Natural analogues to conditions around a final repository for high-level radioactive waste Proceedings of the natural analogue workshop held at Lake Geneva, Wisconsin, U.S.A. (october 1–3, 1984)

John A.T. Smellie (Editor)

Swedish Geological Company
Uppsala Sweden
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SVENSK KÄRNBRÄNSLEHANTERING AB
Swedish Nuclear Fuel and Waste Management Co
MAILING ADDRESS: SKB, Box 5864 S-102 48 Stockholm, Sweden
Telephone: 08-67 95 40

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A list of other reports published in this series during 1985 is attached at the end of this report. Information on KBS technical reports from 1977-1978 (TR 121), 1979 (TR 79-28), 1980 (TR 80-26), 1981 (TR 81-17), 1982 (TR 82-28), 1983 (TR 83-77) and 1984 (TR 85-01) is available through SKB.

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Swedish Geological Company, Box 1424, 751 44 Uppsala

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ABSTRACT

This report documents the proceedings resulting from a Workshop held at Lake Geneva, Wisconsin, USA, from 1-3 October, 1984. The theme of the Workshop was entitled "Natural analogues to the conditions around a final repository for high-level radioactive waste", and was restricted to ultimate disposal in a crystalline bedrock environment. The Workshop provided an important first step in co-ordinating and focussing different national and individual interests and approaches towards natural analogue studies.

One of the points highlighted at the concluding forum of the meeting was the necessity to first define the geochemical processes which are assumed to occur after disposal of the radioactive waste, and then locate suitable analogue systems which can be used to test the mechanisms of one, or a simple combination of these geochemical processes. Even accepting that the choice of which geochemical process(es) to be selected for validation will be sensitive to individual national disposal strategies, far-field radionuclide retardation mechanisms in the geosphere were considered to be a central topic of importance, and should therefore be given high priority.

At this early stage in the development of natural analogue studies it was not possible to cover all the important aspects. In retrospect, the role of the modelles should have received more attention; bridging the gap between geoscientists and the modellers was seen as being of prime importance in future meetings of this nature.

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INTRODUCTION AND SUMMARY OF THE WORKSHOP

INTRODUCTION

The central issue in assessing the long-term performance and safety of a radioactive waste disposal facility is the ability to predict confidently the nature and effect of processes and geological events far into the future. Assessment models which are deterministic require evidence that the processes which they consider will actually occur at the predicted magnitudes and time scale. Probabalistic models require evidence that events will or will not occur, and with what likelihood.

The time-scale over which these predictions are made depends on the wastes and disposal concept involved, but may vary from a few hundred years to several hundreds of thousands of years. In any case the obvious problem is in extrapolating laboratory data, generally obtained over months or at most a few years, out to realistic times into the future.

The processes being studied in the laboratory consider specific aspects of the mobilisation of radionuclides from the waste and their subsequent transport in groundwaters. Fortunately almost all of the processes of interest are also to be found operating in the natural environment, although different elements and different geochemical and hydrochemical regimes may be involved. There is thus an opportunity to use natural analogues to assess these processes over geological time scales.

To be useful a natural analogue must be tightly constrained to a particular process, with the boundary conditions well defined. Analogues of a complete disposal system do not exist. Even in the case of the nearest approach (fossil reactors) the boundary conditions are significantly different or unknown, and the analogue cannot be used as a large scale and wide-ranging control on a rigorously modelled dose calculation. In order to provide either validation or benchmarks the analogue must be tied to a particular process critical to the overall model. The role of a natural analogue should thus be to confirm:

a) that the process is in fact something which can or will occur in practice as well as in theory, and in nature as well as in the laboratory

b) where, when, and under what conditions it can occur

c) that the effects of the process are those envisaged in the model

d) that the magnitude of the effects in terms of scale and time are similar to those predicted for a similar set of conditions

All of the processes of interest are essentially chemical or physico-chemical in nature, and consequently the analogues to seek lie in natural geochemical systems.

Suitable conditions are most commonly encountered in ore deposits (either pre-existing or in the process of formation) and not surprisingly these provide the most accessible and useful analogues. However, any system where a geochemical anomaly exists, implying lack of equilibrium, can be useful. Thus the contact between two bodies of rock of dissimilar composition, or the interaction of porewaters or groundwaters with a rock or mineral can provide good analogues. The essentials to bear in mind when selecting analogues are as follows:

1 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 accountable.

2 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.

3 The magnitude of the various physico-chemical parameters involved (P, T, pH, Eh, concentration, etc) should be determinable, preferably by independent means.

4 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).

5 The timescale of the process must be measurable, since this factor is of the greatest significance for a natural analogue.

Whether an analogue can be applied quantitatively (as an actual control or benchmark on a model), or only qualitatively (as a ´sign-post´ that the model is going the right way) will be strongly dependent on how many of these conditions are satisfied, and with what degree of confidence.

In all cases there will be some limitations owing to inability to define adequately all these conditions. Some important processes appear not to be amenable to natural analogue control. These are generally physical which are site-specific; groundwater flow for example. The only analogue for the study of one flow system is the study of another in a similar environment. Processes not correlated by analogues are thus those which, to be studied, must be observed on the same ´real time´ scale as that of the process. These processes are however, few, and in the chemical field there are no processes or situations for which some of the conditions specified above cannot be satisfied: enough that is to give at least a qualitative assessment.

The last ten years have seen a growing interest in analogues, although little consensus as to how and where to apply the results being obtained. The objective of this Workshop was thus to bring together the analogue workers (mainly geologists and geochemists) to try and agree on some of the main principles of analogue study. The intention is that the conclusions can be transmitted to the analogue users (those involved in predictive modelling) to help them better to apply the data on a more selective basis. Indeed the natural follow up to this Workshop would appear to be more detailed discussion with the modelling and safety assessment groups.

WORKSHOP SUMMARY

Prior to the Workshop there was a consensus among several investigators that natural analogue studies would best be approached by first defining the major geochemical processes involved in the mobilisation and transport of radionuclides. However, there was little agreement on which are the most important in particular circumstances, and consequently where most effort should be placed.

