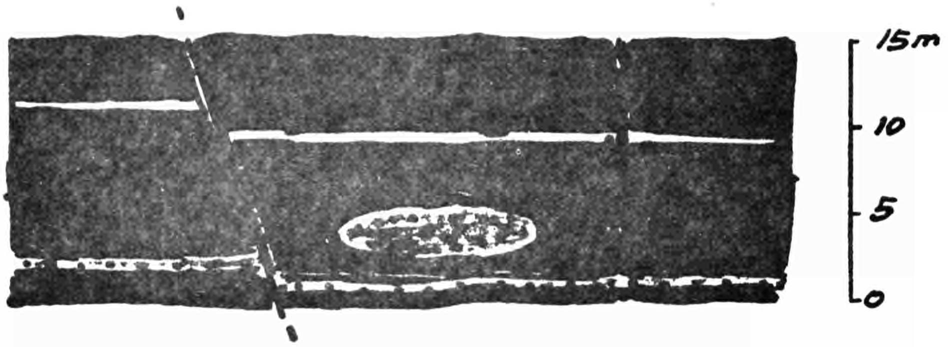
REDUCED LEVEL AT THE BASE OF A SANDY DEPOSIT



TRACE ELEMENTS IN SAND-CLAY SERIES (ORTE)



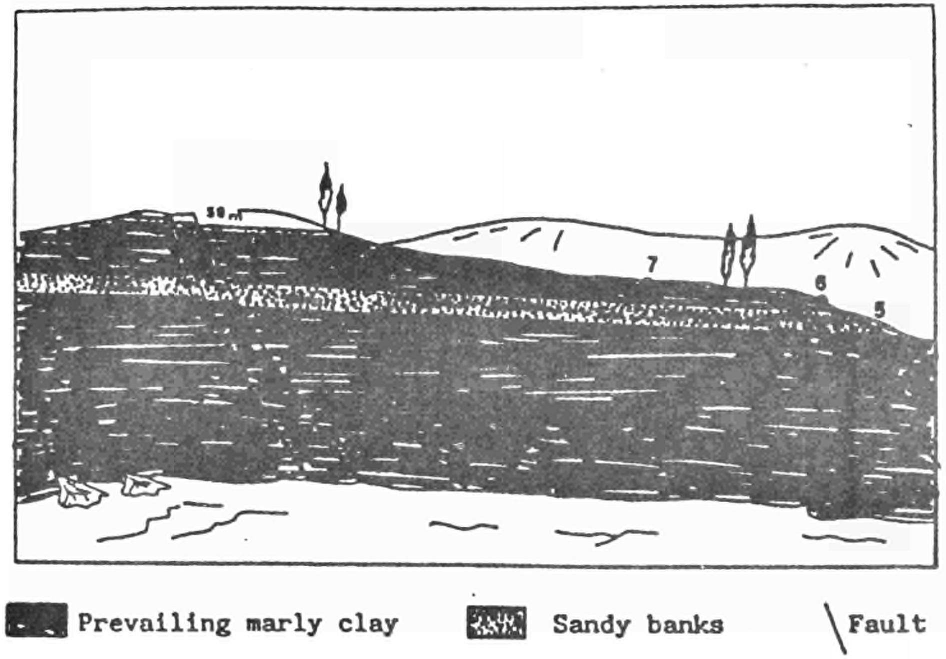
PRECIPITATES AT SAND-CLAY BOUNDARY (ORTE)



OXIDATION BANDS IN CLAY FRACTURE (NARNI)

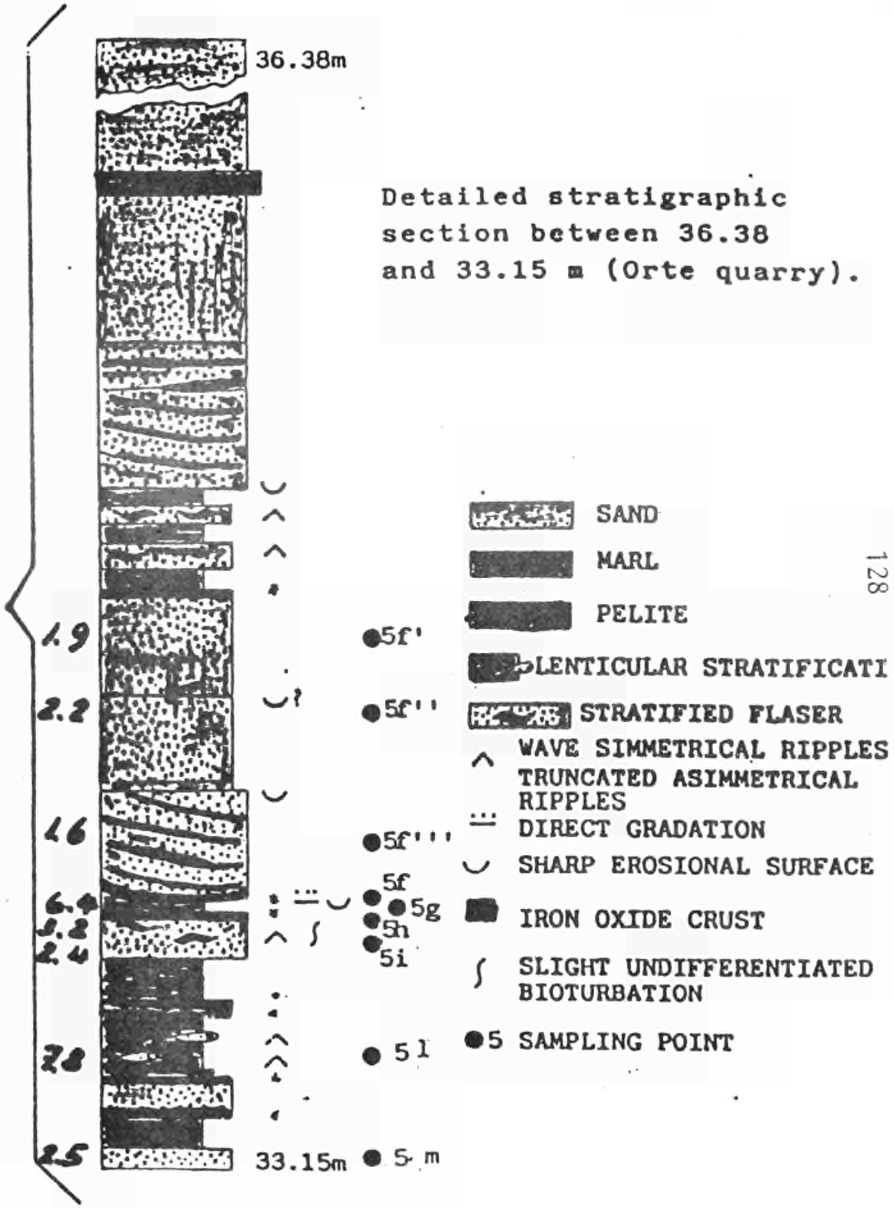
FIG.11

URANIUM DISTRIBUTION IN THE SANDY CLAY UPPER SERIES OF ORTE



Uranium concentration in ppm

SAMPLING MAP



Detailed stratigraphic section between 36.38 and 33.15 m (Orte quarry).

FIG. 12

Natural Analogues Working Group, Brussels, 5 to 7 November 1985

Evidence for field measurements of retardation factors for U/Th/Ra radionuclides

The suitability of a given site for radioactive waste disposal cannot be established reliably in the absence of realistic data relevant to the predictive models designed for safety assessment. Many parameters characteristic of a given geological formation such as permeability, porosity etc. can be measured directly in the field or from field specimens. However many others such as sorption parameters for different radionuclides have not been measured directly until recently. Instead short time-scale laboratory experiments have been carried out yielding data which either cannot be extrapolated reliably to the longer time scales required or cannot be used to model field conditions because of the poorly controlled, artificial and simplistic experimental conditions. Therefore, there is a need to design methods of direct field measurement of sorption parameters such as retardation factors, phase partition coefficients etc.

The simple concept of K_D or retardation parameters required for most radionuclide migration modelling cannot be directly applied to multi-process phenomena occurring in nature without detailed understanding of the processes involved. Thus, it is necessary to study the dependence on Eh, pH, groundwater chemistry, the properties of accessible minerals, groundwater colloids, organic complexes and alpha-recoil mechanism. The coefficients may vary with time due to the long term effects of matrix diffusion and the slow alteration of accessible surfaces. Thus, it becomes imperative to establish a hierachy of principal processes contributing to the sorption of chemicals species in a given groundwater/rock system in order to obtain a meaningful distribution coefficient and therefore, relevant input data for safety assessment codes. To define these processes in detail requires careful generic studies in geochemical systems which could be used as analogues to potential repository site and may even help in defining suitable geological systems for the purpose.

In their short review article on natural geochemical analogues presented at the Chicago workshop, Airey and Ivanovich (1984) attempted to define the essential characteristics of geochemical analogue, to discuss the role of such systems in studying the scientific basis for the long-term prediction of radionuclide transport, and to assess methods of relating findings from the geochemical analogue to the proposed repository site. The authors defined a geochemical analogue as a geological entity exhibiting spatial and temporal discontinuities. They also classified the geochemical analogues according to function:

(1) to elucidate processes or assess mechanisms which affect retardation factors over long periods;

(2) to define the limits of migration of indicator elements under conditions which are frequently more rigorous than those anticipated under repository operating conditions; and

(3) to examine the validity of proposed geochemical analogues to ultra-low abundances of transuranics and fission products (eg Nd as geochemical analogue to Pu^{3+} etc).

Only the first of the above three items has been considered in this short presentation partly because it is the most relevant to the question of quantitative evaluation of input parameters to safety assessment codes, and partly, because the author has spent more time on this aspect of natural geochemical analogues in recent times.

Following the above approach, only a few examples of field work exist in which effective retardation factors have been measured or relevant data were obtained for the calculation of these parameters. These are summarised in the Table.

Although some of the parameters measured by different authors differ by one or two orders of magnitude, it is encouraging to note that the measured retardation factors for uranium and thorium are sufficiently large to confirm the existance of natural retardation processes active in the different geological media under consideration. However, it is not clear whether these apparent differences are a result of diverse geochemical and geological conditions in each case (most likely) or an artifact of assumptions in individual measurements. Perhaps the most disturbing observation is the high mobility of radium isotopes in anoxic brines (an observation made for saline portions of aquifers made earlier by numerous authors e.g. Cuttell et al, 1985).

These approaches encourage this author to think that the natural geochemical analogues have a crucial role to play in not only providing the qualitative data (examples of which are too numerous to consider here) but also in providing quantitative data for input parameters to safety assessment codes and in defining the criteria for selection of potential sites for high, intermediate and low radioactive waste.

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UK

November 1985

ABOUT THE PERMEABILITY OF FAULTS AND FRACTURES IN CLAY FORMATIONS

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ABSTRACT

Clay formations are being considered in a number of European countries as possible geological host rocks for radioactive wastes disposal. Risk analysis studies have pointed out that faulting of the formation followed by water intrusion could constitute a possible radioactivity release scenario.

In this context field studies were undertaken to investigate fractures and faults in clay formations.

The objectives of the present study, conducted on a number of samples taken from clay fractures, were: a) to date existing fractures where percolation of water has occurred, b) to study the diffusion profile on the various elements both sides of the fracture planes.

The results are presented for a series of samples taken from the quarry front of a surface clay formation in central Italy, where a number of fractures exhibiting clear traces of percolation were investigated.

The main achievements of the study were to understand the element migration mechanism in clay across a redox potential discontinuity and to estimate the order of magnitude of the active lifetime of the percolation phenomenon. This latter ranged between some tens to some hundreds years, depending on the considered profiles.

Two types of element concentration profile were identified: Cs, Te, U, Fe, having Kd values strongly dependent on the redox conditions show a stepwise profile in correspondence to the redox front. Co, which is weakly affected by the redox conditions of the medium, shows a more regular profile indicating a depletion near the water percolation plane.

1. INTRODUCTION

The geological formations chosen for hosting repositories of high-level radioactive waste must guarantee isolation from man's environment for extended periods of time. Of many lithological types examined, argillaceous rocks, when properly chosen, appeared among the most suitable geological media because of their plasticity as well as for their low hydraulic conductivity (Bonne et al. 1985).

Three main features make clay attractive as a host formation :

1) the high ion exchange capacity, which ensures a good retention for most of the radionuclides;
2) the intrinsic impermeability;
3) the capability of plastic response to the applied stresses.

The high retention coefficient of clay is a well-known property constituting a barrier against radionuclide migration.

Migration is also prevented by the lack of water movement within compact and homogeneous clays : a permeability as low as 10^{-9} - 10^{-10} m sec^{-1} allows a ground water displacement of a few meters per hundred thousand years, assuming an hydraulic gradient in a common range (0.1 - 0.01) (Bonne et al., 1979).

All these properties can guarantee the isolation of waste until the rock is physically homogeneous and integer.

In fact fracture permeability might be superimposed on the low intrinsic hydraulic conductivity so compromising the efficiency of the above mentioned retention (D'Alessandro and Gera, 1985). Although the possibility of permeable fracture formation in plastic clay is still an open problem (Legrand, 1976) faults and fractures are often seen in clays, not only in outcrops or quarry fronts, but also at depth (Chapman and Gera, 1984). In some cases traces of oxidation found along fissures in quarry fronts seem to indicate that the clay has been affected by ground-water circulation in the past.

The evidence of water percolation through the fractures poses an obvious question related to the lifetime of the phenomenon. Two alternative possibilities are given :

- the oxidation zones are formed over geological time at the original depth of burial as a result of water percolation through the formation; in this case they provide some indications about water movement in depth;

- the oxidation zones are formed rapidly and very close to the surface. In this case they would be of little importance for long-term waste containment since their formation should be regarded as a shallow phenomenon, able to affect a depth of only a few tens of metres.

The problem was tackled in precedent studies (Antonioli and Lenzi, 1984) (Saltelli and Antonioli, 1985) carried out on the plio-pleistocenic blue clays of Monterotondo (North of Rome) where in an active quarry front, several parallel fractures, sandwiched by two red-yellowish oxidation bands, were indicating the occurrence of oxidizing solutions circulation.

The analytical results showed that an oxidation process had been active along fissure borders with no effect on the mineralogical composition of the clay. The only recognizable effect was the change in the trace element content, such as cobalt, sulphur, cesium.

As expected, the total iron was higher in the oxidized than in the reduced zones, with the ratio FeII/FeIII increasing from the fracture to the blue-grey bulk.

Furthermore, the oxidated bands showed a higher retention capability with respect to Cs and Sr than the unperturbed clay.

A preliminary estimate of the life-time of the fractures, carried out on the basis of Sr migration time gave a figure of some hundreds years : thus the order of magnitude of the water circulation time through the fractured clays (i.e. the age of the fractures) seemed to pertain to hystorical, rather than geological time-spans.

Within the present study some results and findings coming from the above mentioned campaign are ckecked and discussed. New samples of clays showing significant oxidation bands (from the same Monterotondo's quarry) have been studied. A set of chemical analysis mainly focussed on the trace elements, allowed the mechanisms of migration to be interpreted. As a result the age of the fault as calculated in the previous study has been verified, and some useful general information about the diffusion phenomena inside clay has been drawn. Furthermore, a model for uranium migration through the fractured clay is proposed, which gives a good fit of experimental data.

For the sample C the activation analysis has only been used for defining uranium concentrations. Destructive chemical analysis (ETAAS and ICPES) was used for Co, Fe, Mn, Sr, V, Zn.

RESULTS AND DISCUSSION

Concentration profiles have been reported for iron, cobalt, manganese, uranium, cesium, tellurium (figs.3 to 8). For all the other elements it was not possible to correlate the profile of the concentration to the leaching phenomenon, either due to a flat profile or to an excessive point scatter.

The sampling scheme is reported in figs.1 and 2. On the first two samples (A and B) concentration elements were determined along a line perpendicular to the fracture plane. For the bigger one (C) three such sampling lines were taken (fig.2). The general trend of figs.3 to 8 exhibits an element enrichment in the oxidized zone, with the only exception of Co and Mn.

Although data points are very scattered for cobalt its depletion in the oxidized zone is rather clear in all the samples.

For all the other elements the enrichment can be explained as a migration from the bulk of the clay to the oxidized zone which is characterized by a higher retention capability (Antonioli e Lenzi, 1984).

Cobalt appears less sensitive to the redox potential and to the exchange capability. As can be expected, iron exhibits the more pronounced enrichment in the oxidized zone due to the precipitation of the colloidal Fe III hydroxide. It is reasonable to attribute part of the enhanced exchange capability of the clay to this colloidal ferric oxide whose concentration reaches 7% in the oxidized zone (Antonioli e Lenzi, 1984). The Cs and Te flat profiles in the sample B -contrasting with those of the sample A- can be explained by the older age of sample B, (larger oxidation band) which might have allowed an element re-equilibration. For the bigger sample (C) the differences in thickness of the oxidized zone are reflected by the shape of the different profiles, α being the sampling direction which crosses the halos in its thicker part and γ in the thinnest one. The manganese depletion in all the three profiles (α, β, γ) can be explained by the higher mobility of Mn in its oxidized form, and to the scarce sensitivity of MnO_4 to the exchange capability of the medium.

Uranium profiles were only determined on sample C (profiles α and γ) due to the very specific irradiation needed for the activation analysis. These two profiles suggest a local maximum concentration within the oxidized zone.

Fracture age assessment

One of the objectives of the present analysis is to estimate the time the fracture was effected by water percolation. Such an information can be obtained by looking at the thickness of the oxidized zone, or more in general, for a given element, by the thickness of the zone effected by diffusion of the same element (Saltelli and Antonioli, 1985). If transport is supposed to obey a simple Fick law

$$\frac{\partial c}{\partial t} = \frac{D\,\partial^2 c}{\partial x^2}$$

diffusion thickness L and diffusion time T are roughly correlated as :

$$L \simeq 2\sqrt{DT}$$

where D is an effective diffusion coefficient.

Table 1 has been obtained computing T from the above relationship, using best estimate values of D (see table 2) and L from the experimental profile.

Profiles			
U	39 - 203	--	0.2 - 97
Co	570 - 1015	?	1 - 36
Fe	194	16 - 99	--
Mn	1015	36 - 99	1 - 36
mean value	506	63	29

Table 1. Fracture age (a) based on migration profiles.

Element	Diffusion coefficient (cm^2/sec)
U	1.2 10^{-8}
Co	2 - 4.8 10^{-9}
Fe	2 10^{-9}
Mn	2 10^{-9}

Table 2. Diffusion coefficient values. From Lanza (1985)

In spite of the considerable scatter the above time spans give an idea of the fracture active lifetime, which seems to pertain to hystorical, rather than geological time scale.

Migration Model

Due to the considerable scatter in the data points for all the profiles a curve fitting exercise appears hardly possible. The difficulty is increased by the heterogeneity of the clay medium, going from an oxidized to a reduced end, which requires different parameters to be used for the different zones, e.g. a retention factor for the reduced zone and a different one for the oxidized. Actually where oxidized/reduced transition is continuous, the retention factor would be better described by a function of space and time ranging between these two extreme values. A complete model should account for the diffusion of oxygen inside the clay with consequent chemical reaction and for the diffusion of a typical metallic constituent outside the clay. In general the two fluxes will be coupled, the activity of the metal being a function of the oxygen activity and viceversa. In fact the chemical interaction between the metal and the substratum will be a function of the oxygen content. For instance most of the metals are likely to absorb on the ferric oxide which is the main product of the oxygen chemical reaction. Without pretention of giving a full description of the system a qualitative fitting was attempted with a simplified model which accounts for :

a) oxygen diffusion inside the clay with fast chemical reaction, independent of the clay constituents diffusion;

b) metal diffusion outside the clay with fast chemical reaction with the substratum, the equilibrium constant being a function of oxygen concentration.

The hypothesis a) is probably an over simplification, as the oxygen is strongly reacting with iron, which is itself diffusing. If the oxygen uptake is considered as a fast reaction, the transport can be modelled with an effective diffusion coefficient rather than with kinetic constant.