This "process-oriented" background formed the basis of a detailed assessment of the potential of natural analogues in predicting system behaviour for a high-level waste repository in crystalline rock (Chapman, et al., 1984). The results of this study were presented at the beginning of the Workshop, and because they were felt to be widely applicable to all types of radioactive waste disposal (not only in crystalline rocks) they formed the basis for the subsequent discussion session. This report is not included in these proceedings but is available as SKB TR 84-16 and NTB 84-41. The conclusions of this study, plus other issues of interest which became apparent during the Workshop proceedings, formed the basis of a concluding forum organised during the final day of the meeting. For discussion purposes a series of topics were presented to the Workshop participants. These topics, together with the general response from the floor, are outlined below:

Whole-system Analogues vs. Process-orientated Analogues

It was considered that process-oriented analogues studies were more acceptable from a practical viewpoint. The chances of locating natural systems exhibiting one or two geochemical processes relevant to radwaste problems are much greater than locating a single system exemplifying many or all the important geochemical processes. Moreover, the more processes that occur in an analogue system the more complex the system is and the more difficult to interpret. It is doubtful in any case that a reliable and unimpeachable ´whole-system´ analogue exists. The time factor is another practical aspect to be taken into consideration, for example, investigative time-scales for process-oriented analogues would probably lie in the range of 2-3 years, in contrast to whole systems which would warrant a much larger scaled programme of up to 10 years. In conclusion, there was general agreement that process-oriented analogue investigations were much more tractable and useful although very complex analogues, if found, should not be neglected.

Ranking of Processes

Which are the most important geochemical processes for study? The following rankings were presented for discussion based on the outcome of available full system safety analyses which allowed the sensitivity of predicted radionuclide releases to specific processes to be identified:

A
- Retardation during far-field transportation of radionuclides.
- Matrix diffusion.

B
- Radiolysis
- Redox equilibration

C Thermal/chemical breakdown of buffer and seal materials (mostly bentonite).

D
- Waste package corrosion.
- Waste-form dissolution and breakdown.

E High-temperature mineralogical fixation.

There was a lack of any spontaneous response to this topic which reflects the complexity of distinguishing between geochemical processes of greater or less importance. To a large extent ranking priorities will depend on individual national radwaste policies and disposal system designs. For example, safety assessments for the Swedish programme emphasise the role of the canister, matrix diffusion, and radiolytic effects, while the U.S. programme will tend to up-grade high-temperature mineralogical fixation processes. In general, however, it can be stated that if, as in all safety assessment evaluations, the assumption is made that canister corrosion will take place, resulting in an eventual release of radionuclides into the geosphere (i.e. cumulative failure of the near-field engineered barriers), then far-field retardation processes would appear to be quantitatively the most important factor in controlling releases to the biosphere, as indicated in the above ranking list.

Chemical Analogues

In order to study the behaviour of critical long-lived radionuclides such as technetium, neptunium, plutonium, americium etc. (i.e. those which do not exist naturally, or if they do, exist only in very small quantities), suitable chemical analogues are required which exhibit similar physico-chemical properties. Based on similarities in vanlence state, speciation, complexation, ionic radius etc., possible chemical analogues for the most important longlived radionuclides are listed in Tables 1 and 2. There is general agreement about the suitability of the chemical analogues presently in use. However, there still exists the problem of the best chemical analogue for plutonium (see Krauskopf, this volume). To accomodate all three valency states of plutonium it was reiterated that Th (IV) is only really suitable for Pu (IV), U (IV) would also be a useful analogue for Pu (IV) and U (VI) (in the presence of carbonate and at a pH greater than 6-7) would be the best analogue for Pu (V). Lanthanide elements, for example Nd, would be more acceptable for Pu (III).

High-temperature Analogues

Even though high-temperature intrusive analogues (> 500°C) are not directly applicable to the physico-chemical conditions expected to characterise a high-level radwaste repository (e.g. up to 300°C in the U.S. context and < 100°C in the Canadian, Swiss and Swedish programmes), the point was made (though not universally accepted) that an understanding of what happens at high temperatures may help to elucidate what happens over the much longer time periods representative of low-temperature conditions. As referred to above, the thermal load expected to result from the waste emplacement programme in the U.S. will initially raise temperatures up to 300°C during its first few hundred years after disposal. As a consequence, high-temperature analogues (e.g. reactions and transport mechanisms for hydrothermal ore deposits) are being given higher priority in the U.S. than elsewhere.

Hydrochemical Analogues

An obvious disadvantage in the general application of such analogue studies is that each site investigated will have a distinct hydrogeological and hydrochemical signature. However, methods of dating groundwaters to assess movement rates and groundwater sources should still be of great value, even though experience has shown it to be difficult to reconcile groundwater dating with hydraulic modelling. Nevertheless, the possibility still exists and it was recommended that for dating purposes as many isotopic methods as possible should be employed (e.g. ^{14}C, ^{2}H, ^{3}H, ^{36}Cl etc.).

Ideally, a repository for radwaste should be located at a level of minimum hydraulic gradient. In this context the presence of deep saline groundwaters and their implications may be of direct relevance. Do these waters really represent zones or levels of minimum hydraulic gradient? Further analogue studies of saline water environments were recommended.

Use of Analogue Data

Although analogue data are available from all types of geological environment, there is no necessity to restrict their application on a rock-type specific bases. If the emphasis is put on process-oriented studies, then the environment frequently becomes of less significance, for example, data on sedimentary aquifer hydrochemistry can be used to varying degrees for all types of groundwater study. In this respect analogues offer general applicability and there is a clear need to collate and catalogue available data so that assessment groups can see what can be used to validate specific aspects of their models.

Modelling and Time-scales

The questions were posed as to whether the geoscientists are catering to the modellers requirements, and are we in fact looking at analogues which are too old, or span too great a time scale.

Regarding the modellers requirements, there was a general lack of response due mainly to the fact that collaboration between geoscientists studying analogues and the safety assessment modeller has rarely been established stisfactorily. There appears to exist, therefore, an overall ignorance in many quarters as to the modellers requirements and, presumably, on behalf of the modellers a general ignorance as to what the geoscientist can offer. This is an important gap which must be bridged.

In response to the second question, it was suggested that both fossil and active analogues should be examined. With regard to suitable time-scales of investigation, there was general agreement that if a system is being perturbed (e.g. near surface uranium deposit), then the uranium isotopes (especially the uranium decay series) should provide a good time-scale of examination (i.e. 1 Ma to the present). For some processes archaeological analogues were clearly more appropriate than geological ones.