The assumption b) has been introduced in the model through the relationship

$$R(x) = R_1 + (R_2 - R_1)\,\frac{C_{O_2}(x,t)}{C^{\circ}_{O_2}} \qquad (1)$$

where

$R(x)$ is the metal retention coefficient at a distance x from the interface (adimensional)

R_1 is the limiting value for the oxidized zone

R_2 is the limiting value for the reduced zone

C_{O_2} is the oxygen concentration (M)

$C^{\circ}_{O_2}$ is the oxygen concentrations at the water-clay interface.

The retention R can be also defined as :

$$R(x) = \frac{\bar{C}_M}{C_M} \qquad (2)$$

where $\bar{C}_M$ and C_M are the metal concentrations in the substratum and in the solution respectively, expressed in the same units (M).

Eq.1) is coupled with the transport equations

$$\frac{\partial C_M}{\partial t} = \frac{D_M}{R(x)} \frac{\partial^2 C_M}{\partial x^2} \qquad (3)$$

$$\frac{\partial C_{O_2}}{\partial t} = D_{O_2} \frac{\partial C_{O_2}}{\partial x^2} \qquad (4)$$

and the boundary conditions

$$\left.\begin{array}{l} C_{O_2}(0, t) = C^\circ_{O_2} \\ C_M(0, t) = C^\circ_M \end{array}\right) \quad \text{(interfacial concentrations)}$$

$$\left.\begin{array}{l} C_{O_2}(x, 0) = C^b_{O_2} \\ C_M(x, 0) = C^b_M \end{array}\right) \quad \text{(bulk concentrations)}$$

In the above formulas D_{O_2} is an effective diffusion coefficient, incorporating a retention factor, while for the metal the effective dispersion is explicitely calculated as $D_M/R(x)$, where D_M accounts for the molecular diffusion, and for the so-called tortuosity factor.

The uranium curves have been chosen for the fitting exercise, as they exhibit a more regular trend, going from a plateau inside the clay, to a concentration increase in the oxidized zone and decreasing again at the fracture plane (fig.8). The fit for the two profiles α and γ is plotted in fig.9 where the C_{O_2} and $\bar{C}_M$ profiles are indicated by the dotted and the full lines respectively.

The local maximum of C_M is due to the competing action of the U leaching out of the clay and of the increased U retention coefficient which follows the O_2 penetration. The parameter values employed in the fit are given in table (2). Because several parameters were adjusted to obtain the fit, even the good results of profile cannot be taken as a proof of the correctness of the model. The results are anyhow encouraging, and suggest that the main features of the physical system have been reproduced.

Conclusions

It has been seen that in spite of the large variability of the system under examination the order of magnitude of the active lifetime of the fracture can be estimated. The hystorical age of the fracture system of Monterotondo is confirmed (Saltelli and Antonioli, 1985). Thus the network of permeable discontinuities in the Monterotondo clay can be explained as local and shallow features, probably due to unloading following the cover removal (by either natural or man-made causes). Such fractures are not likely to enhance the clay permeability in depth as it can be reasonably expected that the clay maintains its former impermeability under lithostatic pressure. On the other side the element profiles can by themselves provide useful information on the migration in clay, when the fracture is considered a long-term migration experiment which cannot possibly be performed on a laboratory time scale.

Due to the high heterogeneity of the system clay/oxygen-clay/water and to the large internal variability of the data points such system can give more qualitative information on the general transport mechanisms than actual quantitative data on the various diffusion parameters.

In other words studying for instance the U profile in the fracture does not easily provide a set of transport parameters (K_D, D ...) but rather points out the relevant predominating transport mechanism and the effect of the redox potential of the medium. In general the indications given by the so-called "natural analogs" about the problem of radionuclide migration through geological media should be regarded with a similar attitude.

Concerning the effects of water circulation through fractured clay, the observations on Monterotondo quarry should be generalized by a survey on other clay formations. The final outcoming should be the identification of a "marker" of water percolation through fractured clays. This should allow permeable fractures in the clays to be recognized also if striking chromatic evidence of the percolation phenomena is lacking.

TABLE 3

PARAMETER VALUES

$C^{o}_{O_2}$ = 0.781 E-4 M

$C^{b}_{O_2}$ = 0

C^{b}_{M} = 0,017 M

C^{o}_{M} = 0.0083 M

D_{O_2} = 7.931 E-9 cm^2/s

D_{M} = 3.448 E-7 cm^2/s

R_1 = 163 (0)

R_2 = 100 (0)

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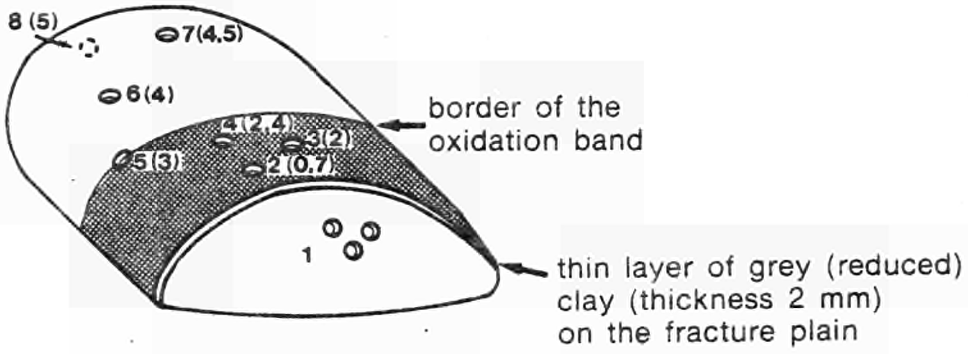
Sample A



Sample B

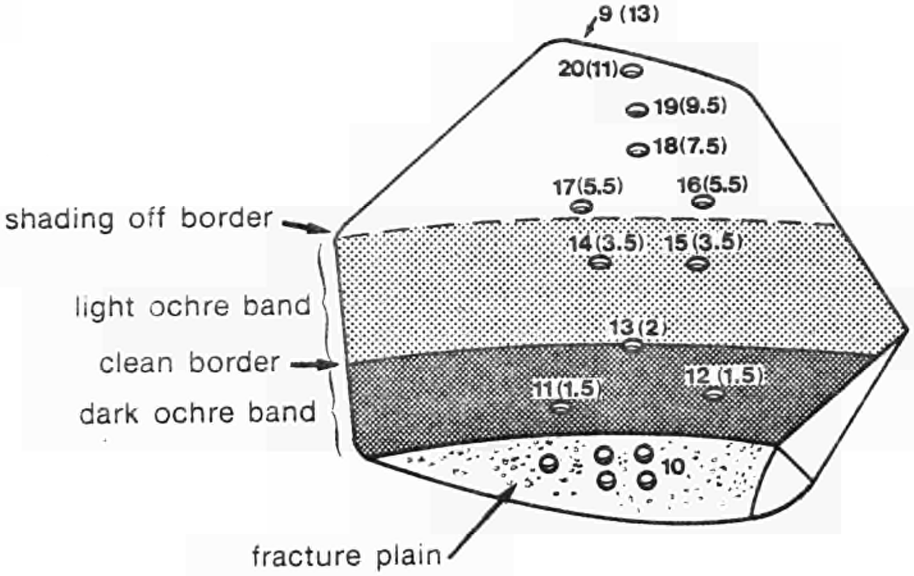


Fig.1 Clay A and B. Scheme of the sampling for the activation analysis - sample numbers and the distance from the fracture plain (cm)

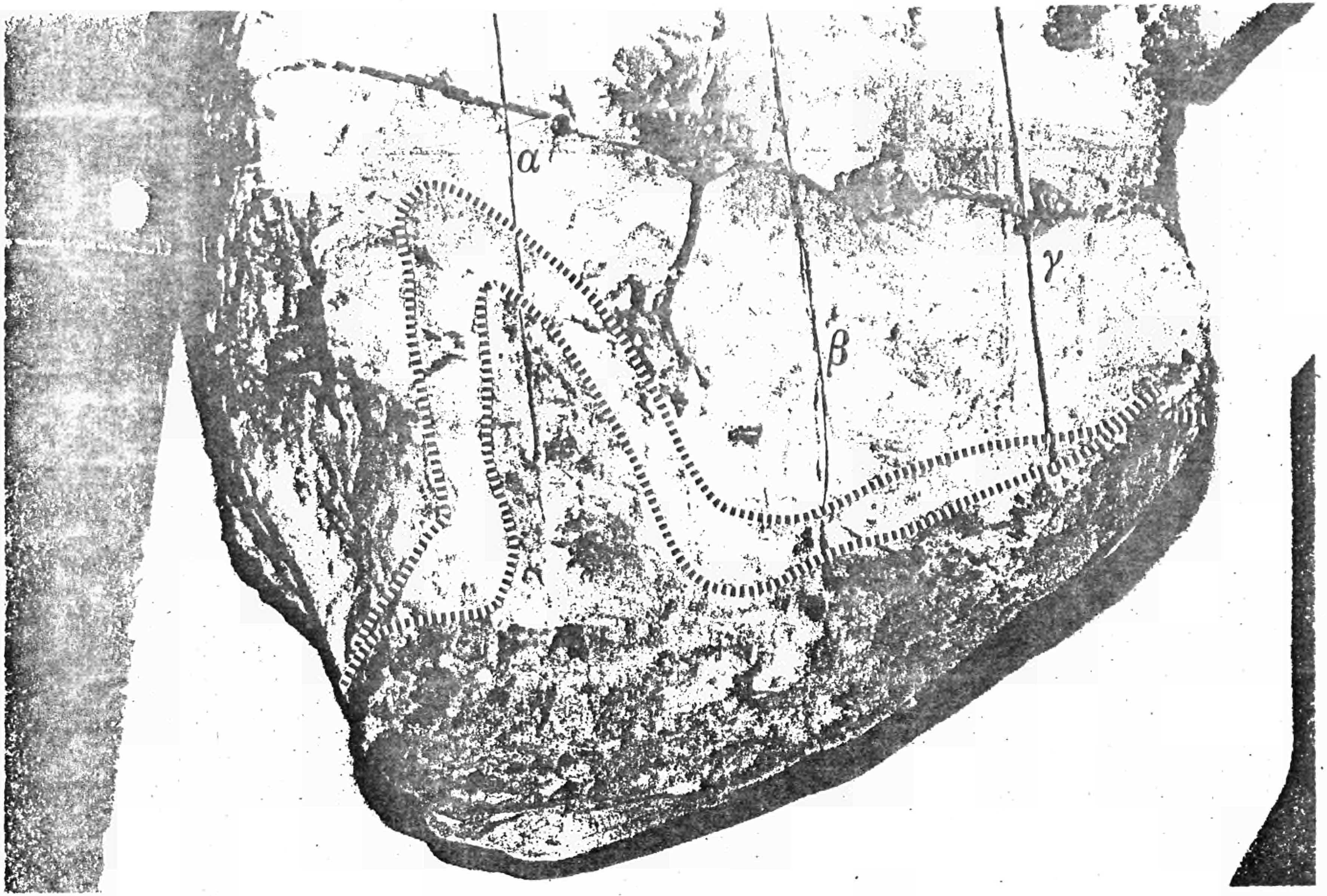


Fig. 2 - Sample C. Showing an irregular oxidation band; α, β and γ being the traces of the different profiles