CONCLUSION

In summary, the Workshop provided an important first step in co-ordinating and focussing different national and individual interests and approaches towards natural analogue studies. In particular, there is a need for more collaboration so that individuals and groups are not working in isolation, and a need to disseminate and catalogue data already available but as yet unused. By co-ordinating natural analogue studies at a national and international level it should be easier to justify the work by explaining their importance to regulatory or funding authorities.

One of the points highlighted at the Workshop was the necessity to first define the geochemical processes which are assumed to occur after disposal of the radioactive waste, and then locate suitable analogue systems (i.e. process-oriented analogues) which can be used to test the mechanisms of one, or a simple combination of these geochemical processes. In addition, although complex analogues tend to be too difficult and time-consuming to investigate, they should not be neglected. The choice of which geochemical process(es) to be selected for validation will obviously be sensitive to each disposal strategy. However, far-field radionuclide retardation mechanisms in the geosphere would appear to be a central topic of importance, and should therefore be given high priority.

Naturally it was not possible to accomplish everything at this early stage in the development of natural analogue studies. In retrospect, the role of the modeller should have been given more attention. With only some indications (i.e. ´sign posts´) from process-oriented investigations such as radiolysis (Oklo; Curtis and Gancarz, 1983) and bedrock radionuclide migration processes (Sweden; Smellie and Rosholt, 1984; Marysvale; Shea, 1984), there exist few documented natural analogue data which can be directly used by the modellers. Bridging the gap between geoscientists and modellers was seen as a prime importance.

With regards to future planning, there is a need for an international steering group of geoscientists and modellers to define joint requirements and to determine which geochemical analogues (i.e. process-oriented) are best suited to fullfill these requirements. In addition, the use of the Nuclear Energy Agency (NEA) Radionuclide Migration Newsletter and other media to disseminate information on research in progress in the field of natural analogues is recommended.

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Neil A. Chapman
British Geological Survey
Keyworth
Nottingham NG12 5GG
U.K.

John A.T. Smellie
Swedish Geological Company
Box 1424
751 44 UPPSALA
Sweden

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TABLE 1: Possible Chemical Analogues for the Long-Lived Nuclides Present in HLW.

Element	Oxidation State in Nature[2]	Ionic Radius[1] (Ang.)	Hydrolysis Coefficient[3] (log K_1)	Possible Chemical Analogue
Tc	Red. IV (o)	0.64		Re (IV) ?
	Ox. VII			Re (VII) ?
Pa	Red. V	0.78	9.5	(Th, U (IV))[4]
	Ox. V			
U	Red. IV	0.76	13.4	U (IV), (Th, Zr, Hf)
	Ox. VI	0.73	8.2	U (VI)
Np	Red. IV	0.87	12.5	U (IV), (Th, Zr, Hf)
	Ox. V	0.75	5.1	U (VI)
Pu	Red. III	1.00	6.5	Lanthanides[5]
	IV	0.86	13.5	U (IV), (Th, Zr, Hf)
	Ox. IV	0.86	13.5	U (IV), (Th, Zr, Hf)
	V	0.74	4.3	U (VI)[6]
Th	Red. IV	0.94	10.8	Th
	Ox. IV			
Am	Red. IV	0.98	6.5	Lanthanides
	Ox. III			
Cm	Red. III	0.98	(6.5)	Lanthanides
	Ox. III			

1) For the 6 co-ordination state, various values are cited in the literature.

2) Reducing: Eh derived from Fe (II)/Fe (III)
Oxidising: Eh derived from O_2

3) For $M^{n+} + OH^- = M(OH)^{n-1}$; various values are cited in the literature.

4) The chemistry of Pa (V) is more similar to the 4 valency actinides than the chemistry of the 5 valency actinides (U, Np, Pu).

5) Lanthanides - best analogue is Nd
- acceptable Ce, Pr, Sm, Eu, Gd, Tb, Dy, Ho
- less acceptable are La (too large), Er, Tm, Yb, Lu (too small); Y.

6) There are no suitable analogues for 5-valency actinides. The best analogue would appear to be U (VI) in the presence of carbonate and at a pH greater than 6-7.

* Elements underlined are those considered most suitable for chemical analogues.

TABLE 2: The Physico-Chemical Characteristics of Potential Chemical Analogues for Long-Lived Actinides Present in HLW.

	Element	Oxidation State in Nature	Ionic Radius1) (Ang.)	Hydrolysis Coefficient2) ($\log K_1$)
	Sc	III	0.73	9.7
	Y	III	0.89	6.3
	La	III	1.06	5.5
	Ce	III	1.03	5.7
L	Pr	III	1.01	5.9
A	Nd	III	1.00	6.0
N	Sm	III	0.96	6.1
T	Eu	III	0.88	6.2
H	Gd	III	0.94	6.0
A	Tb	III	0.92	6.1
N	Dy	III	0.91	6.0
I	Ho	III	0.89	6.0
D	Er	III	0.88	6.1
E	Tm	III	0.87	6.3
S	Yb	III	0.86	6.3
	Lu	III	0.85	6.4
	Ti	IV	0.61	
	Zr	IV	0.72	14.3
	Hf	IV	0.71	13.8
	V	V3)	0.54	
	Nb	V	0.64	
	Ta	V	0.64	
	Re	VII3)	0.63	

1) For the 6 co-ordination state, various values are cited in the literature.

2) For $M^{n+} + OH^- = M(OH)^{n-1}$

3) Other oxidation states probably also occur.

SESSION A

ANALOGUES AND PROCESSES

Chairman: Douglas G. Brookins

THE POTENTIAL OF NATURAL ANALOGUES IN ASSESSING SYSTEMS FOR DEEP DISPOSAL OF HIGH-LEVEL RADIOACTIVE WASTE*

N.A. Chapman[1], I.G. McKinley[2] and J.A.T. Smellie[3]

[1] British Geological Survey, Keyworth, Nottingham, NG 12 5GG, U.K.
[2] Swiss Federal Institute for Reactor Research, CH-5303 Würenlingen, Switzerland
[3] Swedish Geological Company, Box 1424, 751 44 Uppsala, Sweden

ABSTRACT

Many of the processes which will lead to the breakdown of engineered barriers and the mobilisation of radionuclides in a deep waste repository have analogies in natural geological systems. These "natural analogues" are seen as a particularly important means of validating predictive models, under the broad heading of radionuclide migration, which are used in long-term safety analyses. Their principal value is the opportunity they provide to examine processes occuring over geological timescales, hence allowing more confident extrapolation of short timescale experimental data.