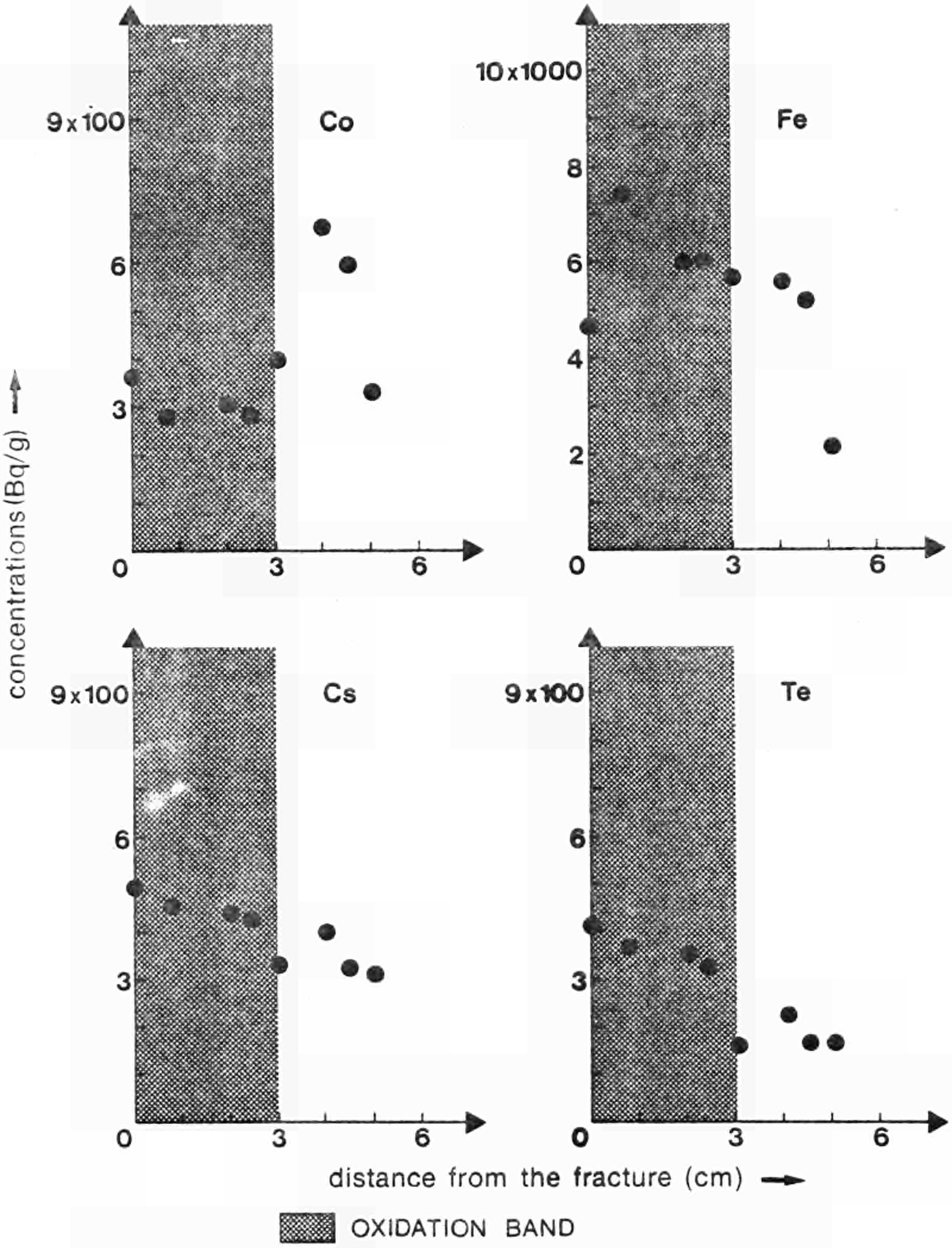


Fig.3 Sample A - profiles of Co, Fe, Cs, Te

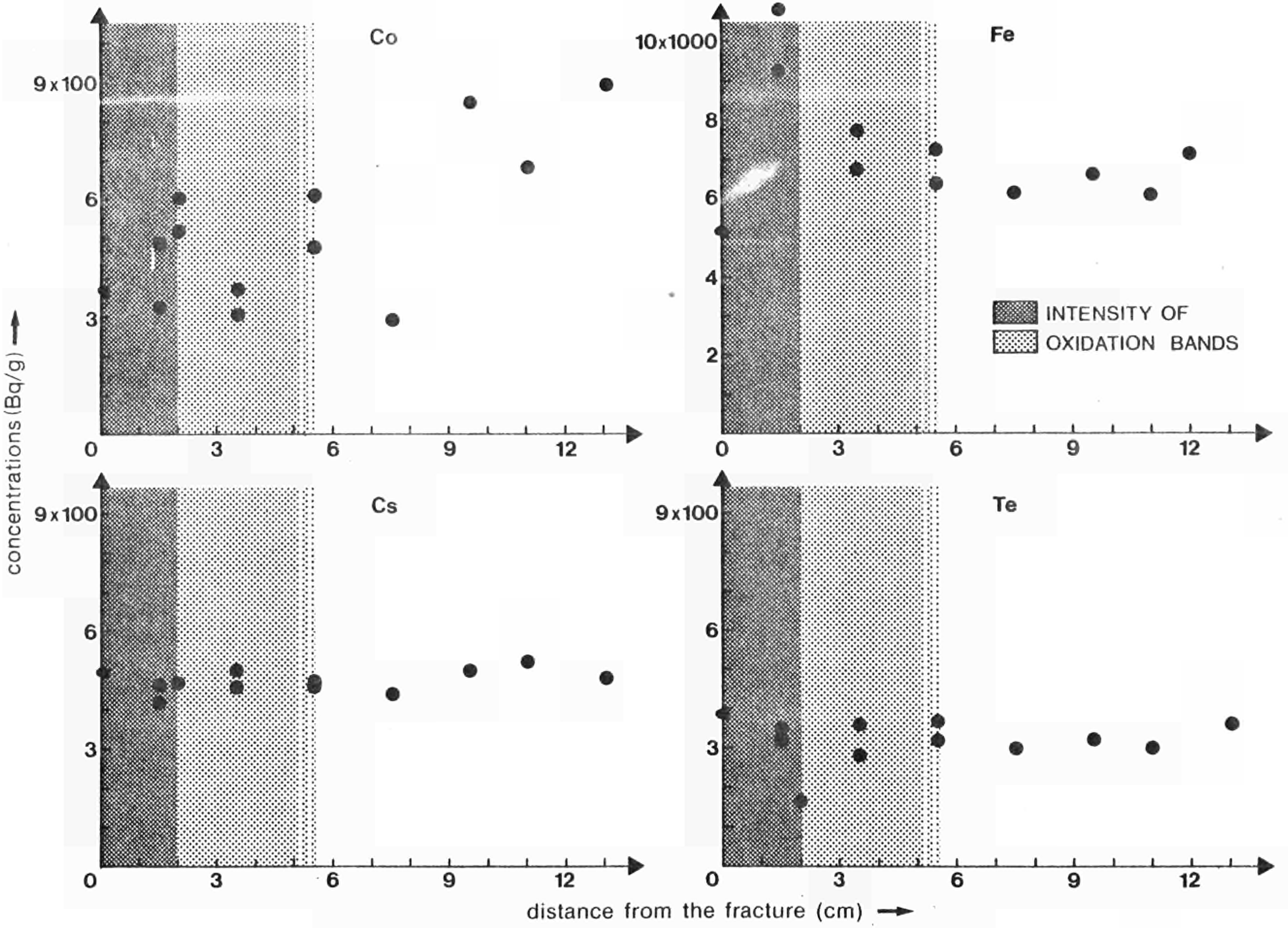


Fig.4 Sample B - profiles of Co, Fe, Cs and Te

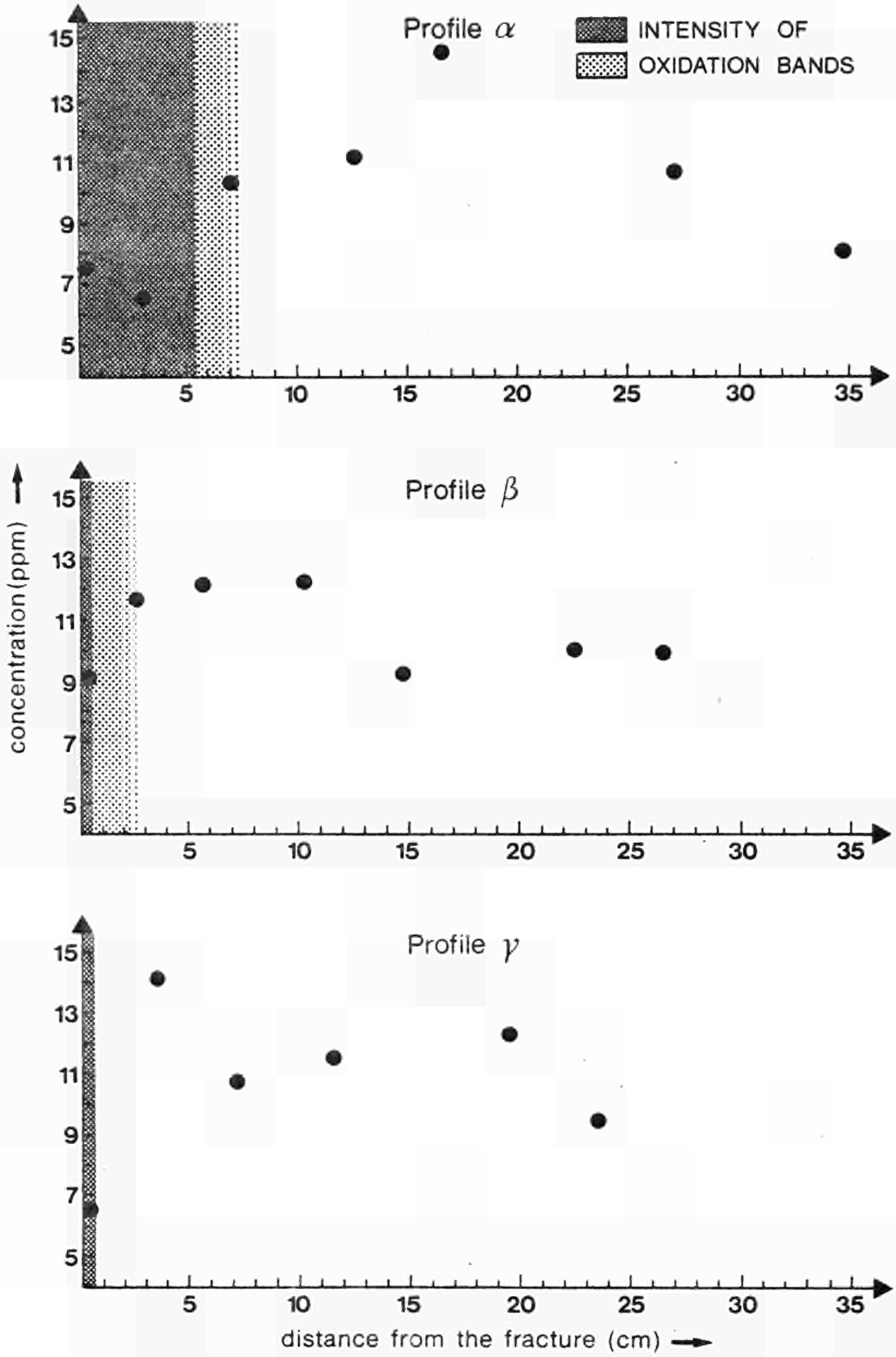


Fig.5 Sample C - Co profiles

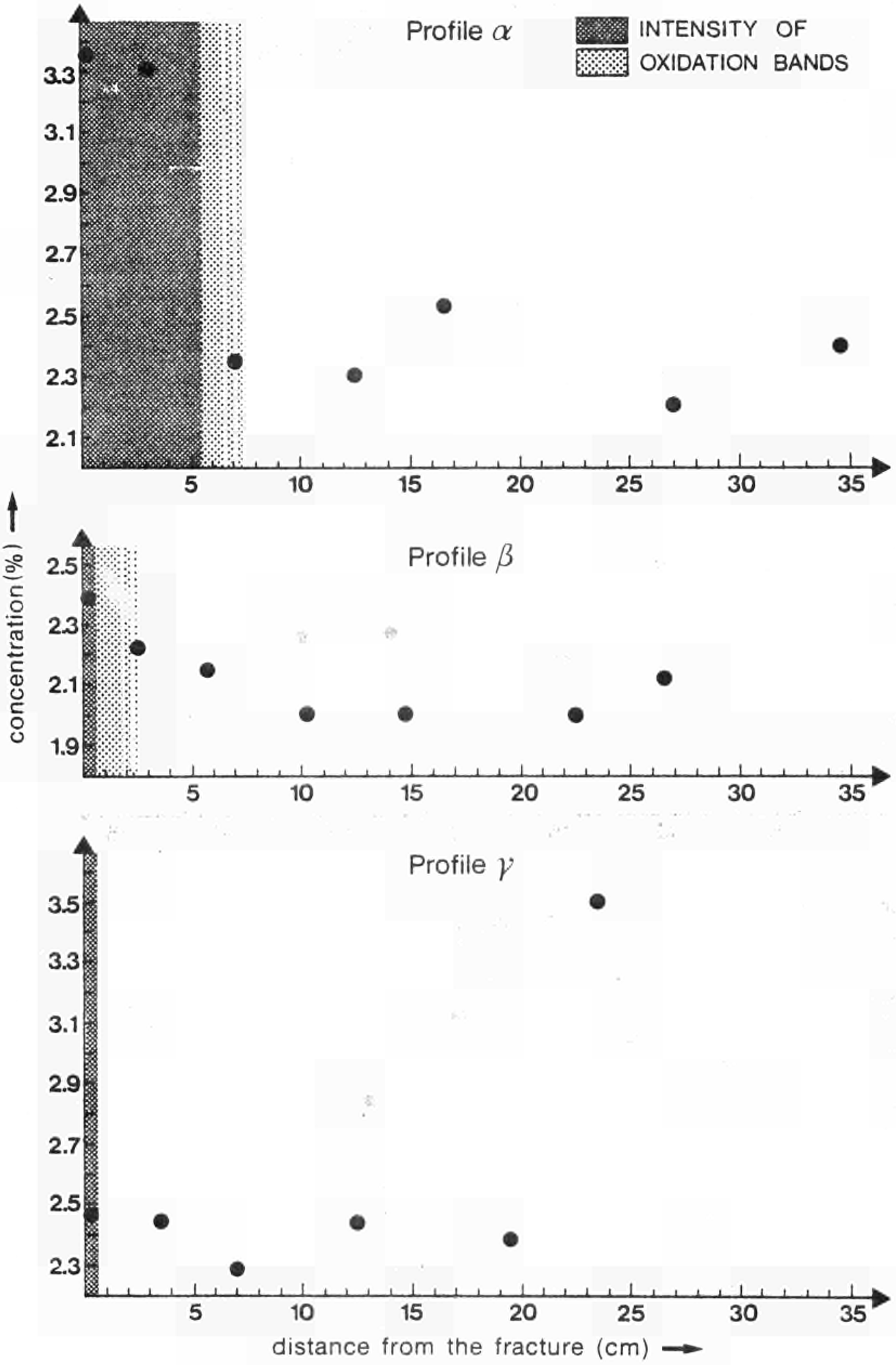


Fig.6 Sample C - Fe profiles

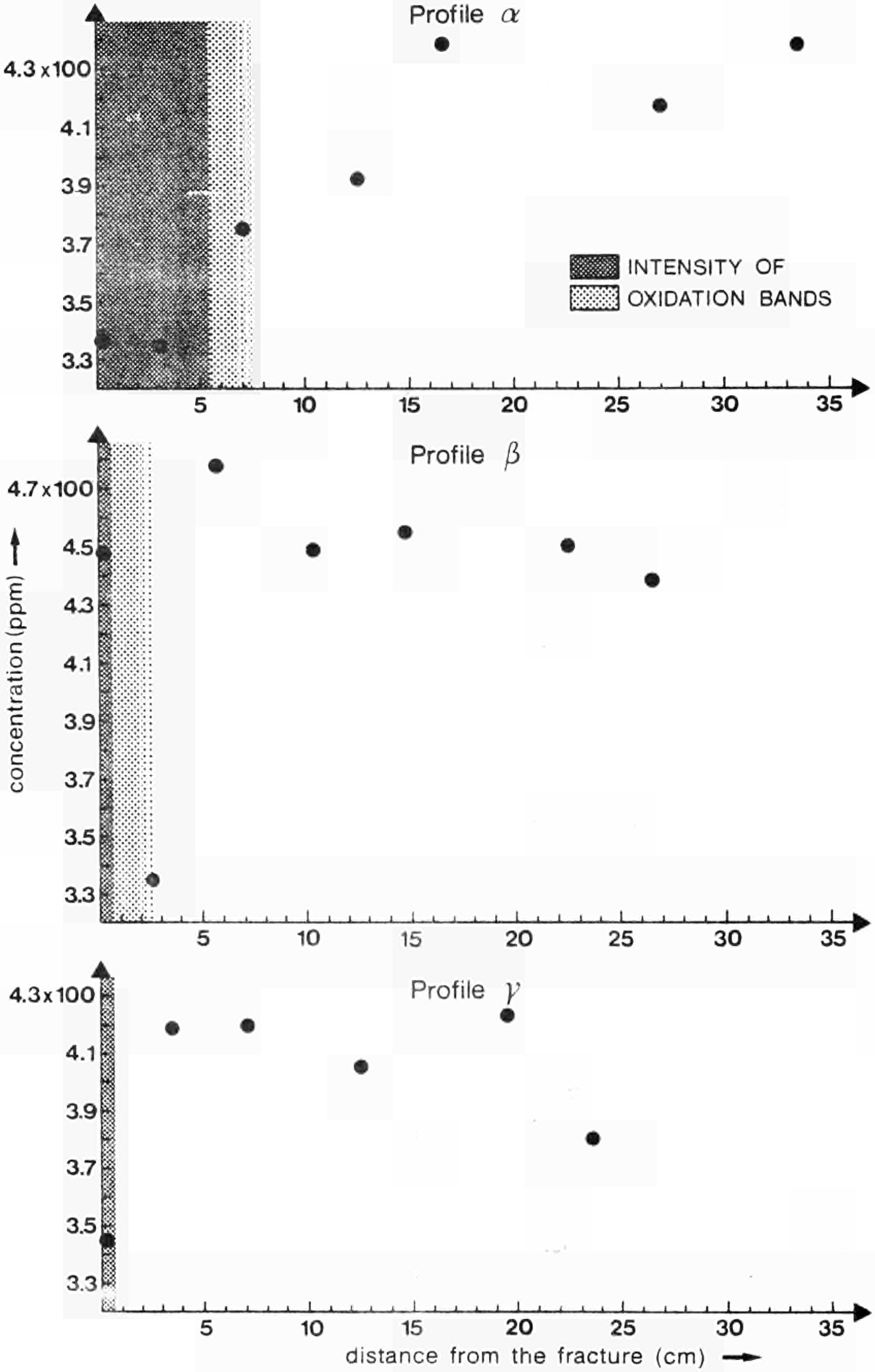


Fig.7 Sample C - Mn profiles

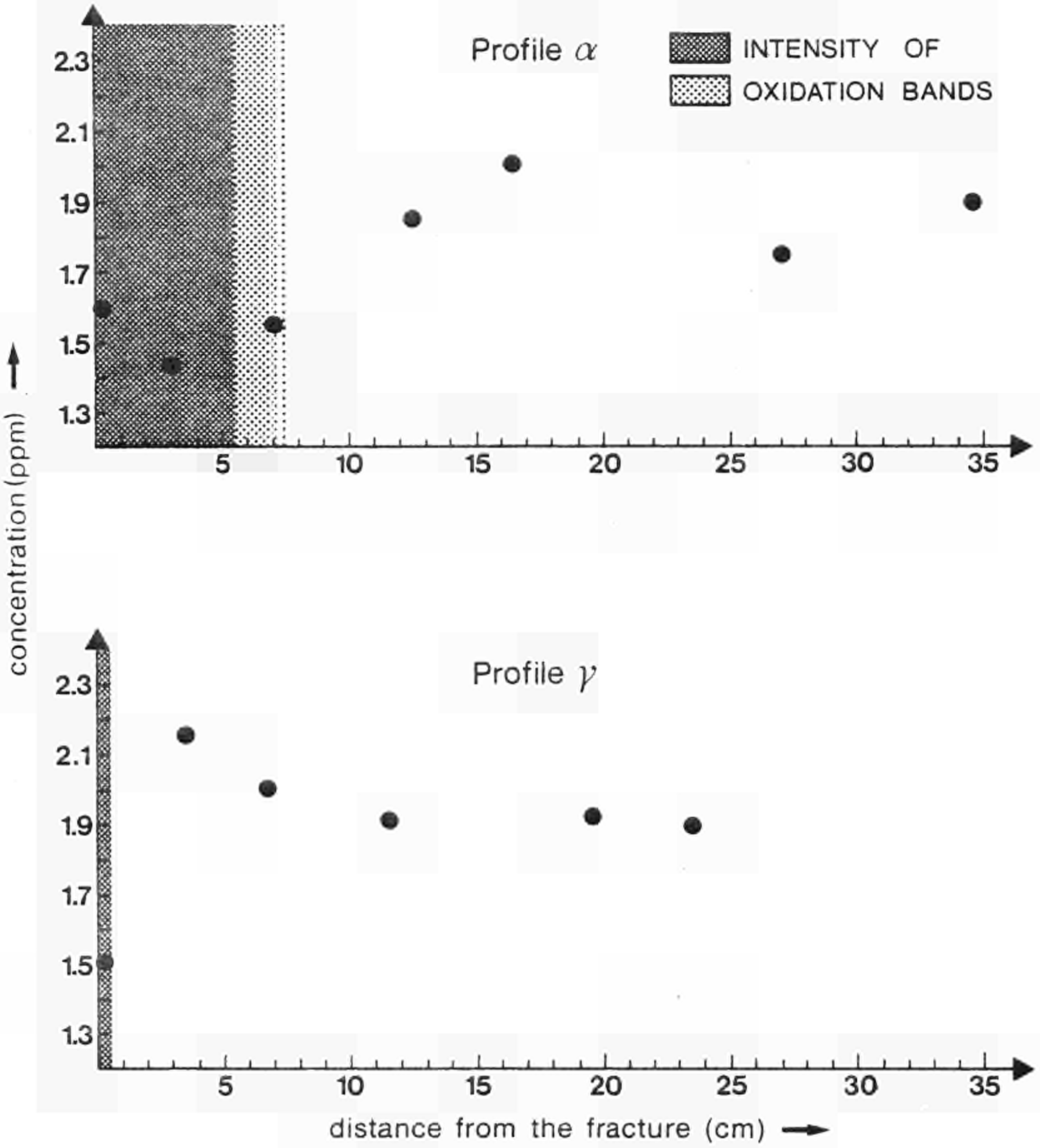


Fig. 8 Sample C - U profiles

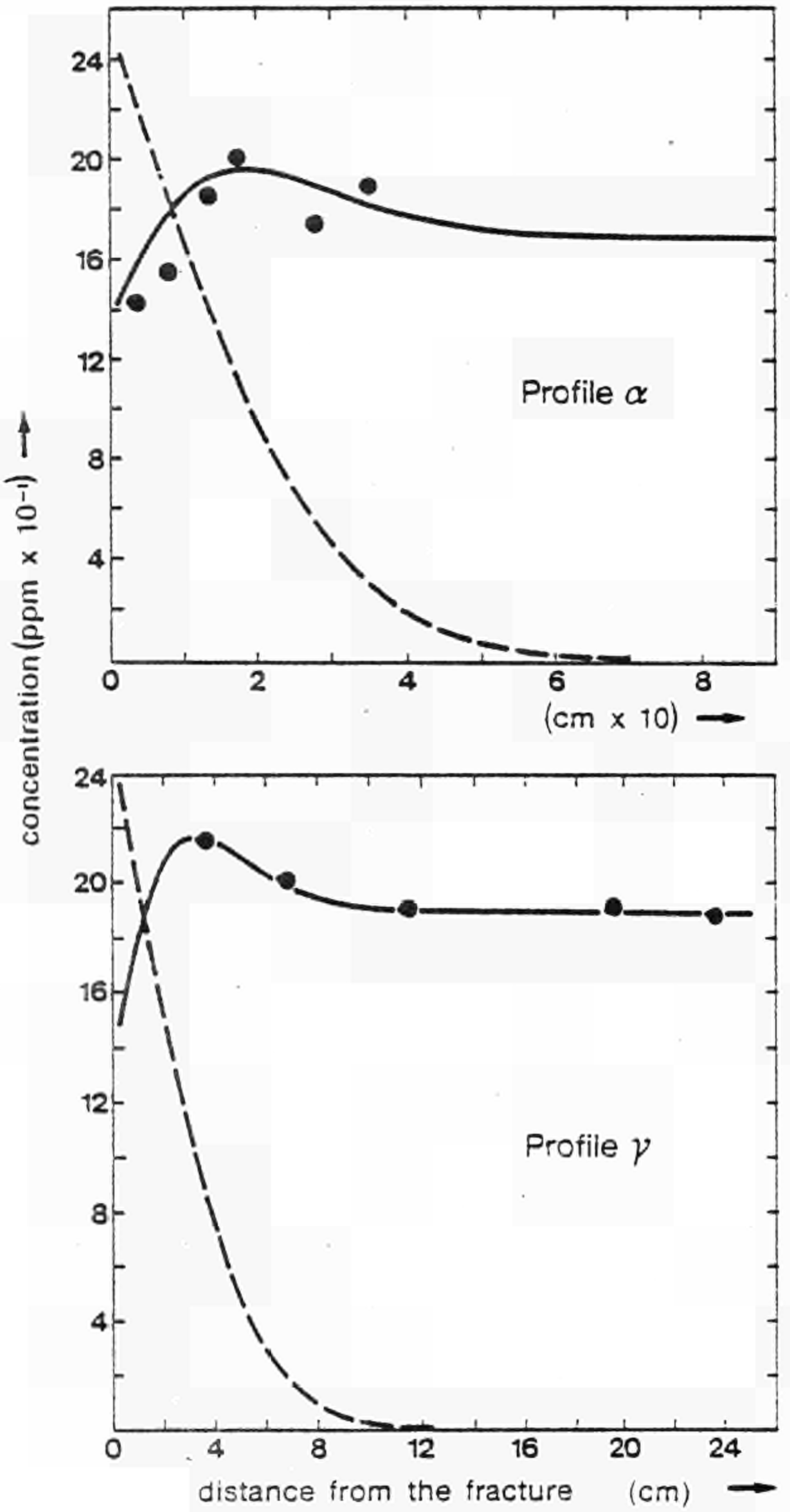


Fig. 9 Results of mathematical model :

—— uranium profile

---- oxygen profile

● experimental data

Analogue of elemental diffusion over 5000 years in sediments; close but not close enough?

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Notes to accompany discussion.

The Loch Lomond natural analogue study has been presented at several meetings over the past couple of years as data were obtained and progress made on interpreting results. The basics have been described in a number of reports to CEC (co-sponsor of the work with UKDOE) prepared by the principal investigators, Mackenzie (SURRC), McKinley and Hooker (BGS). The purpose of this brief presentation is not to look at the large volume of data available on major and trace element profiles in the sediment and pore waters, but to focus-in on bromine in particular, to see how it can be used to produce direct analogue evidence for long-term apparent anion diffusivity to support laboratory experiments. The discussion then looks at how the pleasing outcome of this exercise can be marred by trying to compare the physical model environment of the analogue too closely with that of any waste disposal system. This highlights one of the main short-comings of obtaining reliable quantitative parameter values from natural analogues.

In outline the system examined comprises a one metre thick band of ~5000 year old marine sediments sandwiched by freshwater sediments at a depth of about 4m below the bed of Loch Lomond. Both marine sediments and pore waters,having different compositions to the freshwater,formed a geochemical discontinuity which acted as a source term for diffusive/advective migration out into surroudning sediments. A wide variety of chemical profiles has been determined for various elements, and models constructed to account for them in terms of mobility and fixation processses.

Bromine shows an excellent porewater diffusion profile from a peak in the marine band. This has been modelled to produce a maximum apparent diffusivity of 8 x 10^{-7} cm^2/s assuming an initial concentration in the marine sediment fluids of 60 ppm. If the latter value were to have been 20ppm, then a De of 3 x 10^{-7} cm^2/s is obtained. These values compare well with anion diffusivities in consolidated clays (eg Boom Clay) in the order of 10^{-6} cm^2/s, and could thus be interpreted as providing the much sought-after analogue support for laboratory determinations.

However, despite the physicochemical conditions in the sediments being well characterised, along with the age profile, the boundary conditions are still exceptionally difficult to tie down. Assumptions have had to be made about:

- constant rates of sedimentation
- compaction driven advection in pore-waters
- maintenance of similar physicochemical conditions in the sediments for 5000 years plus
- availability and speciation of Br in the marine band
- initial concentration levels in the whole sediment pile.