This report begins by reviewing the processes leading to breakdown of containment in a high-level radioactive waste repository in crystalline bedrock and the subsequent migration mechanisms for radionuclides back to the biosphere. Nine specific processes are identified as being of the most significance in migration models, based on available sensitivity analyses. These processes are considered separately in detail, reviewing first the mechanisms involved and the most important unknowns then the types of natural analogue which could most usefully provide supporting evidence for the effects of the process. Existing studies are assessed and possibilities considered for additional analogues. Conclusions are drawn, for each process as to the extent to which analogues validate current predictions on scale and effect longevity of function, etc. Where possible, quantitative evaluations are given derived from analogue studies.

A summary is provided of the conclusions for each process and the most important topics for further studies are listed. Specific examples of these requisite analogues are given.

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* This presentation, delivered by N.A. Chapman at the Workshop, is based on a much larger report not reproduced here. The report is available as an SKB Technical Report (TR 84-16) and as a NAGRA Technical Report (NTB 84-41).

The report emphasises throughout the importance of linking analogues to well defined processes, concluding that analogues of complete disposal systems do not exist. While the report is aimed specifically at the NAGRA (Switzerland) and KBS (Sweden) concepts for disposal of high-level wastes or spent fuel the results are seen to be more widely applicable. A considerable amount of the information reviewed and presented could be used in the assessment of disposal of other waste types in other host rocks.

SOME USES FOR NATURAL ANALOGUES IN ASSESSING THE FUNCTION OF A HIGH-LEVEL WASTE REPOSITORY

I. Neretnieks

Dept. Chemical Engineering, Royal Institute of Technology,
S-100 44 Stockholm, Sweden.

ABSTRACT

Radionuclides migrating with the water in fractured rock may diffuse into the porous matrix of the rock and have access to a very large surface for sorption. This will retard their movement very much in excess of what only sorption on the fissure surfaces would do. There are some potential natural systems which might be used to show that this process has been active over very long times. The transport of uranium in the bulk rock, the saltwater content of the micropores of the rock and the interaction of oxygenated water with ferrous minerals in the rock are potential systems to study further.

A simplified analysis shows that the observed leaching of uranium in surficial rocks and the observed oxidizing waters in surficial rock is consistent with the diffusion of oxygen into the rock matrix. The analysis also shows that the observed reducing waters in deeper rock is consistent with the matrix diffusion data.

Oxygenated waters cannot penetrate more than a few meters or tens of meters into rock with hydraulic properties prevailing at depths below a few hundred meters during several million years of exposure.

INTRODUCTION AND BACKGROUND

Final repositories for high level waste (HLW) or spent nuclear fuel (SF) in deep crystalline rock repositories will be influenced by the chemical environment prevailing in the rock. The rock is fractured and there is natural water movement in the fractures. The temperature after an initial temperature increase to 100-150°C (or in some concepts several 100°C) will settle down to well below 100°C in the long term perspective.

The expected water flow rates in the rock at repository depth (500-1500 m) is expected to be on the order of a few ml to a few tens of $ml/m^2 \cdot year$ (KBS-3 1983). The frequency of fractures where the water moves is on the order of 1 fracture per 5 m or more. The composition of the water moving in the fractures is strongly influenced by reactions with the rock and with the fissure filling minerals. Its pH, Eh and concentration of dissolved solids such as sulphide, sulphate, carbonate, fluoride and organic complexing agent will strongly influence the interaction with the canister, backfill and HLW/SF.

Deep groundwaters in the Swedish bedrock have been found to be at near neutral pH and to be depleted of oxygen. This strongly affects the solubility and sorption equilibria of many of the important nuclides (U, Np, Pu, Tc). The solubility is many orders of magnitude less and sorption many orders of magnitude higher in reducing waters than in oxidizing.

The surface waters infiltrating are aerated and thus oxidizing. They are depleted of oxygen by various mechanism. Reactions with dissolved organic matter consume some oxygen and reactions with reducing minerals consumes another part. If mainly organic matter and dissolved reducing ions such as Fe^{2+} is the cause for the change, then the reducing capacity of the system is very low and might easily be upset. The result would be the same if only surficial mineral reactions would control the Eh. If on the other hand the minerals at depth in the rock are accessible and participate in the reactions, then the very large ratio of rock to moving water would ensure that the Eh system is very stable. It may then also accomodate considerable disturbances due to the excavating operations and potential production of oxidizing agents due to radiolysis.

Crystalline rock has been observed to be porous with a connected porosity of usually less than 1%. The pore system permits dissolved species such as oxygen, an-ions and cat-ions including radionuclides to diffuse in and out of the porous rock matrix. Oxygen and other oxidizing species may access the reducing minerals and react, radionuclides may diffuse into the pores and those which sorb may access very much larger surface areas with which to react. Actinides and technetium, if originally in higher oxidation states, may react with reducing minerals and precipitate at the redox front. There is considerable evidence that migration in the pore systems of deeplying crystalline rock takes place. However, this mechanism has such large impact on the prediction of radionuclide migration, that it would be very valuable to have evidence from long term processes in nature to further support it.

High level waste and spent fuel are highly radioactive. The radiation may cause radiolysis of water, producing hydrogen gas and oxidizing agents such as oxygen and hydrogen peroxide. There is a possibility that the small mobile hydrogen molecule will diffuse away without reacting with the oxidizing species and leave these behind to oxidize the actinides and technetium of the HLW/SF. The radionuclides would then be mobilized. They would migrate fast and far if reducing conditions were not reestablished by reactions with reducing minerals in the rock. The reaction with rock minerals goes back to the question of what makes the waters reducing in the first place. The extent of radiolysis may be studied by such naturally appearing parallels as the natural reactors and ore mineralizations.

The above subjects will be treated in more detail below. Some additional areas where long term natural systems may add information are mentioned briefly also.

The mobility of fission products and actinides in natural uranium oxide crystals at known boundary conditions gives information needed for predicting release rates from SF.

The observed high salt contents in deep waters in the Canadian shield and Sweden might be of use as indicators that these areas have very small water movement. Native copper imbeeded in sulphate minerals indicates that sulphate reacts extremely slowly with copper - although this process is thermodynamically possible in the presence of ferrous iron minerals.