While reasonably confident estimates can be made for several of these parameters, the greatest doubt lies in the initial chemical form and concentration of Br and its mobilisation rate; the "source-term". So long as this is unknown, it is difficult to say whether calculated values of De represent mininum or maximum diffusivities. The factors which could control this are discussed in detail in the presentation.

Thus, even in this well characterised, well controlled "single process" example (by normal analogue standards!), difficulties have been found in providing confident quantitative values. The system obeys almost all the "Rules of Analogues" which we laid down in our SKB/Nagra review last year, failing only in fully meeting the second criterion; knowledge of the magnitude of all the parameters involved.

This emphasises the problems of precise analogue control, since the requirements for quantitative application are exacting. It is tempting now to return to this example and do more work to try to plug all the leaks and make a thoroughly confident case. The pros and cons of this approach are discussed, advice is sought from the assembly, and the implications of this experience for modellers is explored further.

PERFORMANCE ASSESSMENT INPUT:
MARYSVALE NATURAL ANALOG STUDY

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The primary purpose of natural analog studies is to clarify the ability of the geologic environment and engineered system associated with an underground radioactive waste repository to mitigate the transport of radionuclides of concern toward the biosphere. The data are obtained through the study of processes affecting the migration and retardation of nuclides associated with natural geologic sytstems. These natural analog studies are selected to be appropriately analogous to some aspect(s) of an underground radioactive waste repository. Natural phenomena that need to be understood in relation to nuclide transport and/or retardation within the geologic environment include (after Chapman et al., 1984) include:

- Rock and mineral thermal and/or chemical stability - as related to canister corrosion, waste form dissolution, buffer stability, rock strength and permeability, and stability of sorptive minerals
- Solubility and speciation of radionuclides - chemical formation of complex molecules and/or colloids comprising actual or proxy elements and/or radionuclides
- Mineralogic fixation/retardation - incorporation of radionuclides into the structure of newly formed minerals from host rock and buffer material
- Mineralogic sorption and retardation - external influence of minerals on the mobility of radionuclide complexes
- Radiolysis - effect of radiation on water, and therefore, the system oxidation potential, related to radionuclide transport

- Redox equilibrium - the changes in solubility of radionuclide complexes of concern as related to changes of oxidizing versus reducing conditions
- Matrix diffusion - ability of microcrack network within the rock to retard migration of radionuclides
- Fracture hydrologic control - the extent to which large-scale cracks and facture systems influence the movement and retardation of radionuclides within ground water
- Radionuclide/water relative migration - the rate of transport of radionuclides relative to the ambient water flow.

The data pertaining to the above natural phenomena of concern will be used in the validation and verification of performance assessment evaluations of a crystalline repository under expected conditions. Performance assessment and licensing activities will require such information on both near-field and far-field repository environments, with input provided by natural analog studies combined with laboratory and field tests. To this end, the U.S. Department of Energy (DOE) calls for natural analog studies to be performed and described in the Site Characterization Plan (SCP) under Section 6.4, Geochemistry, Natural Analogs. Another important contribution of natural analog studies is the ability to demonstate to the general public, as well as regulatory bodies, that geologic systems have the ability to retain nuclides under natural conditions and for times geologic in scale.

The Marysvale Natural Analog Study is being conducted by the Office of Crystalline Repository Development (OCRD) for the DOE. The type of geologic analog being studied is an inactive, hydrothermal uranium/molybdenum ore vein deposit, emplaced within crystalline (granitic) rocks. An inactive ("fossil") hydrothermal system, with significant mineralization, can be considered analogous to a radwaste repository after any canisters have been breached and the interactions between ground water, rock, and radionuclides have taken place, initially at elevated temperatures. A uranium/molybdenum mineralization is advantageous since many of the nuclides expected in the radwaste form are likely to be present. There is also the likelihood that certain elements that can proxy for given radwaste nuclides will be present.

Aspects of the hydrotherml uranium deposit at Marysvale that express the key unknowns of this study include (after Shea and Foland, 1985):

- Spatial extent of the hydrothermal system
- Nature of the hydrothermal fluid
- Thermal gradient around the ore body
- Duration of the ore mineralization
- Suite of nuclides present in the ore
- Extent of the nuclide migration from the vein into the country rock
- Nuclide mobilization within the surrounding country rock
- Hydrothermal effects upon the retentivity (e.g., for uranium) of the refractory minerals
- Hydrothermal effects upon permeability and rock strength
- Role of fractures and microcracks in nuclide transport
- Perturbations to the mineral system since initial emplacement of the ore.

For the purposes of discussion, the natural phenomena relative to radioactive waste isolation performance assessment and investigation parameters of the Marysvale Natural Analog Study have been simplified. These simplified versions are expressed as composites of the fundament parameters temperature (T), distance (d), chemical potential ( ), time (t), and mass (m). A matrix has been generated which attempts to show to what extent the investigation parameters meet the "objectives" of the natural phenomena regarding radioactive waste isolation.

It will be seen that the Marysvale Natural Analog Study does address many of the key natural phenomena regarding radwaste isolation. It will also be seen that it is highly unlikely that any single natural analog study can respond to all the necessary fundamental parameters and thus there is a need for other natural analog studies to address these processes completely.

APPENDIX 4

Major International Programmes

1. Commission of the European Communities' programme (B. CÔME).

2. Pocos de Caldas, Brazil (J. SMELLIE).

3. The Koongarra ore body, Australia (P. AIREY et al.).

4. Cigar Lake Project, Saskatchewan, Canada (J. CRAMER and P. SARGENT).

THE CEC'S ACTIONS IN THE FIELD OF NATURAL ANALOGUES: AN OVERVIEW

B. COME, CEC, Brussels

INTRODUCTION

The Commission of the European Communities has been participating for several years in research activities on natural geological migration systems. This work falls within the co-ordinated project MIRAGE (Migration of Radionuclides in the Geosphere), which brings together cost-shared research contracts in the various Member States as well as activities carried out at the Joint Research Centre, Ispra, Italy (1, 2, 3)

WORK DESCRIPTION

1. Hard Rock Analogues

A group of investigations was carried out by the Bureau de Recherches Géologiques et Minières (F) at two crystalline sites in France. The first site is situated in the Vosges, on the eastern edge of the Ballons granite, in the Langenberg. This is a monzogranite of Visean age, enriched in U, Th and lanthanides, which has been affected by two hydrothermal episodes: a late magmatic one at about 250 - 300° C, and another at about 150° C during the late Permian. The second site is situated in Brittany, in Cambrian acid volcanic rocks enclosed in the syncline of La Telhaie. This has also been affected by two hydrothermal episodes: an early one at 220° C, and a late alteration between 80 and 150° C. These two "hot release" analogues showed increased mobility of rare earth elements under low temperature conditions (4). In parallel to this, the BRGM conducted a study on supergene alteration of analogous mineral deposits (5).

2. Sedimentary analogues

The well-characterised series of clay-rich sediments from Loch Lomond (Scotland, UK) and adjacent freshwater lochs have been studied by the British Geological Survey. The marine band of interest is about 1 m thick, lies at 3 m depth and was deposited between 6900 - 5400 years B.P. Concentration profiles in the solid phase were determined for 17 elements. The study showed that evidence of post-depositional migration out of the marine band was not found, with the possible exception of ^{234}U; there is also strong evidence for the organic fixation of I, Ra on biogenic particulates in the clays (6).

The second sedimentary analogue study focussed on the sedimentary sequence at Orte (I), and was operated by the ENEA. The clay sequence (10 million year old) is overlain by a sand unit which in turn is covered by a layer of volcanics with a high natural series radionuclide content. Groundwaters percolating through these volcanics are expected to have leached rare earths, U, Th, Ra and transported them down through the oxidized sands to the upper part of the clay. The study can thus be considered as a direct analogue of diffusion processes in the far-field (reducing conditions) and in the near-field where the possibility exists of a radiolysis - induced oxidation zone surrounding leaking waste containers (7).

A companion study on fractures in clays, where groundwater percolation was shown to exist, was conducted by the JRC - Ispra and the ENEA in a clay quarry. Existing fractures were dated and the diffusion profile of elements, both sides of the fracture planes, was measured (8).

Finally, the uranium series disequilibrium method was used to characterise the groundwater flow patterns in the sedimentary layers at the Mol site (B). This pilot study was carried out by the UKAEA - Harwell. Samples of groundwater derived from shallow and deep sand layers above and below the Boom clay formation, at five locations, have been analysed for U, Th, and Ra isotopes. Considerations of circulation/mixing patterns are still under way. However, analysis of bulk clay samples indicates no mobility of any of the uranium, thorium and radium isotopes in that material (4).

CONCLUSIONS AND PROSPECTS

Very encouraging results have been obtained from these preliminary investigations of natural geological migration sytems. It is planned to continue this effort in the framework of the third Community R&D Programme on Radioactive Waste Management; closer attention will be paid to the modelling of the phenomena studied.

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(4) COME, B et al: "The MIRAGE Project: large-scale radionuclide transport investigations and integral migration experiments" Proceedings of the Second CEC Conference on Radioactive Waste Management and Disposal, Luxembourg, 1985 (EUR 10163)

(5) SUREAU, J.F., 1985 (this report, Appendix 3)

(6) CHAPMAN, N.A., 1985 (this report, Appendix 3)

(7) BRONDI, A., 1985 (this report, Appendix 3)

(8) D'ALESSANDRO, M., et al., 1985 (this report, Appendix 3)

PROPOSED PROGRAMME OF INVESTIGATION AT POÇOS DE CALDAS, MINAS GERAIS, BRAZIL

Natural analogues to the radionuclide mobilisation processes and geochemical/hydrogeological conditions in and around a deep repository for radioactive wastes were recently brought into focus by Chapman et al (1984). This evaluation was closely followed by an Analogue Workshop held at Lake Geneva, Wisconsin, USA, in October 1984, and the first meeting of the more formally constituted CEC Natural Analogue Working Group (NAWG) held a year later at Brussels in November 1985. As a result, the important near- and far-field processes which will occur in the geosphere after disposal, and which require data from analogues to allow their incorporation into assessment models, have now been identified, and the necessary involvement of the modelling and safety assessment fraternities at every stage of natural analogue studies has been stressed.

The first NAWG report listed the processes or mechanisms considered by the Group to be of most significance to the majority of waste disposal concepts. These included:

- Solubility limitation of radionuclide concentrations.
- Groundwater accessibility to the waste.
- Radiolysis of groundwaters.
- Material thermal stability (e.g. backfills).
- Colloid formation in the near-field.
- Dispersion in porous and fractured media.
- Channeling ⎤
- Short-Circuits ⎬ Pathways for groundwater movement.
- Fracture Hydrology ⎦
- Diffusion of radionuclides in:
  Matrix of the rock
  Intra-crystalline
  Backfill (e.g. clay pores)
- Redox behaviour of radionuclides.

- Sorption of radioactivity on:
  Fracture surfaces
  Minerals

The Group discussed all available analogue studies and concluded that detailed study of these processes in a variety of geological environments would provide much useful information to support and justify the use of specific detailed research models, and the means of their simplification for incorporation into large assessment codes. One of the localities considered to have great potential for the study of many of these processes, particularly when carried out in parallel to complementary projects elsewhere, is the Poços de Caldas region in Brazil.

The Poços de Caldas Region

This region, which consists principally of alkalic intrusive rocks, chiefly nepheline syenite and phonolite, is generally anomalous with respect to concentrations of uranium, thorium and the rare-earth elements (REE). Chemically, these elements can be considered analogous to neptunium, plutonium and americium/curium respectively. A considerable amount of basic geological information is already available in the area, and has been presented elsewhere (see for example, Frayha, 1962; Wedow, 1967; Santos, 1976; Barretto and Fujimori, 1984). Two sites are available for study:

- Morro do Ferro	(U, Th and REE)
- Osamu Utsumi Mine	(C-09 Uranium Mine; U with subordinate Th and REE)

These sites, which are situated within about 5 km of each other, are connected by a good road system with the nearby town of Poços de Caldas. The Morro do Ferro site has already been the focus of extensive analogue studies considering the behaviour of thorium (as a chemical analogue of Pu) in oxidising surficial groundwaters and in the biological environment (Eisenbud et al, 1984). As a result of this work,

NATURAL ANALOGUE WORKING GROUP MEETING, BRUSSELS
5-7 November 1986

Koongarra Ore Body: A Natural Analogue of Radionuclide Migration in the Far Field of HLW Repositories

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KOONGARRA ORE BODY: A NATURAL ANALOGUE OF RADIONUCLIDE MIGRATION IN THE FAR FIELD OF HLW REPOSITORIES

ABSTRACT

A brief overview is presented of uranium ore bodies as natural analogues of radionuclide migration in the far field of HLW repositories. Particular reference is made to the secondary mineralization associated with the Koongarra ore body. Attempts have been made to assess the validity of generating equations which form the basis of transport codes. The effect of these phenomena - time dependent sorption coefficients, colloid transport and α-recoil effects - which are not adequately described by many codes - are discussed. An approach to modelling the distribution of uranium series through separable mineral phases within the host rock is presented. Current attempts to extend the analogue to fractured rocks are outlined. Finally, an approach is suggested for applying the results of natural analogue studies to HLWR site assessment.

TABLE OF CONTENTS

Page

1. INTRODUCTION 183

2. THE NATURAL ANALOGUE APPROACH 184

3. THE STUDY REGION 185

4. PRELIMINARY APPROACH TO THE ASSESSMENT OF TRANSPORT CODES 186

5. EVIDENCE FOR TIME-DEPENDENT TRANSPORT PARAMETERS 187
   - 5.1 Laboratory Adsorption Experiments 187
   - 5.2 Distribution of α-recoil Products 188
     - 5.2.1 Uranium series fractionation between phases - multiphase modelling 188
     - 5.2.2 Direct experimental evidence for α-recoil 189
   - 5.3 Effect of Mean Residence Time on Radium Distribution Coefficients 190

6. EVIDENCE FOR A TIME INVARIANT GROUNDWATER PARAMETER (^{234}U/^{238}U ACTIVITY RATIO) 191

7. COLLOID TRANSPORT 192

8. EXTENSION OF THE ANALOGUE 194
   - 8.1 Fractured Rock Studies 194
     - 8.1.1 Multi-element distribution (PIXE/PIGME) 194
     - 8.1.2 Fission track and α-track studies 195

9. APPLICATION OF NATURAL ANALOGUE STUDIES TO SITE ASSESSMENT 197
   - 9.1 Migration Rates of Transuranic Elements and Fission Products, Relative to Uranium 197
   - 9.2 Some Implications to Model Verification 199

REFERENCES 201

LIST OF FIGURES

FIGURE 1 Uranium ore bodies as natural analogues of far field radionuclide transport.

FIGURE 2 Uranium ore bodies as natural analogues of HLWR in the far field - application to the assessment of the long-term prediction capabilities of transport codes.

FIGURE 3 Uranium ore bodies as natural analogues of HLWR in the far field - application to site assessment.

FIGURE 4 Location of uranium ore bodies within the Alligator Rivers region of the Northern Territory of Australia.

FIGURE 5A Location of the sampling wells at the Koongarra deposit (adapted from Figure 10, reference [13]).

FIGURE 5B A section between wells 78 and PH 94 showing the location of a major fault, the extent of uranium deposits, the boundary of surface oxidation and the groundwater flow paths (adpated from Figure 1, reference [12]).

FIGURE 6 The effect of the selective phase extraction procedure (Table 1) on (a) the percentages of ^{236}U and ^{238}U in the aqueous phases, and (b) the ratio of the percentages in the aqueous phases.
Sample: Ranger One drill core S1/146, 2.7 m.

FIGURE 7 The flux of uranium between specified separable phases within the weathered ore.

FIGURE 8 Variation of the ^{234}U enrichment in the clay/quartz phase R_{CQ}-1 (part A) and (R_{CQ}-1)/$^{8}U_{CQ}$ (part B) with $^{8}U_{AX}/^{8}U_{CQ}$. $^{8}U_{AX}$ and $^{8}U_{CQ}$ are the ^{238}U levels in the amorphous and crystalline iron (AX) and clay/quartz (CQ) phases respectively.

FIGURE 9 Variation of the reciprocal of the ^{226}Ra, ^{224}Ra, ^{223}Ra adsorption coefficient with the decay constants.

FIGURE 10 Variation of the ^{230}Th/^{234}U activity ratio with ^{238}U, i.e. with distance from the uranium deposits.

LIST OF TABLES

TABLE 1 Selectively Extracted Phases from Weathered Ore

TABLE 2 Rate and Adsorption Parameters (Radium)

1. INTRODUCTION

The design of high level radioactive waste repositories involves multi-barrier concepts[1]. These include:

- immobilization of reprocessed waste in glass or, perhaps SYNROC,
- encapsulation of the immobilized waste or spent fuel elements in metal containers,
- minimization of groundwater access and migration in the near field by site selection, engineering design and the use of buffer materials,
- natural retardation of radionuclide migration in the geosphere.

The greater the period of isolation of waste products from the environment, the greater the inherent protection due to radioactive decay, dispersion and isotopic dilution. The United States Environmental Protection Agency[2] has published a criterion for the maximum dose commitment to the public over 10 000 years.

Demonstration of compliance with this type of regulation involves the proponents of repository design with a new class of problem. A performance assessment methodology is being developed to examine the total system. Of the various elements in the total repository concept, retardation of radionuclides in the far field is one of the most significant[3,4]. In principle, mathematical models are capable of precise description of radionuclide transport; in practice their predictive capability is limited by the necessity of using lumped parameters to describe:

- aquifer properties,
- the mineralogy of accessible surfaces,
- solute adsorption and dispersivity.

In addition, at least two other factors need to be taken into account:

(i) Changes in the geological environment. When considering the long-term future, possible changes in the geological environment must be taken into account. Szoreen and Kocher[5] have recently pointed out that "Within 1000 years, near surface bore holes may be disrupted by erosion. By 10 000 years extensive continental glaciation could occur . . . For time periods greater than 100 000 years, it is possible that temperature and pressure fields at the repository site might be significantly different and that the chemical and mechanical properties might change as a result."

(ii) Migration of man-made elements. Many of the elements which are assessed to contribute most to long-term dose commitment (^{237}Np, ^{239}Pu, ^{241}Am, ^{99}Tc) do not occur in nature at concentrations which can ordinarily be measured and hence their geochemistry is unknown.

2. THE NATURAL ANALOGUE APPROACH

Long-term prediction is based, to a significant extent on subjective judgment. The aim of natural analogues is to reduce the level of subjectivity in one of the following ways[6]:

(i) Detailed understanding of the cumulative effect of transport in the distant past can provide a basis for prediction.

(ii) Since local geological environments associated with the natural analogue were frequently more rigorous than those in repository systems, the observed migration of indicator elements may provide an upper bound of the extent of transport of key radionuclides.

(iii) Natural analogues may be used to assess the assumptions underlying geochemical transport codes. Processes which are significant for long-term prediction, but not observed over laboratory timescales, may become apparent. Examples will be presented below.

In this study, uranium ore bodies in the Alligator Rivers Region of the Northern Territory of Australia are being evaluated as analogues of radionuclide transport in the far field[7,8]. Uranium deposits have the following potential advantages:

(a) They comprise a wide range of radionuclides and heavy metals including actinides, radium isotopes, lead isotopes and rare earth elements,

(b) Ultra-low levels of significant transuranic elements (^{239}Pu, ^{237}Np) and fission products (^{99}Tc, ^{129}I) are also present.

(c) Depending on the process studied, the accessible timescales range from <1 year to about 500 000 years. This range is particularly appropriate in studying processes determining the extent of radionuclide transport over 10 000 years.

(d) As uranium series elements are ubiquitous and can be measured at very low levels, the possibility exists of transferring information from the analogue to the proposed repository site.

Natural analogues of far field transport based on uranium ore bodies are not without problems. Because of the age of the deposits, virtually all daughters are authigenic, i.e. they are produced in situ by radioactive decay. On the other hand, products leached directly from repositories are allogenic. Many significant nuclides, e.g. ^{234}U, ^{230}Th, ^{226}Ra are formed by α-decay. Their distribution throughout the accessible minerals is determined not only by adsorption kinetics but also by the physics of the recoil process.

The investigation is currently structured to address the following issues (Figures 1-3).

(1) Is there a need, based on experimental evidence, to reassess geochemical transport codes for long-term prediction? In particular,

  - Is there evidence for a systematic time-dependence of transport code parameters?
  - Are there factors (e.g. colloid transport) which are not adequately described by the generating equations?

(2) Can natural analogue studies contribute directly to the assessment of far field transport at actual repository sites?

3. STUDY REGION

The uranium deposits of the East Alligator River (Figure 4) are the most significant mineral resources of the Pine Creek geosyncline[9]. The geosyncline comprises about 14 km of Lower Proterozoic sediments with interlayered tuff units, and rests on granitic late Archean complexes[10]. The sediments were regionally deformed and metamorphosed at 1800 My BP. Cover rocks of Middle Proterozoic and younger ages rest unconformably on these rocks. The Lower Proterozoic sediments are mainly pelites (75 per cent) which are commonly carbonaceous, lesser psammites and carbonates and minor rudites. The environment of deposition ranges from shallow marine to supratidal and fluvial for most of the sequence.

In the Alligator Rivers region, most of the uranium mineralization is in the base of the Cahill Formation which forms part of the Namoona group within the Lower Proterozoic sediments. The deposits are located in zones of chloritization and adjacent to lenses of massive dolomite and/or magnetite. It has been suggested that the common proximity of the uranium deposits to the carbonate rocks may be relevant to ore genesis[10]. It is also believed that association with the granitic Archean basement is also important[11].

The study region, in common with much of far northern Australia, has a monsoonal climate. Almost all the rainfall occurs in the wet season between November and March. Both the East and the South Alligator Rivers have their headwaters in a rugged sandstone formation in the south-east of the region, which rises about 250 m above adjoining lowlands. Wet season flow comprises a series of peak floods superimposed on a base flow which, in a normal year, begins about December and ends in June.

To ensure the generality of the results, a number of ore bodies were studied including Ranger One, Jabiluka One, Nabarlek and Koongarra. Virtually all of the results described in this report were obtained at Koongarra.

Koongarra Deposit

The uranium mineralization occurs in two distinct ore bodies separated by a barren gap. Both consist of primary zones containing uraninite veins within steeply dipping quartz-chlorite schists of the lower member of the Cahill Formation[12]. In the No 1 ore body (Figure 5), which is the subject of the investigation, secondary mineralization is present in the weathered schists running almost from the surface to the base of the weathering at depths of 25 m and 30 m. The secondary mineralization in the weathered schists forms a tongue-like fan of ore grade material extending down-slope for about 80 m.

The groundwater hydrology in the area of the Koongarra deposits has been studied extensively by Australian Groundwater Consultants and McMahon, Burgess and Yeates[13]. Their data, interpreted by Snelling[12] are shown schematically in Figure 5B. The groundwater is believed to recharge along a major fault line and flow in a generally southerly direction away from the escarpment. The location of the sampling wells is shown in Figure 5A.

4. PRELIMINARY APPROACH TO THE ASSESSMENT OF TRANSPORT CODES

Attempts are being made to analyse problems associated with assessment of the validity of the SWIFT (Sandia Waste Isolation Flow and Transport) code for long-term prediction of radionuclide transport in the far field[14].

SWIFT is a fully transient three-dimensional model which solves coupled equations for the following processes in geological media:

- fluid flow,
- heat transport,
- major species and radionuclide transport.

In this work emphasis is placed on assessing the validity of the generating equations for radionuclide transport. Particular attention is paid to the assumption that the interaction between the 'dissolved' radionuclides and the host rock can be described by a linear isotherm. Evidence has been obtained for:

- the time dependence of adsorption coefficients,
- the role of colloids in the transport of some uranium series elements.

The implications of these findings to aspects of model validation is discussed in Section 9.2.

5. EVIDENCE FOR TIME DEPENDENT TRANSPORT PARAMETERS

5.1 Laboratory Adsorption Experiments

Indirect evidence for the time dependence of the adsorption coefficient for uranium on weathered ore has been obtained by comparing the distributions of the pre-existing uranium-238 and artificial uranium-236 through various selectively extracted phases. Results for drill core 146 from Ranger One (Figure 4) are shown in Figure 6. The ^{236}U was added to the aqueous phase. The reagents, and the corresponding phases are listed in Table 1.

Also listed in the table are:

- the fraction of uranium in each phase for all samples measured,
- the average ^{234}U/^{238}U and ^{230}Th/^{234}U activity ratios relative to those in the amorphous iron phase.

It is seen from the figure that, relative to the ^{238}U, the ^{236}U activity is essentially restricted to the aqueous phase and to the uranium associated with ion exchange and the amorphous iron (predominantly ferrihydrate) sites. Over laboratory timescales, there is essentially no access to the crystalline iron (goethite) phase and to the clay/quartz. Clearly, a substantial fraction of uranium exists in the goethite. It would appear that this phase will not contribute to the retardation of radionuclides over short timescales. However, within a geological timeframe, the processes of α-recoil, diffusion or solution/recrystallization of the iron may lead to the incorporation of radionuclides into the goethite.

$$\underset{\text{aqueous}}{\text{U}} \xrightleftharpoons{\text{rapid}} \underset{\substack{\text{amorphous}\\ \text{(largely}\\ \text{ferrihydrate)}}}{\text{U}} \xrightleftharpoons{\text{slow}} \underset{\text{goethite}}{\text{U}}$$

The slow process, which is significant for long-term prediction is discussed below.

5.2 Distribution of α-recoil Products

Extensive investigations have been made of the distribution of α-recoil products in selectively extracted phases from weathered samples obtained from the Ranger One and Koongarra deposits. The following observations were made:

(i) In all but 1 out of 15 samples the $^{234}U/^{238}U$ activity ratios in the DCB extracted phase (goethite) were greater than those in the TAO phase (ferrihydrate, amorphous Fe, Al).

(ii) In all but 1 sample the activity ratio was greater than in the clay/quartz phase than in the goethite phase.

The average values of the activity ratios, normalised to the observed value for the TAO extracted phase (ferrihydrate, amorphous Fe, Al) are listed in Table 1, and are discussed in the following section.

5.2.1 Uranium series fractionation between phases - multiphase modelling

The observed activity ratios in each phase are the net effect of:

- the initial $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ ratios at the defined zero time point,
- transport between phases due to α-recoil, diffusion and phase alteration, and
- radiogenic decay.

Because of the inherent complexity of the system, a modelling approach is essential. As will be discussed below, modelling on this scale provides a basis for transferring information from the analogue to the repository site. For simplicity uranium fluxes only will be considered (Figure 7). Since neither diffusion nor phase alteration can lead to the large $^{234}U/^{238}U$ fractionations listed in Table 1, it will be assumed that α-recoil is an important process. A full account of the model is presented in Chapter 3 of reference [7] and in Chapter 4 of reference [18]. The simplified approach in this presentation has been used to illustrate the experimental basis for the concepts.

Assuming steady state conditions -

$$\frac{d\,{}^{4}U_{CQ}}{dt} = 0 = (1 - {}^{CQ}\rho)\ {}^{8}U_{CQ} + {}^{AX}\rho^{CQ}\ {}^{8}U_{AX} - {}^{4}U_{CQ} \qquad (1)$$

where AX and CQ are the amorphous + crystalline iron phases and clay/quartz phases respectively, ${}^{\beta}\rho^{\gamma}$ is the probability that an α-recoil product arising from decay of a parent in phase α will lodge in phase β. The absence of a subscript indicates all other phases.

From (1)

$$R_{CQ} - 1 = {}^{AX}\rho^{CQ}\ ({}^{8}U_{AX}/{}^{8}U_{CQ}) - {}^{CQ}\rho \qquad (2)$$

Where $R_{CQ} = {}^{4}U_{CQ}/{}^{8}U_{CQ}$ activity ratio.

From equation (2) it is predicted that ^{234}U excess in the clay/quartz phase increases with the ratio of the uranium in the iron and the clay/quartz phases (Figure 8(A)). Linearity would not be expected as the parameters ${}^{AX}\rho^{CQ}$ and ${}^{CQ}\rho$ would depend on the uranium concentration and distribution.

However, it was found empirically that the linearity was very substantially improved by plotting $(R_{CQ} - 1)/{}^{8}U_{CQ}$ against ${}^{8}U_{AX}/{}^{8}U_{CQ}$ (Figure 8(B)). Mathematically this implies that both ${}^{CQ}\rho$ and ${}^{AX}\rho^{CQ}$ are proportional to the concentration of uranium in the clay/quartz phase. The line of best fit intersects the X axis at 3.0 ± 0.5, i.e. no recoil-induced fractionation will occur when the ratio of the amounts of uranium in the two phases is of this order. Since the recoil distances are small (∿ 20 nm), the result implies that the uranium concentrations in the region of the phase boundary are comparable when the fractionation is small despite large differences in the average concentrations (Table 1). Since the iron minerals which amount to between 1 and 4 per cent of the total (say 2 per cent average) contain about 85 per cent of the uranium, the relative concentrations U(iron)/U(clay/quartz) are roughly (85/15)(98/2), i.e. 280/1. Clearly there is a non-uniform distribution of uranium throughout the clay/quartz phase.

This result, and the laboratory observation (Section 5.1) that uranium-236 added to the aqueous phase in batch adsorption experiments is not readily accessible to the clay/quartz phase, is consistent with the scheme shown in Figure 7. It would appear that dissolved uranium is adsorbed rapidly and reversibly onto amorphous iron and enters other phases by the slower processes of diffusion or mineral alteration.

5.2.2 Direct experimental evidence for α-recoil

Particular attention is paid to the role of α-recoil as a mechanism of transport of daughter products from one phase to another. Direct experimental evidence for the effect of α-recoil on the distribution of radium through clay particles has been obtained. The concept involved the addition of a solution of ^{228}Th and ^{226}Ra to dilute suspensions of illite, kaolinite and montmorillonite. The thorium isotope adsorbed on the clay surface and the ^{224}Ra was formed by α-recoil. The $^{224}Ra/^{226}Ra$ activity ratios were measured, by using high activity ratios were measured, by using high resolution α-spectrometry[19] in the aqueous phase and following the application of successively increasingly aggressive reagents. In extreme cases, when the residual radium was less than 0.1 per cent, ^{224}Ra enrichments exceeding 100 were observed. Of greater potential interest is the ratio of the distribution coefficients (^{224}Ra formed by α-recoil/ ^{226}Ra). They were found to vary from 1 for montmorillinite to 3.4 for illite.

5.3 Effect of Mean Residence Time on Radium Distribution Coefficients

Indirect evidence for the time dependence of distribution coefficients has come from laboratory adsorption studies and from observed uranium series fractionation in drill core. Further confirmation has been sought through a systematic study of the parent/daughter couples $^{232}Th/^{228}Ra$, $^{230}Th/^{226}Ra$ and $^{228}Th/^{224}Ra$ in groundwater from Koongarra. The half-lives of the thorium isotopes vary from 2.28 y to 1.4×10^{10} y and of the radium isotopes from 3.6 d to 1680 y.

Experimentally, thorium and radium were isolated from the groundwater and assayed by α-spectrometry. Radon was measured in the field.

The data was interpreted in terms of the procedure of Krishnaswami et al.[20]. Details are discussed in Chapter 8 of reference [7]. The theory is based on the following assumptions:

(i) A substantial fraction of the levels of α-decay products in the aqueous phase are derived by direct recoil.

(ii) Following recoil, the daughter product distributes between the aqueous phase and the surface.

(iii) The level of the inert gas radon is a monitor of the recoil injection process prior to adsorption.

The following parameters are calculated:

(a) Ω, the ratio of the rate of decay to the rate of production in the groundwater.

(b) F, the effective $^{232}Th/^{238}U$ activity ratio.

From these parameters, it was possible to estimate the variation of the radium adsorption K with the decay constant λ. The results are shown in Table 2. The adsorption coefficients increase with increasing mean residence time of the radium species (Figure 5). If this result is found to be general, it follows that estimates of retardation factors based on laboratory measurements will be conservative. Interestingly the values of K (dimensionless) calculated from the theory vary from $153<K<284$ in the sandstone environment around KD 1, to $915<K<6300$ in the weathered schists around PH 55 and PH 58 (Figure 5). In addition, the value of F (the $^{232}Th/^{238}U$ activity ratio) is approximately 0.5 at KD 1 and PH 58 (up-gradient and down-gradient of the deposit) and 0.06 at PH 55 which intersects the mineralization. That the computed parameters are consistent with the geology provides excellent support for the principal tenets of the Krishnaswami et al. theory.

6. EVIDENCE FOR A TIME INVARIANT GROUNDWATER PARAMETER ($^{234}U/^{238}U$ ACTIVITY RATIO)

A significant body of evidence was presented in Section 5 that adsorption coefficients, and hence retardation factors are likely to increase with time. Of equal importance, in any attempt to verify the long-term predictive capability of codes is the identification of time independent parameters. One example appears to be the $^{234}U/^{238}U$ activity ratio in water intersecting the Koongarra deposit. The evidence is as follows.

Down-gradient of the primary ore body in the Koongarra One deposit is a region of secondary mineralization exhibiting kinetic features of a roll front. Although the accumulation has clearly been occurring for very long periods of time, systematic variations of $^{230}Th/^{234}U$ and $^{234}U/^{238}U$ are occurring throughout the region indicating that significant uranium redistribution has occurred over recent geological time and is probably continuing to occur. The observed fractionations can be accounted for qualitatively by the procedure developed by Osmond and Cowart[21] provided the ^{234}U retardation factor is greater than ^{238}U. This is consistent with the observed ^{234}U deficit in groundwater. The weighted average $^{234}U/^{238}U$ activity ratio in all wells intersecting the the deposit is 0.79.

A simple quantitative model for the evolution of the zone of secondary mineralization is being developed by Lever[22]. This includes the effects of transport by flowing groundwater and linear equilibrium sorption (described by a constant retardation for each nuclide in the decay chain). When the concentration of uranium in the groundwater varies only slowly with distance, an approximate solution for the disequilibria between the activities of ^{238}U, ^{234}U and ^{230}Th on the rock can be obtained. It is found experimentally[7] that, except in the region where they are close to equilibrium, the activity ratios on drill core samples of $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ are either both greater than one (on the upstream side of the deposit) or both less than one (on the downstream side). This is consistent with both R_{234} (the retardation factor of ^{234}U) and R_{230} being greater than R_{238}, but is inconsistent with R_{234} being less than R_{238} (which was found by Osmond and Cowart[21]). Further it is found that ^{230}Th is much less mobile than the ^{238}U and ^{234}U, and with this assumption, the retardation factor of ^{234}U is estimated to be 1.2 times that for ^{238}U. Using estimates of the spatial variation of ^{238}U from drill core, the disequilibria can be used to estimate the time that the ^{238}U has been migrating from the primary ore body to be of the order of 3×10^6 y.

7. COLLOID TRANSPORT

The potential significance of colloids in groundwater transport is becoming increasingly widely recognized. J I Kim[23] recently wrote "Without exaggeration, it may be said that the geochemistry of actinides in groundwater is controlled predominantly by colloid chemistry." For instance, in a study of two different groundwaters from Gorleben using ultra-filtration techniques, it was found that:

- the solubility of ^{241}Am decreased by almost three orders of magnitude, and
- the sorption of ^{244}Cm on Gorleben geomatrices increased by almost two orders of magnitude,

as the filter pore size decreased from 3 nm to less than 1 nm[24].

Colloids may be classified as follows:

- true radiocolloids - aggregates of the radionuclide,
- pseudocolloids - radionuclides adsorbed on pre-existing colloids.

Indirect evidence for the role of colloids in the sub-surface transport of thorium-230 is shown in Figure 10, where the ^{230}Th/^{234}U activity ratios are plotted as a function of the uranium concentration for wells down-gradient of Koongarra, Ranger One and Nabarlek. The dissolved uranium concentration decreases with increasing distance from the deposit. If the activity ratio were solely due to the ratio of the sorption coefficients, they should be independent of the location of the sampling well. Again, recoil effects cannot account for the observations since both ^{230}Th and ^{234}Th (which leaves ^{234}U by β-decay processes) are formed by α-decay. The most likely explanation is that:

- uranium is transported predominantly in solution, while
- thorium is transported partly in solution and partly associated with colloids.

If thorium on the colloids has a lower retardation factor than that in solution the activity ratio ^{230}Th/^{234}U would tend to decrease with increasing distance from the ore body as observed.

A technique has been adapted for separating colloids from groundwater filtered through prefilters ranging down to 1 µm. The water is passed through an Amicon H.10P100 anisotropic hollow fibre ultrafiltration cartridge (0.88 m^2 area; 5.3 nm cut-off). Pressure gradients across the membrane are adjusted so that the colloid concentrate is between 1 and 2 per cent of the total. The advantages of this system are as follows:

- colloids from large volumes of water may be concentrated; in a recent experiment up to 10 000 L were used in an attempt to isolate the colloidal component of environmental plutonium,
- colloids are not exposed to air prior to concentration,
- it is technically feasible to select colloids of different size ranges.

A detailed discussion is presented in Chapter 5 of reference [7]. The following results may be reported:

(i) Less than two per cent of the uranium is associated with colloids in the size range 0.005-1 µm. The uranium was in isotopic equilibrium with that in the aqueous phase.

(ii) Up to 40 per cent of the thorium was concentrated with the colloids; in contrast to the uranium there was no evidence of isotopic equilibrium between the aqueous phase and the colloids.

Work is proceeding in order to better characterize the colloids, to extend the range of elements which can be studied on the colloids and to develop methods for 'dating', i.e. determining the mean residence time of the colloids.

8. EXTENSION OF THE ANALOGUE

8.1 Fractured Rock Studies

The effectiveness of crystalline rocks as barriers to the migration of radionuclides depends on:

- the extent to which groundwater can diffuse into the bulk rock through microcracks and fissures,
- the mineralogy of the accessible surfaces,
- the efficiency of colloid migration through fractures.

Three mechanisms of transport through fractured rock are currently under investigation:

- advection - dispersion - surface sorption,

- advection - dispersion - matrix diffusion, and

- advection - channelling - matrix diffusion.

Clearly, establishment of the correct mechanism in each proposed repository site is essential for the long-term prediction of radionuclide transport. A number of laboratory experiments, and elegant single fracture tracer studies have been performed[25]. Although the general features of matrix diffusion theory have been confirmed, it has not been possible to distinguish between the three mechanisms. An endeavour is therefore being made to assess the issues by considering the net effect of transport in the vicinity of pre-existing fractures over geological time. Three techniques are being employed:

- PIXE/PIGME multi-element assay,
- fission track/α-track distributions.

8.1.1 Multi-element distribution (PIXE/PIGME)

In a preliminary investigation the PIXE/PIGME facility at the AAEC has been used to study the distribution of elements in schist samples from the Jabiluka One and Two and Ranger One and Three ore bodies[26]. The samples were sectioned with a diamond saw and polished. The X-ray emission spectrum provides information on both the major elements Si, K, Ca, Ti and Fe and the trace elements Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb and U; the γ-ray spectrum is used to assay Na, Mg, Al, Li, B and F. Particular attention was paid to to a sample from Ranger Three, S3/114, as individual grains were often about 1 mm, the current resolution of the proton beam.

Signficant (5%) simple correlation coefficients (r) were found between uranium and K ($r = 0.960$), Rb (0.959), Zn (0.920), Sr (0.826), Th (0.779), Ga (-0.673), Si (-0.605) and Ni (-0.420). The association with K and Rb suggests that mica (a major K mineral) near uranium bearing veins is rich in Rb. The negative correlations imply that the uranium bearing veins are low in quartz, Ga and Ni.

The ultimate aim of the project is to map the distribution of indicator elements as a function of distance from pre-existing fractures and to interpret the data in terms of the cumulative effect of migration over geological time. Of particular importance to the assessment of repository sites is the retardation of transuranic elements such as ^{237}Np, ^{239}Pu, ^{241}Am and the fission products ^{99}Tc and ^{129}I. The significance of the PIXE/PIGME approach is that assay of a number of acceptable chemical analogues is possible. These include:

- for a range of transuranics - lanthanides or uranium,
- for ^{99}Tc - Re(IV) in the reduced state, and Re(VII) in the oxidized state,
- for ^{129}I - I or Cl.