MATRIX DIFFUSION

Many investigations have shown that the matrix of crystalline rocks is porous (Brace 1965; Norton and Knapp 1977; Skagius and Neretnieks 1982, 1983a: Bradbury 1982) and that ions and other dissolved species may migrate in the pore system either by molecular diffusion or due to a superimposed electric field. Figure 1 shows a conceptual picture of a porous matrix of crystalline rock. Porosities have been found to vary between 0.06 - 1.5% (Skagius and Neretnieks 1982, 1983a; Bradbury et al. 1982) and effective diffusivities between $1 \cdot 10^{-14}$ and $75 \cdot 10^{-14}$ m^2/s for unaltered rock. These data are consistent with those of Brace (1965) who measured samples under confining stresses of up to 500 bars. Skagius and Neretnieks (1983) found that the electric conductivity and diffusivity decreased by somewhat more than 50% at confining stresses of 280 bar. This would be the stress due to the rock overburden at about 1000 m.

Two in-situ experiments in the granite of the Stripa mine at more than 360 m depth with nonsorbing tracers gave values of the effective diffusivity of $1 \cdot 10^{-14}$ - $50 \cdot 10^{-14}$ m^2/s. These experiments had been specifically designed to access the rock that was still essentially in its natural stress condition during the experiment. Figure 2 shows a concentration profile of iodide as it migrated out from a 20 mm diameter hole into the rock during 6 months (Birgersson and Neretnieks 1982, 1983). Water flow is very slow in the porous rock matrix under natural hydraulic gradients because the matrix has a very low hydraulic conductivity ($< 10^{-13}$ m/s). The movement of dissolved species will take place practically by diffusion alone. Nonsorbing species will not be retarded by interaction with the surfaces of the micropores. Sorbing or precipitating species will penetrate smaller distances due to the interactions.

For a case with a constant concentration C_o at the surface of a fissure the concentration profile of a sorbing (or nonsorbing) species in the rock matrix can be calculated from

$$C/C_o = \text{erfc} \frac{x}{2\sqrt{D_a t}} \qquad (1)$$

where x is the distance and t the contact time for constant apparent diffusivity D_a and linear sorption:

$$D_a = \frac{D_p \varepsilon_p}{\varepsilon_p + K_d \rho_p (1-\varepsilon_p)} \qquad (2)$$

The expected values of $D_p \varepsilon_p$ for unaltered crystalline rocks is in the range $1 - 70 \cdot 10^{-14}$ m^2/s, porosities are 0.1-0.4% and typical $K_d \rho_p$-values (Allard 1982; Andersson et al. 1983) for actinides are $10^4 - 10^5$ under reducing conditions. For oxidizing conditions uranium is expected to have a $K_d \rho_p$ 2-3-order of magnitude lower.

Figure 3 shows penetration depths $\eta_{0.01}$ (the distance from the surface with $C = C_o$ at which $C = 0.01C_o$) as a function of time for species with varying sorption coefficients $K_d \rho_p$. The figure indicates that at oxidizing conditions the penetration depths for uranium may be on the order of tens of meters for time scales of millions of years. Under reducing conditions on the other hand penetration depths of the order of a meter might be expected. A case may thus be envisaged where oxidizing surface waters may leach shallow parts of the rocks very deeply into the matrix, whereas at the redox front where the uranium precipitates, very shallow penetration depths can be expected. There is of course also the question if bulk diffusion into the deeplying rocks will take place at all with this mechanism, because the pore waters of the rock matrix may well be at uranium saturation due to its own native uranium content. Disequilibrated uranium might however still be detected.

Nonsorbing species such as most anions eq. Cl^-, Br^-, I^- would migrate several meters to tens of meters during time spans between 10^4 and 10^5 years. If sites could be found where salt water had intruded and become isolated the resultant concentration profile into the rock might be seen. Efforts in this direction have been undertaken around a fissure with salt water (0.6% Cl^-) in the Finnsjö area in Sweden (Skagius and Neretnieks 1983b). The concentration differences were sometimes quite large between the water in the fractures and the water in the matrix porosity but no conclusions could be drawn so far.

The potential of the matrix diffusion to retard migration radionuclides is very large (Neretnieks 1980). This is easily visualised by considering that penetration depths of a cm to tens of cm can be made accessible for sorption if the long lived actinides diffuse into the matrix, whereas fractions of a mm will react only (porous altered surface coating on fractures) if no diffusion were to take place. The nuclides are retarded in proportion to the amount of material they sorb on. A sample calculation for Np-237 indicated an effluent concentration to the biosphere 5000 times lower when matrix diffusion was assumed as compared to the case with only "surface" sorption (Neretnieks 1981).

Evidence for uranium movement from a highly mineralized zone into granitic rock has been found by Smellie and Rosholt (1984) in the Björklund uranium occurence. They found in one sample that U-234 had migrated about 20 cm from the source into the rock during the last 0.5 million years. Other samples also showed uranium movement in the granitic matrix. Because there was no overall uranium leaching it was concluded that the conditions during which the uranium was mobilized were reducing.

This seems to be a very sensitive method to determine uranium movement over a time span up to one million years. A higher spacial resolution of the samples and a more detailed investigation of the rock matrix as regard fissures, porosity and matrix diffusivity might give information on disequilibrations as a function of distance from the mineralized zone. Such information could be used to determine the diffusivity of the rock matrix over long times and distances.

REDOX ENVIRONMENT

Rain water or ice melt water infiltrating the ground is usually nearly saturated with dissolved oxygen. The solubility of oxygen depends on the temperature and is between 9 and 14 mg/l for the temperature range 25°C - 0°C. During infiltration through soils containing organic matter most of the oxygen is consumed by organic reactions. Water infiltrating directly into permeable fractured rock often has detectable oxygen (> 0.05 mg/l) at shallower depths. Measurements to depths of about 600 m indicate (Laurent 1983 a,b) that the waters are reducing (Eh < -100 mV, Wikberg et al. 1983) at 100 m depths and below. They still contain considerable amounts of dissolved organic matter 1-5 mg/l (in some samples up to 50 mg/l) fulvic acids (Laurent 1983 a,b) and 0.1 - 8 mg/l Fe^{2+}. These species constitute the major dissolved reductants of the deep waters. The ferrous iron originates from the ferrous iron minerals in the rock. The ferrous iron minerals constitute 1 - 9% by weight of the rock (Torstenfelt et al. 1983).