The system is being further developed by:

(i) improving the beam resolution from about 1 mm to about 50 μm,

(ii) introducing the capability of two-dimensional scanning and optical location of the proton beam.

It will thus be possible to correlate the areal distribution of indicator elements with those of the uranium and uranium daughter products determined by the fission track and α-track techniques outlined below.

8.1.2 Fission track and α-track studies

Fission track and α-track techniques have been used to map the distribution of uranium and of uranium daughter products on a set of four petrological slides sectioned normal to a pre-existing fracture:

Ranger S3/114	27.2 m
Ranger S1/35	13.7 m
Ranger S1/146	2.0 m
Jabiluka DH 3	33.0 m

The Ranger and Jabiluka ore bodies are vein deposits in which uraninite was deposited 700 to 1200 million years ago. Particular attention was paid to the S3/114 sample where it was confirmed from fission track and electron microprobe analysis that uranium as the mineral saleeite was confirmed to the veins.

Since the surrounding chlorites, micas and quartz do not contain significant phosphorus, it appears that the phosphate needed for saleeite formation was transported by the solutions causing weathering of the veins. Considerations of differences in the density and the uranium composition of uraninite and saleeite lead to the conclusion that <u>either</u> a substantial proportion of the uranium was transported to a location remote from the vein, <u>or</u> that the pressure in the vein during saleeite formation was sufficient to enhance the vein volume to accommodate the weathering products.

Interestingly, neither the electron microprobe, nor the optical study provided evidence for weathering along the margin of the vein. In addition, comparison of fission track and α-track patterns for all partially weathered samples showed that the uranium daughter products had not diffused out of the veins into the surrounding crystalline matrix.

It is not yet possible to draw substantive conclusions on the mechanism of radionuclide transport through fractured rock. However, sufficient has been achieved to confirm that the concept of combining α-track, fission track and multiple element mapping using PIXE/PIGME on chosen material near pre-existing fractures is a promising approach.

9. APPLICATION OF NATURAL ANALOGUE STUDIES TO SITE ASSESSMENT

The aim of the Alligator Rivers, and many other natural analogue studies is to contribute to the assessment of high-level waste repository sites, in particular the long-term rate of radionuclide transport in the far field. Two approaches will be discussed.

(i) Relating the rate of transport of designated transuranic elements and fission products to, say that of uranium,

(ii) the verification of geochemical transport codes for long-term prediction.

9.1 Migration Rates of Transuranic Elements and Fission Products, Relative to Uranium

Two distinct stages are involved. Firstly, using the procedure outlined in (i) to (iv) below, an estimate is made of the long-term retardation of key transuranics and fission products, relative to that of uranium, and interpreted in terms of the sorption properties of the host rock. The second stage involves site specific studies of the hydrology and the uranium series distribution and sorption properties of the host rock. Using the principles underlying the development of the multi-phase model (Section 5.2.1) estimates may be made of the retardation factor of uranium; using the relationship between uranium and key transuranics and fission products obtained from the analogue, the retardation factors for the latter key radionuclides at the proposed site may be found.

The first stage, outlined above, involves the following steps:

(i) *Establish, at the analogue site, retardation factors for uranium over geological time.* By correlating systematic variations of $^{234}U/^{238}U$ activity ratios of dissolved uranium with groundwater travel times obtained from carbon-14 dating, retardation factors of <250 down-gradient of Ranger One and ∿30 down-gradient of the deposit within the Carizzo[17] aquifer, Texas, were estimated. By contrast, a value of $>10^4$ was calculated from estimates of the rate of migration of secondary mineralization associated with Koongarra. The difference is of particular significance because

- the last mentioned value was calculated from equations forming the basis of many geochemical codes, and
- it is not considered that the differences can be accounted for in terms of the groundwater geochemistry.

Briefly, it is now believed that the measured $^{234}U/^{238}U$ variation in groundwater is not simply due to decay but also to the cumulative effect of exchange with uranium on the ferrihydrate, and of in situ ^{234}U production. The relative magnitude of the authigenic component will increase with distance down-gradient of the deposit. It will lead to a reduction in the change of $^{234}U/^{238}U$ with groundwater travel times and a decrease in the estimated uranium retardation factor.

(ii) *Interpret the data in terms of sorption coefficients.* Studies of the rate of advance of the secondary mineralization at Koongarra have indicated that retardation factors valid over geological time can be adequately predicted by laboratory sorption coefficients. These measurements refer to accessible minerals, predominantly amorphous iron (manganese and aluminium) and ferrihydrate. To be valid for very long radionuclide residence times, it may be necessary to increase the sorption coefficients by the ratio U(total)/U(accessible minerals). In the case of the weathered zone of the Ranger deposit, the magnitude of this ratio is about 4. Work on assessing the residence time at which the adjustment should be made is continuing.

(iii) *Establish the role of groundwater colloids in the migration of key elements.* As indicated in Section 7, techniques have been developed to establish the fraction of uranium series nuclides, especially thorium on groundwater colloids. Attempts are being made to extend the work to include environmental plutonium-239 and to determine the residence times of colloids, i.e. the ratio of colloid to groundwater transport rates.

(iv) *Establish the validity of proposed chemical analogues of key transuranic and fission product elements.* Since the levels of a number of key transuranic elements and fission products can be measured at the analogue site, direct geochemical evidence may be sought for the applicability of their proposed chemical analogues. If the validity of the analogues is confirmed, they may be used to predict the long-term rate of transport of the transuranics and fission products under far field conditions.

The second stage involves relating the finding at the analogue and the proposed repository sites. The following elements need to be considered:

- the regional hydrology,
- the hydraulic properties of the host rock,
- the groundwater chemistry,
- the levels (and if possible the nature) of the colloids,
- the sorption properties of the accessible minerals within the host rock for actinides, radium and fission products,
- the distribution of uranium series elements and the chemical analogues of transuranics and fission products through the host rock.

The principles outlined in Section 5.1.2 are used to estimate the retardation factor at the repository site relative to that at the analogue (provided the mineralogy at the two sites is sufficiently similar). The uranium retardation factor is then related to that of the key transuranic elements or fission products either through chemical analogues or through measured sorption coefficients.

9.2 Some Implications to Model Verification

As indicated in Section 4, an important aim of the natural analogue studies is the assessment of the generating equations which form the basis of the transport codes such as SWIFT. There are two classes of uncertainties:

(i) those resulting in our lack of knowledge of the -

  - groundwater hydrology,
  - hydrogeochemical parameters, and the
  - variation of both parameters over the timescales of interest,

and

(ii) those resulting from the fact that the models represent an imperfect description of the transport process.

The first class of uncertainties can only be reduced by detailed study of the proposed repository site. Retardation factors associated with the transuranic elements and fission products can be estimated from:

- direct laboratory measurements, and
- the observed distribution of analogue elements on the host rock and in the groundwater.

The importance of colloids on, say, the transport of thorium-230 can be assessed directly. Arguments that a lack of precision in the knowledge of some parameters e.g. dispersivity, is of little consequence, may be developed.

Of greater relevance to analogue studies is the second class of uncertainties, i.e. those relating to the validity of the generating equations. For instance, in the SWIFT code it is assumed that, under specified conditions, the interaction between the dissolved radionuclides and the rock is described by a simple linear isotherm determined by a time independent adsorption coefficient. Three examples of phenomena which cannot be so modelled will be cited.

(i) Direct evidence has been obtained that the radium sorption coefficient increases with increasing residence time. However, kinetic effects will only be important if the time constant of the rate determining step is of the same order as that of the overall process. Unfortunately, this condition does not apply at Koongarra as the timescale associated with the transport of uranium through the region of secondary mineralization is 10^6 years, which is three orders of magnitude greater than the time constant of ^{226}Ra. Another time dependent process is the alteration of the accessible minerals. Attempts are being made to model the distribution of uranium series elements through the amorphous iron, crystalline iron and clay/quartz phases of the weathered schists in order to determine the timescales.

(ii) Colloid transport has also been shown to be important. Again, the impact on modelling will depend on the residence time T, of the radionuclide on the colloid. If the residence time is short compared with radionuclide migration time, the transport process can be modelled with a single retardation factor R, the magnitude of which will be determined not only by the sorption coefficient, but also by the colloid/groundwater velocity ratio. On the other hand, if the residence time is much greater then the migration time, solute and colloid transport may be modelled independently.

(iii) A third phenomenon which may affect the generating equation is α-recoil. This is only important for key radionuclides formed in the far field by decay of parents leached from the repository. The effect of α-recoil is to increase the sorption coefficient. For radium on clays, increases of up to a factor of 3.7 were observed.

The 'residence time' and 'α-recoil' effects will increase retardation factors; colloids, on the other hand may lead to a decrease and are hence particularly significant.

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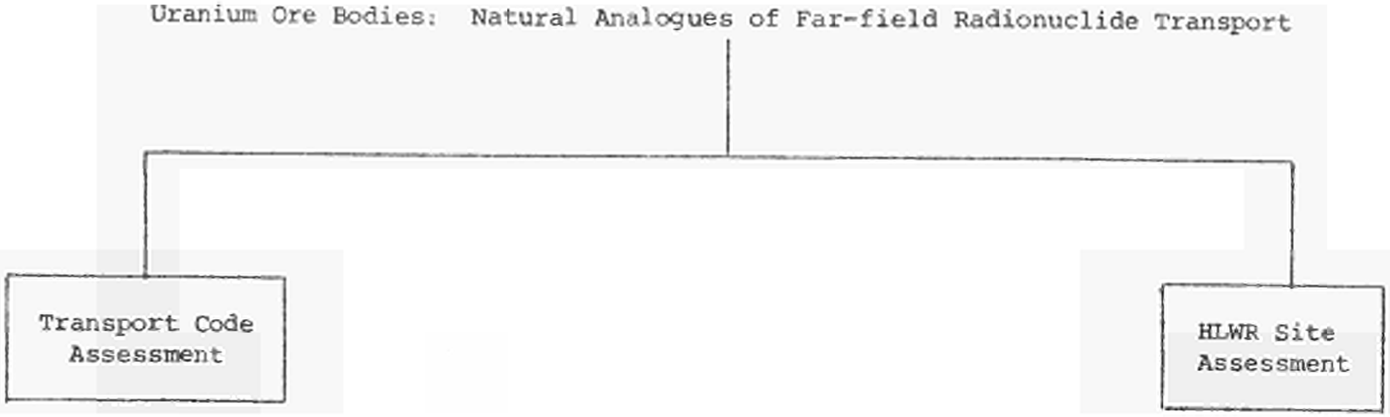


FIGURE 1 Uranium ore bodies as natural analogues of far field radionuclide transport.

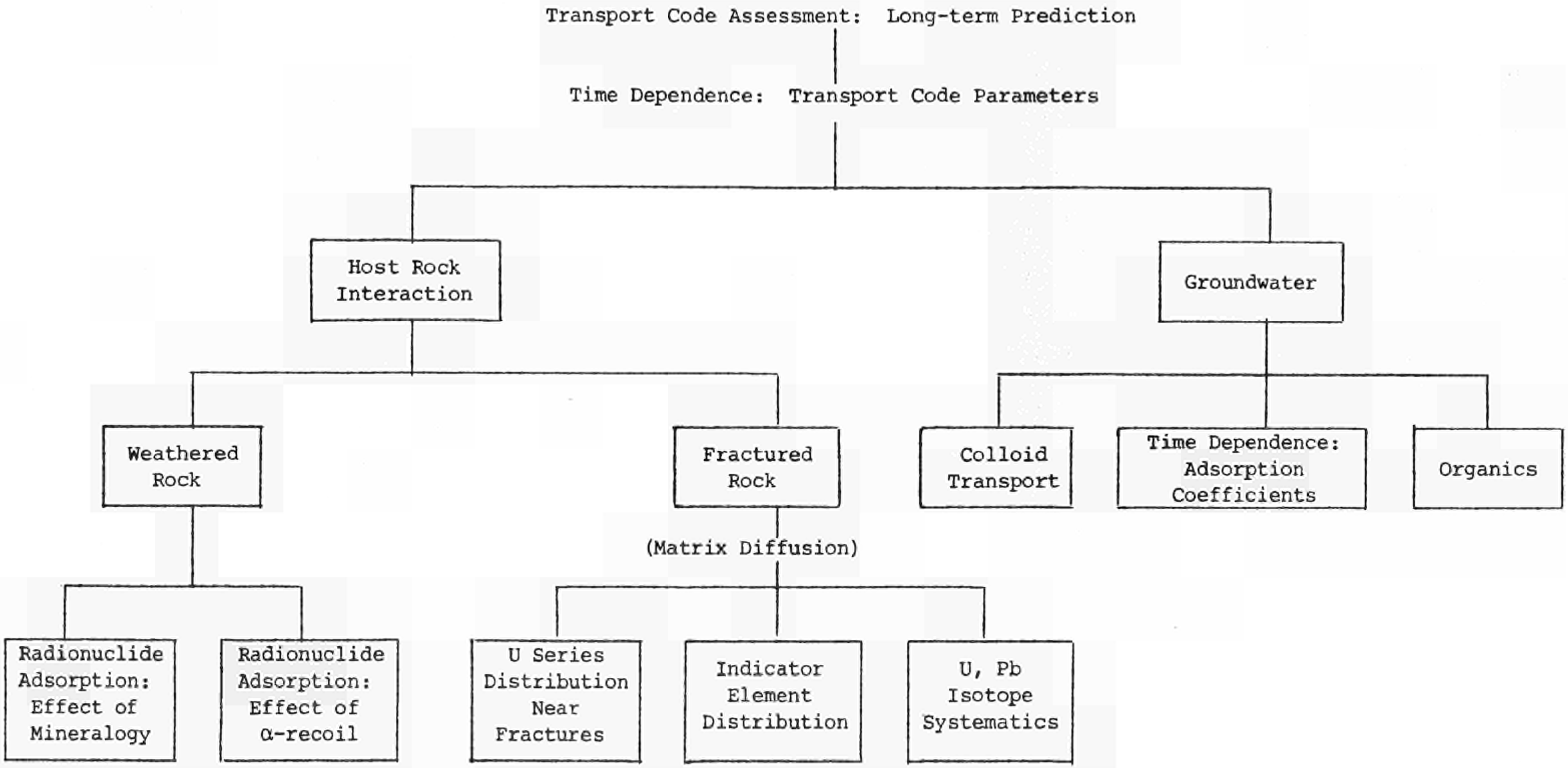


FIGURE 2 Uranium ore bodies as natural analogues of HLWR in the far field - application to the assessment of the long-term prediction capabilities of transport codes.

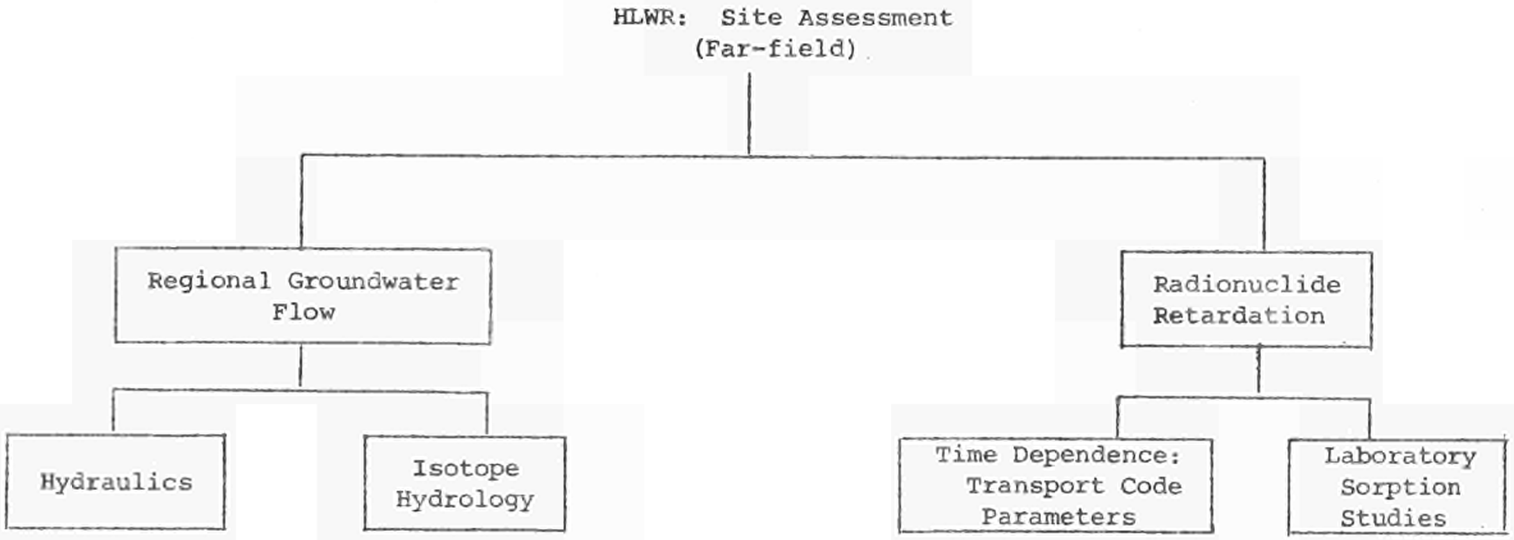


FIGURE 3 Uranium ore bodies as natural analogues of HLWR in the far field - application to site assessment.