Intruding oxygenated water in the deep rock will be reduced by the dissolved ferrous iron and possibly by the organic matter including the fulvic acids. The ferrous iron ion reacts very quickly with oxygen at near neutral pH (Stumm and Morgan 1981). The intruding oxygen will be quickly depleted. Once the dissolved ferrous iron and that immediately adjacent to the fissure surface is depleted, the iron must be transported from the bulk of the rock by diffusion, or the oxygen must move into the bulk and react with the minerals. The rate limiting steps will be the dissolution rates of the minerals and/or the transport of the dissolved species through the rock matrix. If the ferrous iron minerals in the rock matrix can participate in the reduction reactions, a very large reduction capacity is available to buffer any short term disturbances and ensure that the deep waters will stay reducing.

The available data will be used to analyse penetration depths of oxygen into the matrix as well as down through a fracture with infiltrating water.

The time scale of interest ranges over times since the last glaciation, approximately 10^4 years ago, back to hundreds of millions of years during which time there was a considerable regional land uplift of north western Scandinavia ranging up to 1250 m. Erosion during this period was also considerable, documented by sometimes thick (1000 m) clayey sediments and sand layers. The regional land uplift lasted from 50-3 million years b.p. In the other parts of Scandinavia the uplift and levelling was less. Most of the large fracture zones seen today were formed more than 650 million years ago when the rocks were lifted to their present near surface position. During the glaciation periods beginning some 3 million years ago, large parts of Scandinavia were depressed by up to km depths. Between 4 and 11 glaciations have been distinguished. The glaciation periods lasted more than 100 000 years (KBS-3, p. 8:7).

The present bedrock (100 m) may then have become surficial 3-50 million years in north west Scandinavia and up to 650 million years in the south east. During this time it can be assumed to have been exposed to the atmosphere and oxidizing waters only part of the time and to have been subject to very different climatic conditions.

Figures 4a, b, c show a simplified view of oxygen diffusing into the porous matrix of the rock. In Figure 4a the concentration of the oxygen at the surface of the sample is comparable to the dissolution equilibrium concentration of Fe^{2+}. There is a large surplus of Fe(II) minerals in the rock. The reaction front is sharp because of the fast reaction. If either of the two concentrations are much less than the other the one with the higher concentration will dominate the process. The infiltrating oxidizing water in a fissure will be gradually depleted and a penetrating redox front will develop as depicted in Figure 5.

A similar case has been analysed by Neretnicks (1983) where analytical solutions are given for the propagation of this type of front into the rock matrix. Solutions are available both for the case where the surface concentration is constant at the rock interface (surface case) and for the case where oxygenated water flows along a fissure and is depleted along its flow path (fissure case). Simplifying the solutions for the purposes of this paper, to give depth of the reaction front x_r, equation (3) is obtained for the surface case

$$x_r = \sqrt{2\,\frac{D_e^{O_2}\,t}{K}} \qquad (3)$$

where $D_e^{O_2}$ is the effective diffusivity of dissolved O_2 in the matrix, t the exposure time and

$$K = \frac{f\,q_o^{Fe}}{C^{O_2}} \qquad (4)$$

f is the stoichiometric factor. f = 1/4 for the reaction $4Fe^{2+} + O_2 + 4H^+ \rightleftarrows 4Fe^{3+} + 2H_2O$. q^{Fe} is the concentration of available and readily reacting Fe(II) minerals in the rock matrix. The penetration distance of the mineral boundary x_b is obtained from

$$x_b = x_r \cdot \frac{D_e^{O_2} \cdot C^{O_2} + f \cdot D_e^{Fe} \cdot C^{Fe}}{D_e^{O_2} \cdot C^{O_2}} \qquad (5)$$

D_e^{Fe} is the effective diffusivity of the ferrous iron ion and C^{Fe} its equilibrium solubility. When $C^{Fe} << C^{O_2}$ then $x_b = x_r$.

Equations 3 to 5 may now be used to investigate to what depths the ferrous minerals could have been oxidized since the latest glaciation period ~ 10^4 years ago. Torstenfelt et al. (1983) found that the 1-9% by weight ferrous iron minerals in the Swedish crystalline rock are readily oxidized by dissolved oxygen in ground up rock samples. We assume here that also whole rock pieces have reactive iron although possibly in lesser quantities. Intact rock can be expected to have an effective diffusivity $D_e^{O_2}$ between $1 - 70 \cdot 10^{-14}$ m/s. Using C^{O_2} = 10 mg/l and a rock density of 2700 kg/m^3 K is obtained to be K = 380 mol/mol for $D_e^{O_2} = 10 \cdot 10^{-14}$ m^2/s and q_o^{Fe} = 1% be weight.

The reaction depth x_r = 0.013 m from equations (3) and (4). The solubility of the ferrous iron C^{Fe} is less than 10 mg/l. Assuming that the effective diffusivity is of the same order of magnitude as that for oxygen, equation 5 gives x_b somewhat larger than x_r. Mineral alteration depths of a few centimeters barely be expected to be detectable because of weathering and abrasion of surface rock over the long time span of up to 100 000 years.

The water infiltrating a fissure would eventually be totally depleted of oxygen. The distance z_e along a fissure to which traces of oxygen still could be found, can be assessed by the available analytical solutions (Neretnieks 1983a). For a case when the rock between the fractures is not yet fully reacted

$$z_e = \delta\, v \sqrt{\frac{t}{2D_e{}^{O_2} \cdot K}} = \frac{U_o}{S}\sqrt{\frac{t}{2D_e{}^{O_2} \cdot K}} \qquad (6)$$

Equation (6) neglects the diffusion of the ferrous iron (case b in Figure 4). δ is the fissure width and v is the water velocity in the fissure. U_o is the average flux (Darcy velocity) and S is the fracture spacing. The fracture opening can be estimated to be a tenth of a mm or more (Snow 1968) for surficial rock with hydraulic conductivities of $K_p = m^{-6}$ m/s and fissure spacings of about 1 m. The avearage flux U_o at the surface and thus v can be obtained approximately from infiltration. This is taken to be $U_o = 0.1\ m^3/m^2 \cdot$ year (15% of the rainfall in Sweden at present). With a flow porosity of

$$\varepsilon_{flow} = \frac{\delta}{S} = \frac{10^{-4}}{1} = 10^{-4}$$

the velocity $v = U_o/\varepsilon_{flow} = 10^3$ m/year. z_e becomes 203 m. This could not apply to downward flow as the rock properties (K_p, S) change strongly with depth. The distance z_e can be seen as the travel path along a line in the surficial rock.