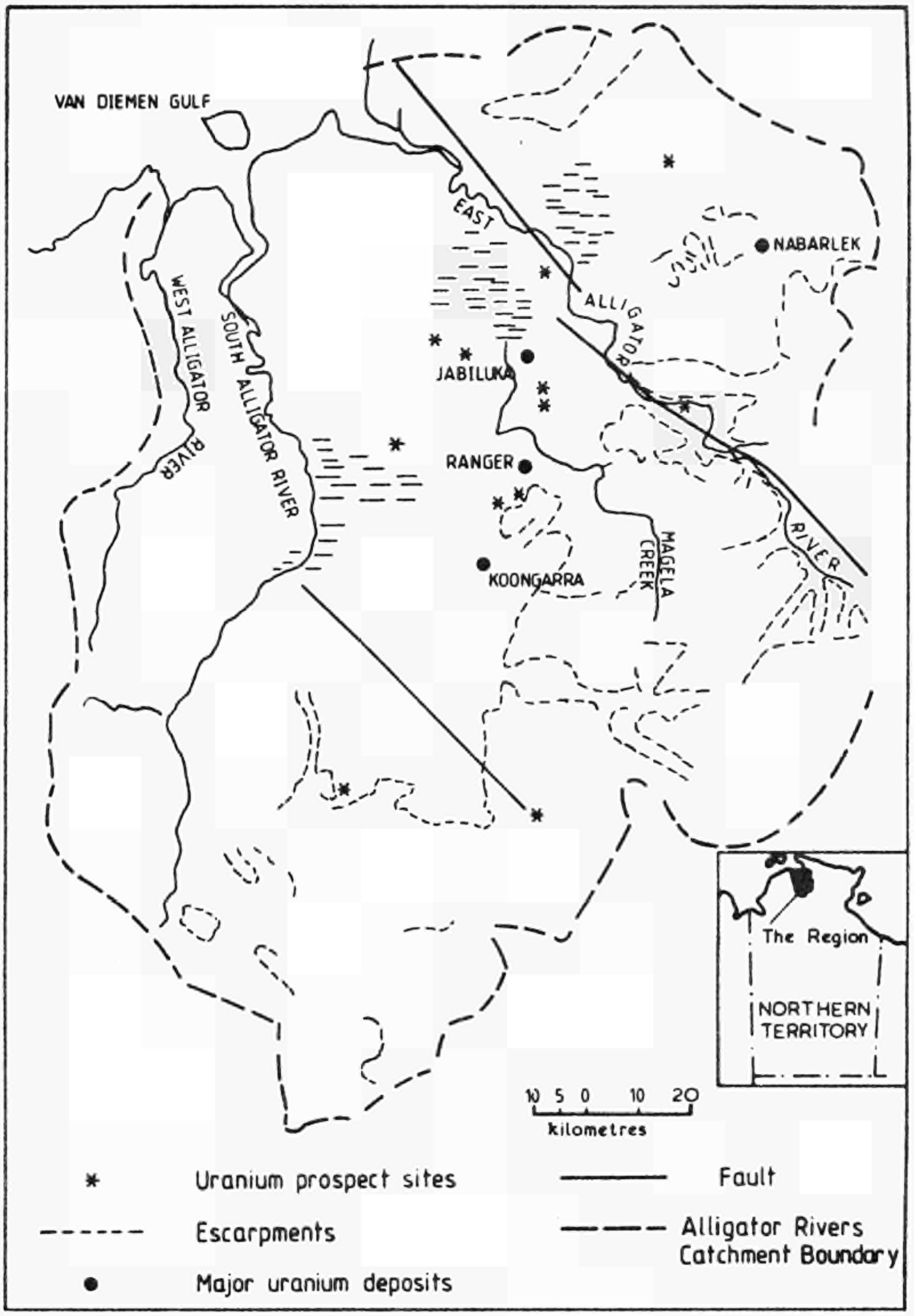
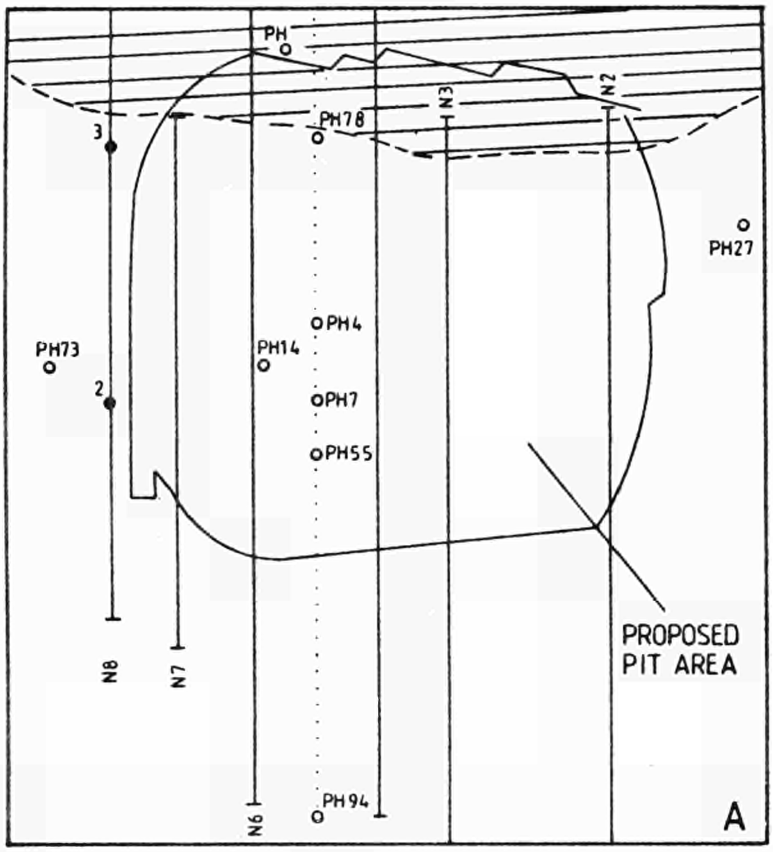


FIGURE 4 Location of uranium ore bodies within the Alligator Rivers region of the Northern Territory of Australia.



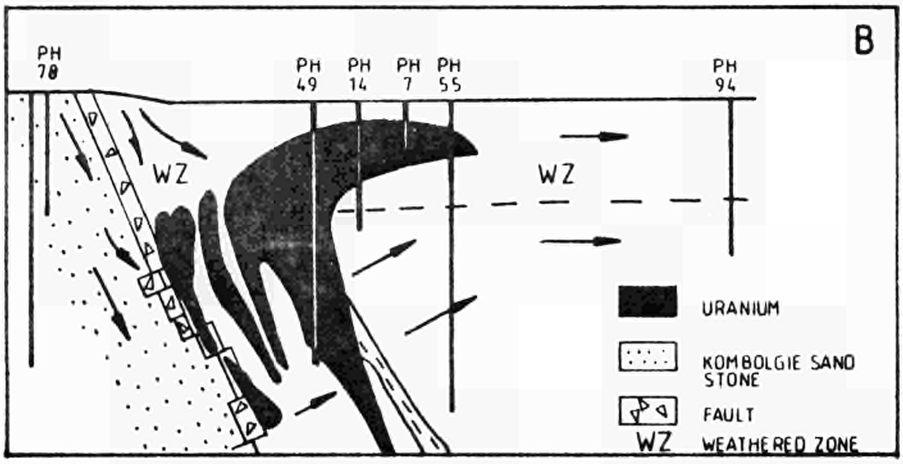
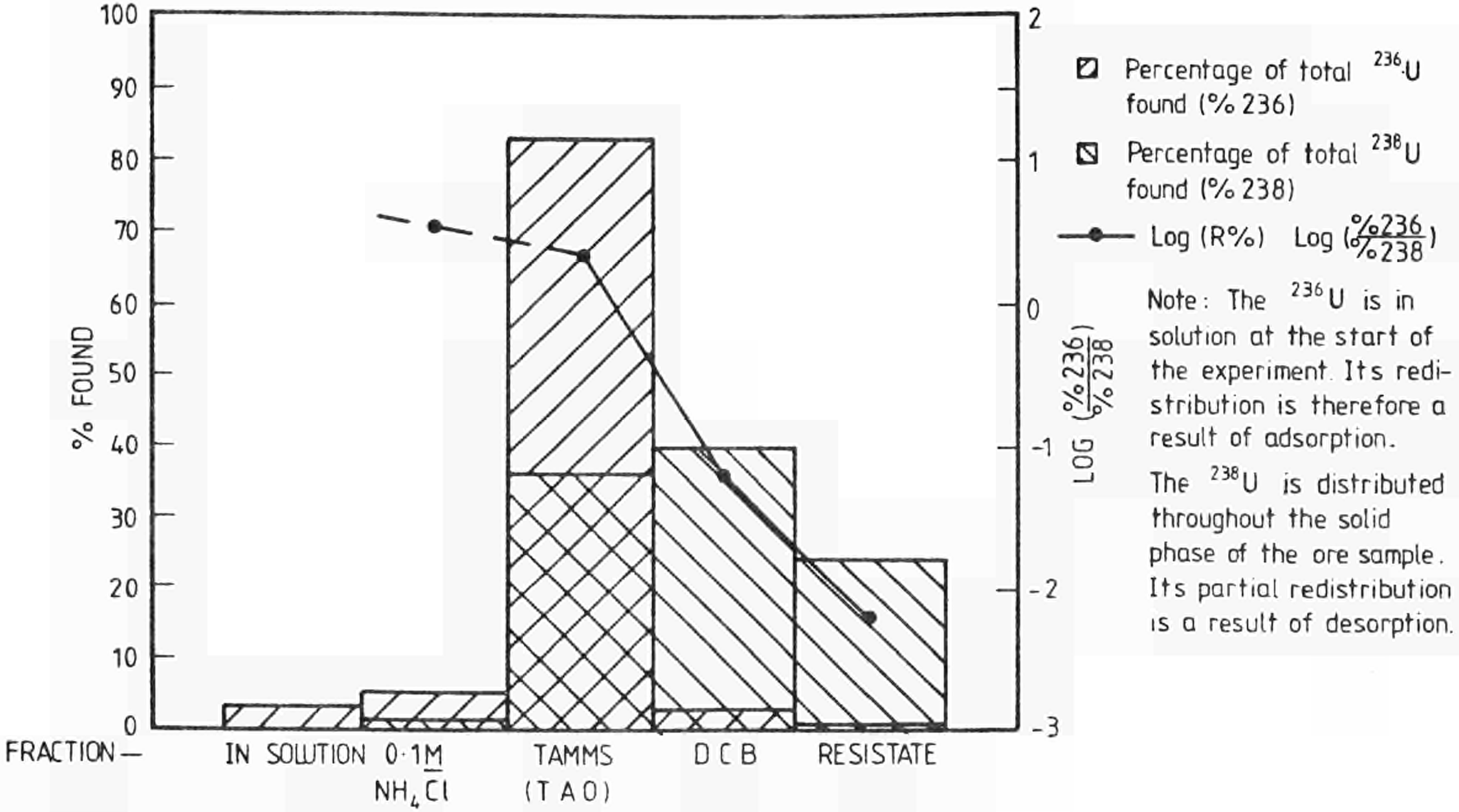


FIGURE 5A **Location of the sampling wells at the Koongarra deposit (adapted from Figure 10, reference [13]).**

FIGURE 5B **A section between wells 78 and PH 94 showing the location of a major fault, the extent of uranium deposits, the boundary of surface oxidation and the groundwater flow paths (adpated from Figure 1, reference [12]).**



Note: The ^{236}U is in solution at the start of the experiment. Its redistribution is therefore a result of adsorption.

The ^{238}U is distributed throughout the solid phase of the ore sample. Its partial redistribution is a result of desorption.

FIGURE 6 The effect of the selective phase extraction procedure (Table 1) on (a) the percentages of ^{236}U and ^{238}U in the aqueous phases, and (b) the ratio of the percentages in the aqueous phases. Sample: Ranger One drill core S1/146, 2.7 m.

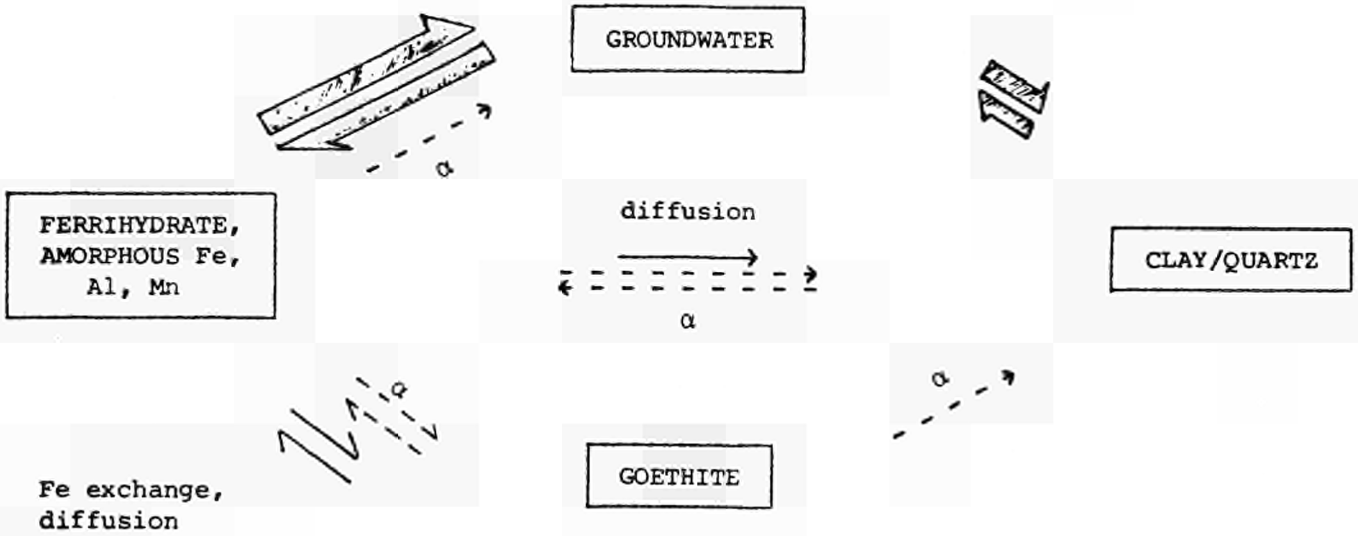


FIGURE 7 The flux of uranium between specified separable phases within the weathered ore.

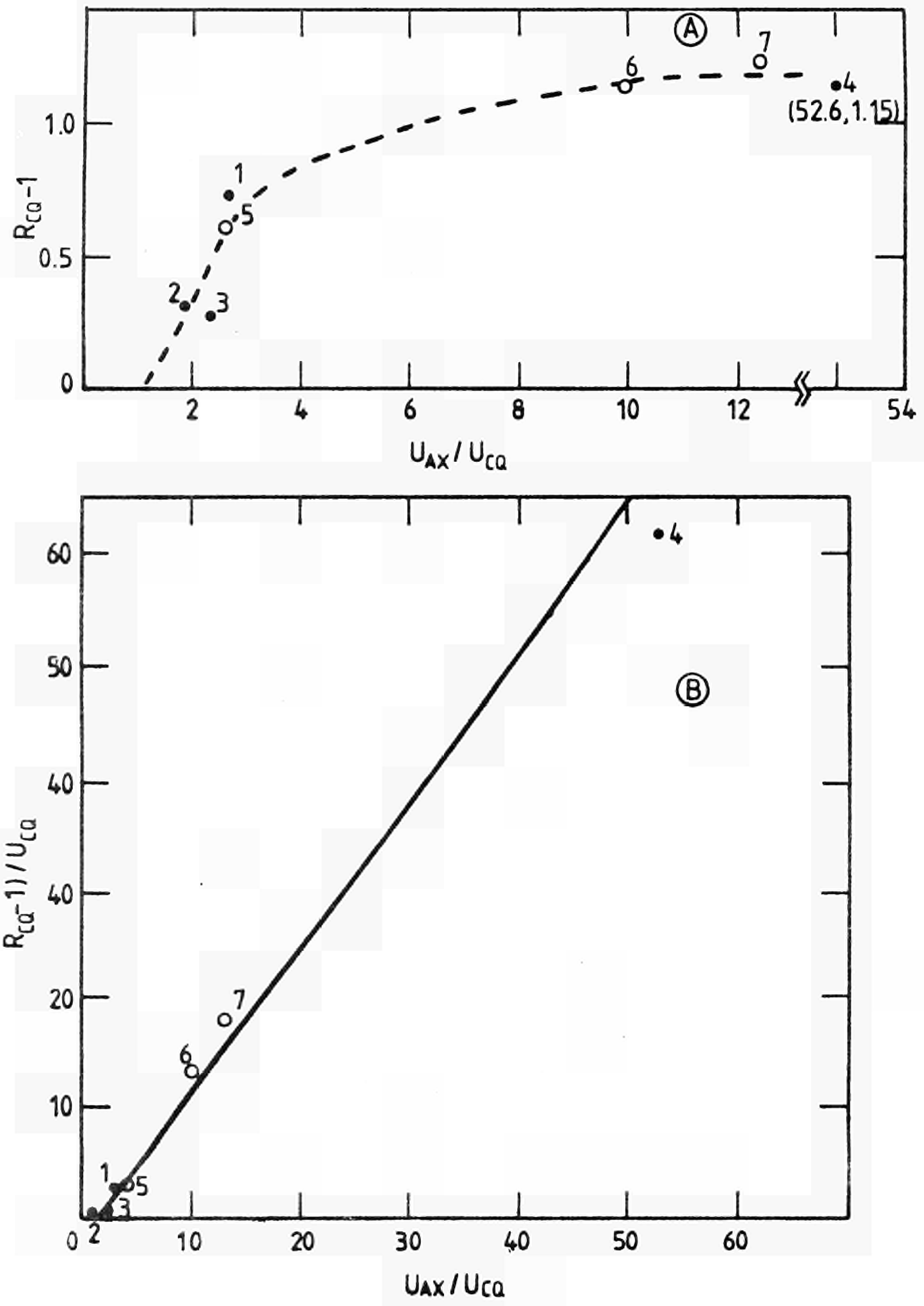


FIGURE 8 Variation of the ^{234}U enrichment in the clay/quartz phase $R_{CQ}-1$ (part A) and $(R_{CQ}-1)/{}^{8}U_{CQ}$ (part B) with ${}^{8}U_{AX}/{}^{8}U_{CQ}$. ${}^{8}U_{AX}$ and ${}^{8}U_{CQ}$ are the ^{238}U levels in the amorphous and crystalline iron (AX) and clay/quartz (CQ) phases respectively.

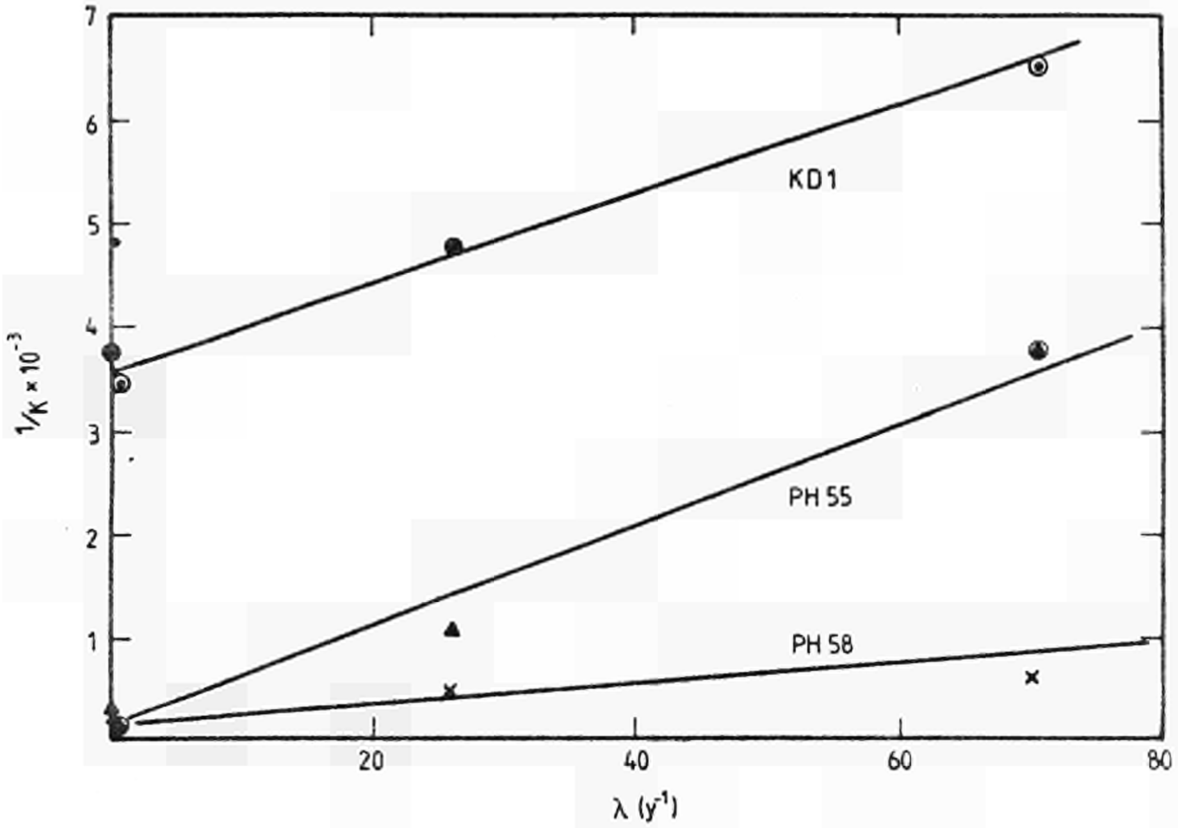


FIGURE 9 Variation of the reciprocal of the ^{226}Ra, ^{224}Ra, ^{223}Ra adsorption coefficient with the decay constants.