The hydraulic conductivity decreases by orders of magnitude with depth and consequently also the flow. Figure 6 gives a compilation of measured data on conductivity and calculated data on fluxes versus depth. As indicated in Figure 6, the flow paths do not have to be vertical and the water can travel considerable distances subhorisontally.

The flux is estimated to be $10^{-3}\ m^3/m^2 \cdot$ year at depths of 100 - 200 m and the fissure spacing on the average increases to become 5 m at 500 m depth. The travel distance z_e for oxygen if the process were to take place in rock with properties like those at 100 m depth becomes $z_e = 10$ m. At even larger depths (500 m) the fluxes of water have been calculated and are estimated to be between $5 \cdot 10^{-6} - 60 \cdot 10^{-6}\ m^3/m^2 \cdot$ year. These calculations are based on extensive measurements of hydraulic conductivities in nearly 50 boreholes 150 - 800 m deep. For these permeabilities z_e becomes 0.05 and 0.6 m respectively if the inlet concentration of oxygen to the fissure again is 10 mg/l. These examples indicate that flow paths travelling short distances, some 100 m, through surficial rock may not be depleted of oxygen even if they travel through fresh fractures. On the other hand deeply lying rock with low hydraulic conductivity will over time spans of 10^4 years deplete the waters of oxygen within a few meters.

For the "surface case" where C_o is constant at the rock surface, equations (3-5) the influence of Fe^{2+} migration could be assessed in a very simple way. This is not as straightforward in the "fissure case" because the ratio of the O_2 concentration C^{O_2} in the fissure, to the iron solubility concentration C^{Fe} changes along the fissure. At low C^{O_2} the impact will be large and speed up the depletion of the oxygen.

Measurements of the ratio of Fe(II)/Fe(III) in the Götemar granite indicate that surficial (~ 250 m depth) crystalline rocks have a smaller ratio than more deeply lying rocks (Smellie and Stuckless, 1985). The shallower granite is considerably more fractured than the deeper granite. The shallower samples are also depleted in uranium, indicating that the bulk rock has been exposed to some oxidizing agent. The projections made by equation (3) indicate that for the oxidizing agents to reach depths of a few hundred m directly by diffusion from the surface, the time needed is far in excess of the existance of the earth. Obviously this is not possible and other explanations must be sought. An increased Fe^{2+} solubility or mobility might extend the depth of influence considerably but not enough (equation (5)). Clearly with the data available it is not possible to explain an average penetration of oxidants down to a few hundred meters in crystalline rock by diffusion-penetration from the surface only. If on the other hand water seeps down the fractures and the oxidants penetrate from the fissures, the distances to be traversed are much shorter. Crystalline rock has been observed to have water bearing fractures at distances of about 5 m at larger depths (500 m) (Carlsson et al. 1983) and higher fracture frequencies are found at shallower depths.

A sample calculation for a fracture frequency at 1/m is given below. The diffusing fronts from each fracture will in this idealized case meet in the middle of the rock between the infinite plan planar fractures. Figure 7 shows how the rock will be oxidized between the fractures. The front velocity V_{front} is again obtained by a mass balance (Neretnieks 1983a) to give

$$V_{front} = \frac{v}{1 + \frac{K}{m}} = \frac{v\varepsilon_f}{\varepsilon_f + K(1 - \varepsilon_f)} \simeq \frac{U_o}{K} \qquad (7)$$

as $\varepsilon_f << 1 << K$. It applies only for times long enough for the fronts from both fractures to have met i.e.

$$t > t_{min} = \frac{(S/2)^2 K}{2 D_e O_2} \qquad (8)$$

derived from equation (3) again assuming that $x_b = x_r$ (negligible Fe^{2+} diffusion). For S = 1 m, $t_{min} = 15 \cdot 10^6$ years. After this time the broad front will start to move with fully penetration of all the rock between the fractures. To fully oxidize all the rock at shallower depth between the fractures to a distance of 1000 m takes (equation 7) an additional $3.8 \cdot 10^6$ years.

Equation (7) can also be used to illustrate the case where only a surface coating on the fractures react with the water. A fracture which has 0.2 mm of minerals containing 1% by weight of reactive Fe^{2+}, has a K in this case 5000 times smaller than in the previous example. This would result in all waters becoming oxidizing at a distance of 100 m in 76 years. Fractures down to several hundred meters would be totally oxidized in 10^4 years. In $10 \cdot 10^6$ years the finer fissures down to 500 - 600 m would also be affected.

The above analysis and projections are based on data which have a large variability and include some assumptions which must be tested in the field (e.g. availability of reactive iron minerals). Because the question of readily available redox capacity for moving groundwaters may have such a large impact on radionuclide migration if is felt that some effort should be directed to this area.

The availability and mobility of dissolved ferrous iron also has direct bearing on the potential reaction between copper, sulphate and iron. If the reaction rate were nonnegligible, then the availability of either sulphate or ferrous iron - which ever is smallest - would limit the corrosion of a copper canister (Corrosion Institute 1983).

The availability of the ferrous iron is also of importance for limiting the movements of potential radiolytic oxidizing agents as well as oxygen introduced during the mining operations.

RADIOLYSIS

High level waste and spent nuclear fuel buried in deep geologic repositories may eventually be wetted by water. The alfa-radiation will radiolyse the water and produce hydrogen and oxidizing agents, mainly hydrogen peroxide and oxygen. The hydrogen will escape by diffusion and the oxidizing agents may attack the canister materials, oxidize the uranium oxide matrix or diffuse out and oxidize reducing agents in the surrounding rock.

The rate of radiolysis has been computed recently (Christensen and Bjergbakke 1983). It is strongly influenced by the amount of available water and by the presence of dissolved iron. The movement of the oxidizing agents out from the canister and their reaction with the reducing agents (mainly ferrous iron) in the Swedish crystalline rock has been modelled as well as the movement of the radionuclides within and past the redox front. Some substances such as uranium, neptunium and technetium will precipitate at the redox front and will be withdrawn from the water to a considerable extent (Neretnieks 1983b).

The movement of the redox front is slowed down considerably by the reactions of the oxidizing agents with the ferrous iron in the rock in the same way as infiltrating surface waters are depleted of dissolved oxygen.