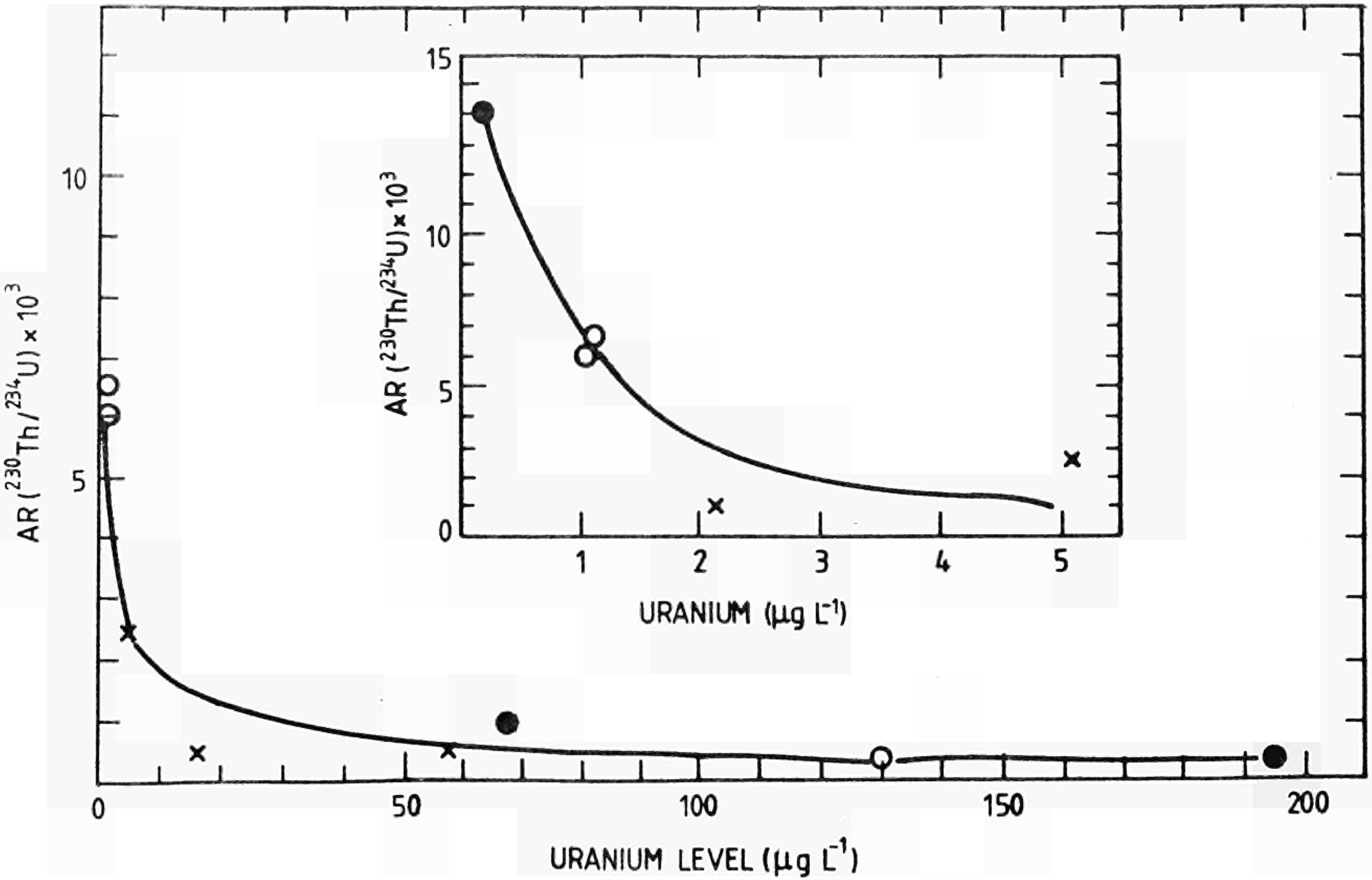


FIGURE 10 Variation of the ^{230}Th/^{234}U activity ratio with ^{238}U, i.e. with distance from the uranium deposits.

TABLE 1

SELECTIVELY EXTRACTED PHASES FROM WEATHERED ORE*

Reagent	Composition	Phase Description (Abbreviated)	U (%)	$^{234}U/^{238}U$	$^{230}Th/^{234}U$
Tamms Acid Oxalate [15,16]	0.2 M ammonium oxalate, 0.2 M oxalic acid, pH 3.25	ferrihydrate, amorphous Fe, Mn, Al	31±10	0.75±0.1	0.61±0.5
CDB[17]	citrate, dithionite bicarbonate solution, 80°C	crystalline Fe (goethite)	54±7	1.09±0.12 (1.45)	1.23±0.13 (2.01)
Digestion - fusion	digest with HNO_3, HF, $HClO_4$ - fuse with Na_2O_2	clay/quartz	15±9	1.7±0.5 (2.26)	1.4±0.2 (2.30)

* Samples from Ranger One and Koongarra Ore Bodies.

TABLE 2

RATE AND ADSORPTION PARAMETERS (RADIUM)

Well	^{223}Ra			^{226}Ra			^{224}Ra			^{228}Ra		
	P (dpm/L)	$\Omega \times 10^3$	K	P (dpm/L)	$\Omega \times 10^3$	K	P (dpm/L)	$\Omega \times 10^3$	K	P (dpm/L)	$\Omega \times 10^3$	K
Koongarra												
KD 1	207	4.83	206	4536	3.77	264	4536F (1829)	2.74/F (6.52)	364F (153)	4536F (1905)	1.48/F (3.52)	677F (284)
PH 55	5488	1.09	915	120194	0.236	4228	120194F (7572)	0.236/F (3.74)	4228F (2266)	120194F (7572)	0.097/F (1.54)	1.0×10^5F (6300)
PH 58	584	0.456	2191	12797	0.274	3647	12797F (6526)	0.268/F (0.523)	3717F (1896)	12797F (6526)	0.140/F (0.275)	7115F (3629)
Nabarlek												
OB 25	2322	0.50	1972	50872	0.0087	11457				50872F*	0.0056/F	17627F

* Parameter F cannot be estimated.

CIGAR LAKE PROJECT :
A U-DEPOSIT NATURAL ANALOG.

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at the Analog Workshop, Brussels, November 1985 hosted by CEC.

Introduction

Since 1982 the Canadian Nuclear Fuel Waste Management Program (NFWMP) has conducted natural analog studies to complement the experimental generic research towards safe underground disposal of fuel wastes in plutonic rock. A major component of the natural analog work is centred on using the sandstone-hosted U-deposits in northern Saskatchewan as analogs of disposal vaults. Through cooperation with the exploration and mining companies, studies have so far been conducted on the U-deposits at Dawn Lake, Key Lake and Cigar Lake (Figure 1).

The justification for a natural analog study of unweathered sandstone-hosted U-deposits is summarized by the following characteristics of these deposits :

1. There are no detectable indicators at surface of the unaltered Precambrian U-deposits. Even for shallow deposits (~ 200m depth) direct signals such as radiation, dissolved or dispersed ore-elements, and daughter gas are not detectable at surface.

2. The deposits consist of massive, highly concentrated ore bodies containing between 1 and 65 % U_3O_8.

3. The pressure (>700bar), temperature (150-200°C) and the salinity (200-350g/L TDS) of the ore-forming solutions were similar or higher and lasted much longer compared to projections for the first half-life of a disposal vault within the regime of deep saline groundwaters.

4. A clay-rich halo in the sandstone hostrock surrounds the massive ore bodies in a fashion similar to the buffer and backfill in a disposal vault.

5. Several hundred meters of sandstone hostrock plus several tens of meters of overburden perform the same role as the farfield and the biosphere, respectively, of a disposal vault.

6. The intersection of the ore bodies by fractures, the lack of engineered containment barriers and the higher porosity and permeability of the sandstones compared to granite, make such a deposit an open system for groundwater flow compared with a disposal vault.

7. The Pb-isotopic record shows that these ore bodies have survived several major groundwater-interaction events since ore formation at around $1x10^9$ years ago.

The sandstone-hosted deposits thus provide an excellent opportunity to study the specific processes and parameters that control trace-element mobilities in a system similar to or more open than that expected for a disposal vault.

Furthermore, it is recognised that many features as well as genetic parameters of certain sandstone-hosted deposits in northern Saskatchewan are similar to those for the Archean U-deposit at Oklo in Gabon, west Africa. The younger age of these Saskatchewan deposits precludes the occurence of a spontaneous nuclear reaction in these deposits. However, observations and data from these Saskatchewan deposits can provide insight to the conditions and compositions of the Oklo deposit prior to the onset of the nuclear reactions.

The Cigar Lake Deposit

The Cigar Lake deposit is the biggest and richest deposit of U-ore in northern Saskatchewan to date. The geology and geometry of the deposit are very simple (Figure 2). The deposit occurs within the Proterozoic Athabasca Sandstone Formation just above the contact with the underlying high-grade rocks of the Archean Shield. The horizontal ore body is surrounded by a clay-rich halo and overlain by flat lying sandstone plus a thin veneer of glacial overburden. Many subvertical fractures intersect both the ore body and the hostrocks.

The ore body lies at a depth of 430m and occurs as an irregular-shaped lens (~ 2000m L x 50-100m W x 1-20m H) inside a 10-50m thick clay-rich halo. The age of primary mineralization has been dated at 1.3×10^9 years. The average ore grade is 14% U_3O_8 with a maximum of more than 60% U_3O_8. The present ore reserve is calculated at 147×10^6 kg U which is comparable to a disposal vaults contents for used fuel.

In addition to these characteristics, the Cigar Lake deposit is particularly valuable to conduct a comprehensive analog study because of the present status of development of the deposit. The deposit has been extensively drilled with more than 180 drillholes for a total of 80 km of core. Mine development is scheduled to start not before 1989. In addition to exploration data, extensive mineralogical and geochemical information already exists and is being collected by the exploration and mining companies. Environmental impact studies have included investigations of the hydrogeology and groundwater chemistry, as well as many aspects and processes at surface and in the glacial overburden.

AECL's Present Analog Program

Natural analog studies on the Cigar Lake deposit have been conducted for the last 2 years. The main studies are:

1. Trace-element distribution in the sandstone hostrock around the ore body. This study includes the infillings of the fractures in the sandstone as well as the rock matrix adjoining these fractures. It addresses the following aspects : importance and extent of matrix diffusion, importance of and changes in Eh and pH in matrix dissolution over long periods of time, and stability plus sorption parameters of secondary minerals. The following techniques are being employed : chemical analysis (XRF, INAA, microprobe), petrographic analysis and XRD, fluid inclusion analysis on suitable phases, and stable plus radiometric isotope analysis.

2. Trace-element distribution in the clay-rich halo surrounding the ore body. This study addresses the composition, stability and sorption characteristics of the mineral phases comprising the clay-rich halo. The clay mineral component of this study is contracted out to Carleton University in Ottawa. The following techniques are being employed : chemical, mineralogical and isotope analyses, mineral separation, and selective extraction of trace elements.

3. Groundwater interaction and trace-element migration. A study on present groundwater compositions to analyse the dissolution of the ore minerals, the parameters controlling their stability and the parameters controlling the transport of dissolved trace-elements. The following techniques are being employed : sampling and analysis of groundwaters including dissolved gases, colloids, isotopes, organics and bacteria.

4. Migration of selected radionuclides. This study attempts to determine the extremely small quantities of fission products and transuranics and their distribution in and around the ore body. These radionuclides (e.g. ^{99}Tc, ^{129}I and ^{239}Pu) are expected to be relatively enriched in the very high-grade ore. It is planned to use ultra-sensitive mass spectrometry on ore, rock and water samples.

Scope for Improvements and Expansion of Activities

Results and experience of the first two years of study on the Cigar Lake deposit have both confirmed the importance of this deposit as a natural analog, and identified scope for improvements and expansion in research activities.

An improvement is required in the quality of groundwater samples in particular for a better characterization of colloids and organics. Presently groundwater samples are collected from piezometers in exploration holes. These piezometers are primarily installed for hydrogeological measurements and do not always meet the quality standards for geochemistry. The best option for improvement is the installation of "clean" piezometers dedicated to groundwater geochemistry. This requires a larger diameter drillhole for a packer-equipped piezometer which minimizes the potential for contamination. In addition, a hollow-fiber filtration system combined with a down hole pump is being considered for improving the collection of colloids. This filtration system requires the use of packer-equipped piezometers.

An expansion of activities is required to allow the completion of studies on certain aspects, such as the flow and composition of groundwater, before the deposit is being disturbed by mining activities. This expansion should include a better hydrogeological characterization of the site, more on-site analyses on groundwater samples, and an expanded analytical program for fission products, transuranics and other isotopes.

Possible International Involvement in the Cigar Lake Project

(not to be discussed in Workshop forum)

It is suggested that countries interested in the Cigar Lake project and its results, formalize an international involvement in the project. The objective of this involvement is to optimize the range and activity of the natural analog studies on the Cigar Lake deposit before the onset of mining activities. Results of these studies will be used both for a better understanding of the evolution of the Oklo deposit, and in assessing many aspects of underground disposal of high-level waste.

The suggested format for involvement is that AECL continues to operate the project assisted by technical and financial input from participating countries. Cigar Lake Mining Corporation (CLMC), as owner and operator of the deposit, has indicated its preference for AECL's role as coordinator and operator of the analog project. The duration of the project will be for at least three years or until mining activities begin. The project could involve the coordination and execution of the technical program, the organization of at least one meeting per year to report results and review the technical program, and the organization of field trips. These possibilities will be explored outside the workshop with various international agencies and states.

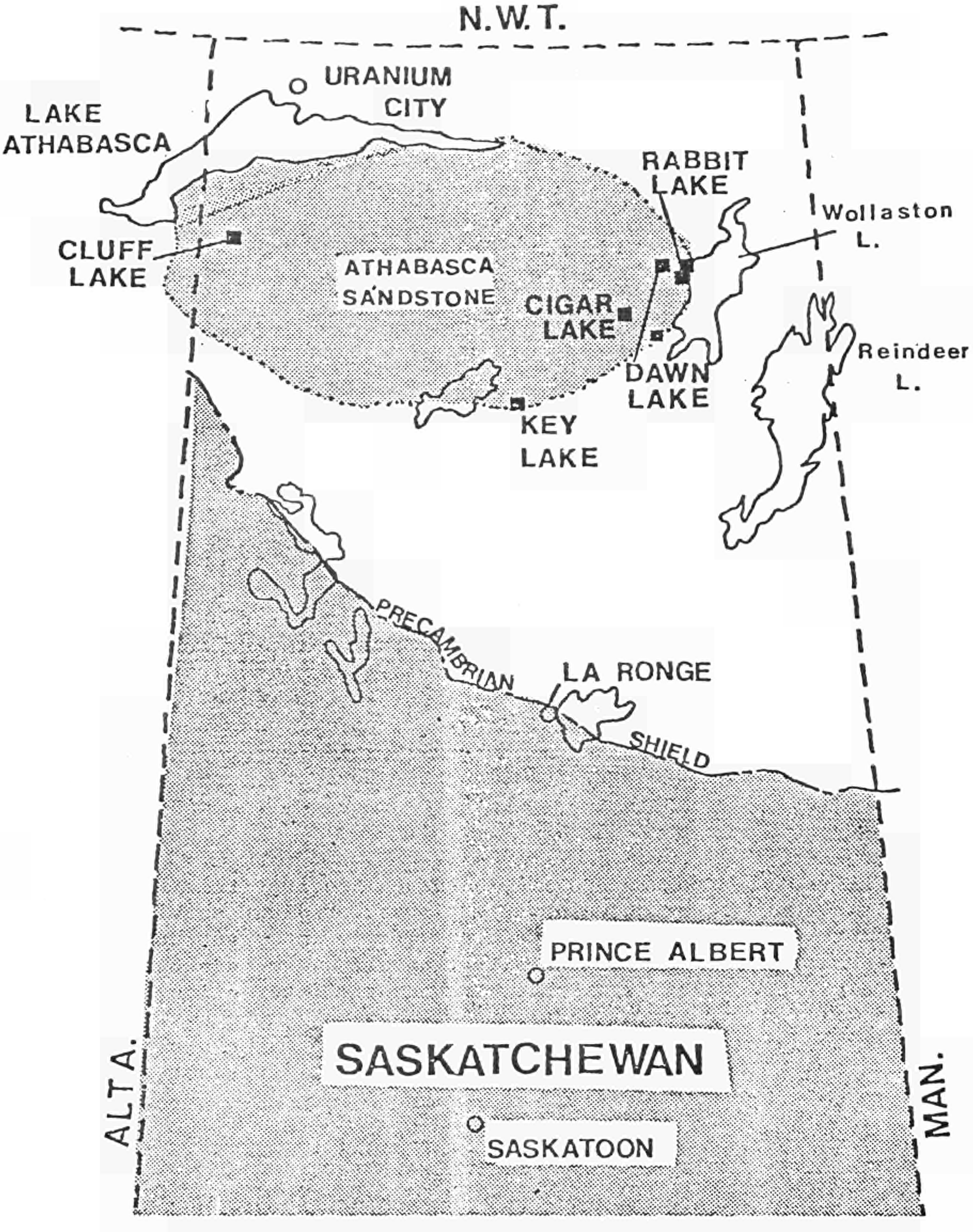
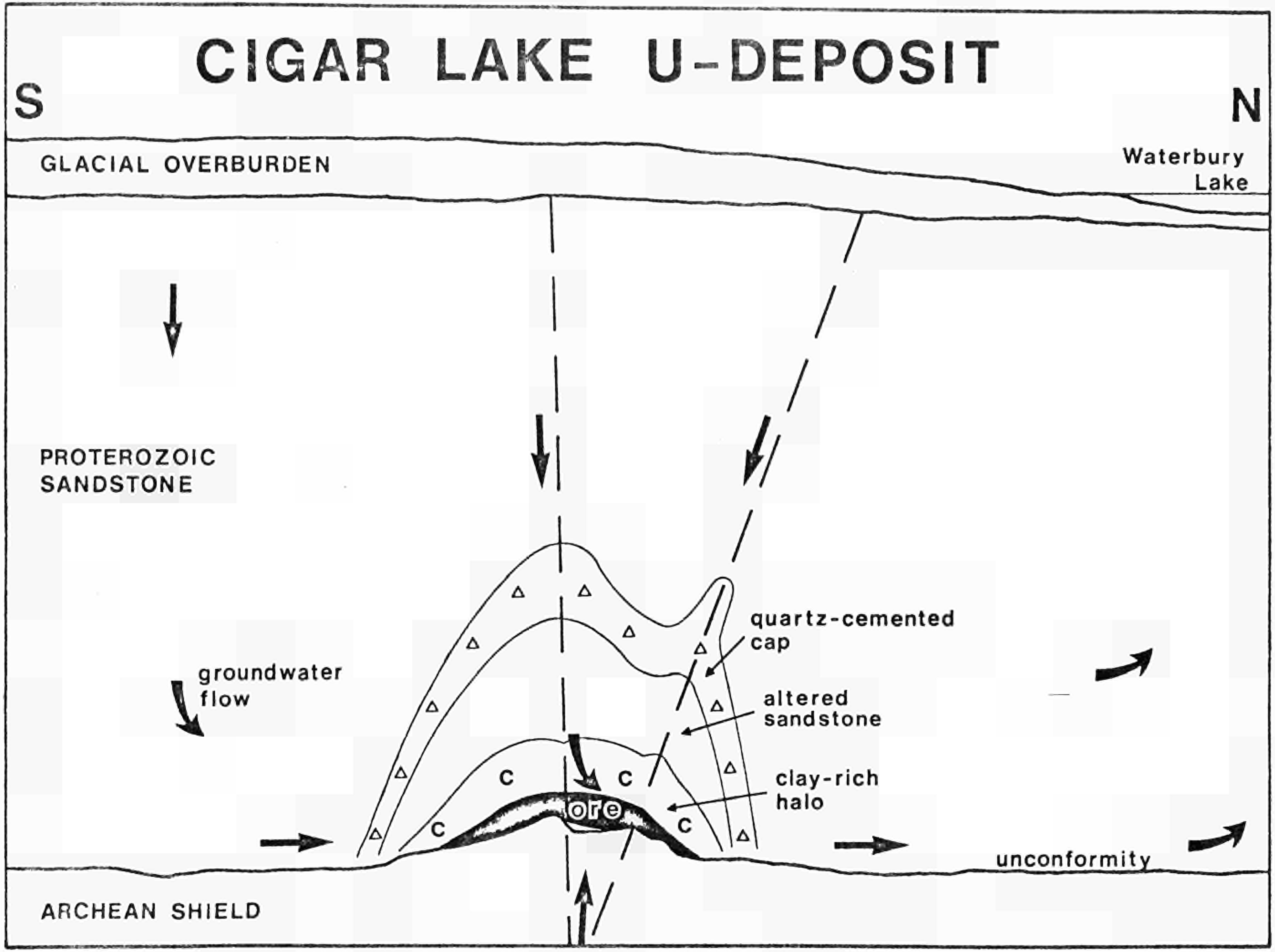


Fig 1

GURE 1: Location of Some Important Sandstone-Type Uranium Deposits in the Athabasca Sandstone Basin of Northern Saskatchewan

Fig 2.


CIGAR LAKE U-DEPOSIT