The rate of production of oxidizing agents and the escape of produced reducing agents (H_2) will depend on several factors. The available surface area of the waste and thickness of the water films in the waste are of prime importance as they determine how much water may be penetrated by the α-particles. Recombination reactions may aid considerably. Potentially a factor of 200 (Christensen and Bjergbakke 1982) reduction of the net production of oxidants can be achieved.

Figure 8 shows a sample calculation of the extent of the redox front downstream from a canister for spent fuel (Neretnieks 1983b). In this case a maximum production of oxidants is assumed. At the redox front the dissolved uranium will precipitate. Several other nuclides (Np, Tc in some circumstances Pu) will also precipitate because of their vastly smaller solubilities in reducing waters.

These processes have been observed and investigated for one of the Oklo reactors (Curtis and Gancarz 1983). This has given very valuable information and confirmation of the expected processes. It would, however, be valuable to find similar analogues in crystalline rock surroundings.

DISCUSSION AND CONCLUSION

The existence of a porous matrix in crystalline rocks has a strong impact on the retardation of many important radionuclides. There is strong evidence from laboratory measurements and a few in-situ measurements that the pore system of the matrix is open and connected even when the rock is under lithostatic load comparable to that expected in a repository. There are several potential analogues which might give evidence that these processes have been occurring over long times and are still taking place. So far the attempts to find some very clearcut indisputable analogues has not been entirely successful because of the complexity of the systems studied and the variability of the natural systems.

The processes which determine the redox potential of deep groundwaters must be understood better because the chemistry of especially many of the actinides is strongly dependent on the electrochemical potential. The very simplified analysis given in this paper seems to indicate that the ferrous iron minerals in the bulk rock participate in the reactions.

This would be of importance because it would ensure that the reducing properties of deep crystalline ground waters are very difficult to upset by natural as well as man induced disturbances. The radiolytically produced oxidizing agents would be quickly neutralized and only influence the rock nearest to the waste.

NOTATION

A	surface for mass transfer	m^2
C	concentration of oxidant in liquid	mol/m^3
C_o	concentration at inlet of fissure	mol/m^3
C_s	concentration at surface of fissure	mol/m^3
D_a	apparent diffusivity	m^2/s
D_e	effective diffusivity = $D_p \varepsilon_p$	m^2/s
D_p	pore diffusivity	m^2/s
D^*	$D_p \varepsilon_p C_o / q_o f (S/2)^2$	$1/s$
f	stoichiometric factor for oxidation reaction	-
K	volumetric capacity ratio	-
K_d	sorption equilibrium constant	m^3/kg
m	$\varepsilon_{flow}/(1 - \varepsilon_{flow})$	-
N	mass of species	mol
q	concentration of reducing species in solid	mol/m^3
q_o	original concentration in solid	mol/m^3
Q	dimensionless concentration	q/q_o
r	distance from center of slab	m
r_b	location of redox front in slab	m
S	thickness of slab	m
t	time	s
u_o	flux of water in bedrock	$m^3/m^2 \cdot s$
v	velocity of water in fissure	m/s
v_{front}	velocity of redox front	m/s
x	distance into solid	m
x_r	depth of reaction front	m
x_b	depth of the mineral transformation front	m
z	distance along fissure	m
z_e	distance along fissure of leading edge of redox front	m
Z	dimensionless distance	-
δ	fissure width	m
ε_{flow}	flow porosity of bedrock	-
ε_p	diffusional porosity of rock	-
Θ	dimensionless time	-
ρ_p	density of rock minerals	kg/m^3

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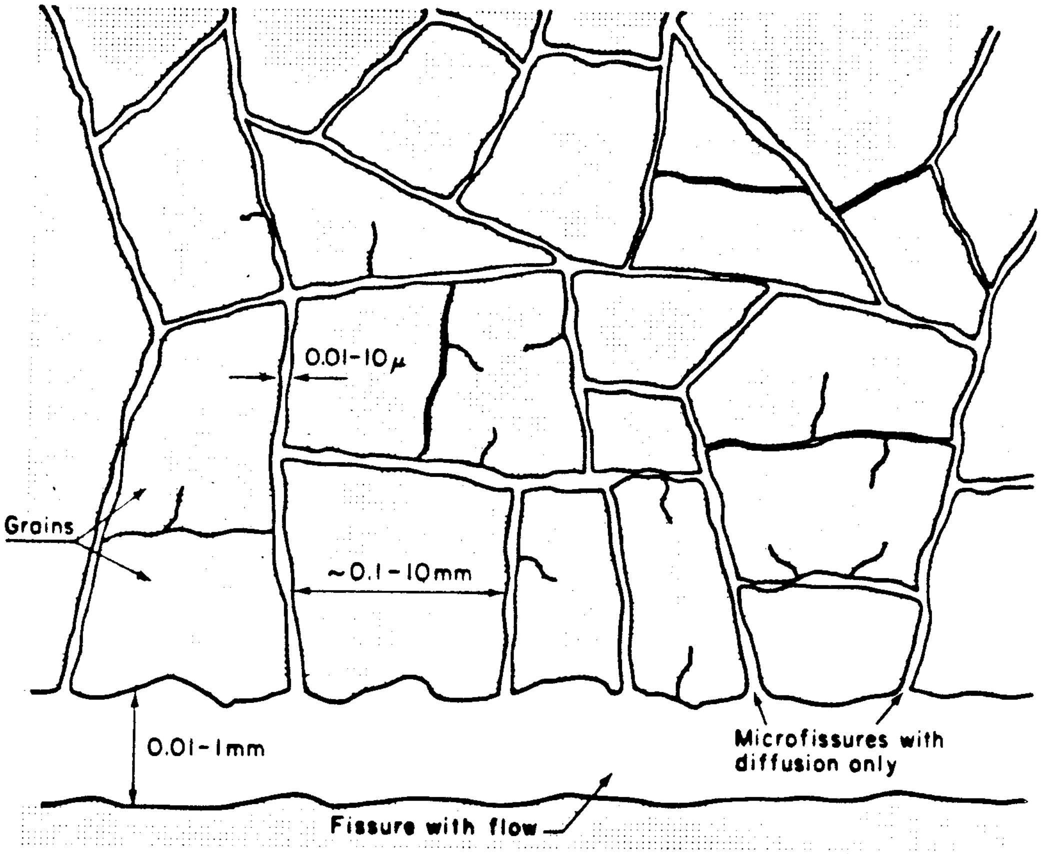

Figure 1. Conceptual picture of a porous matrix of crystalline rock

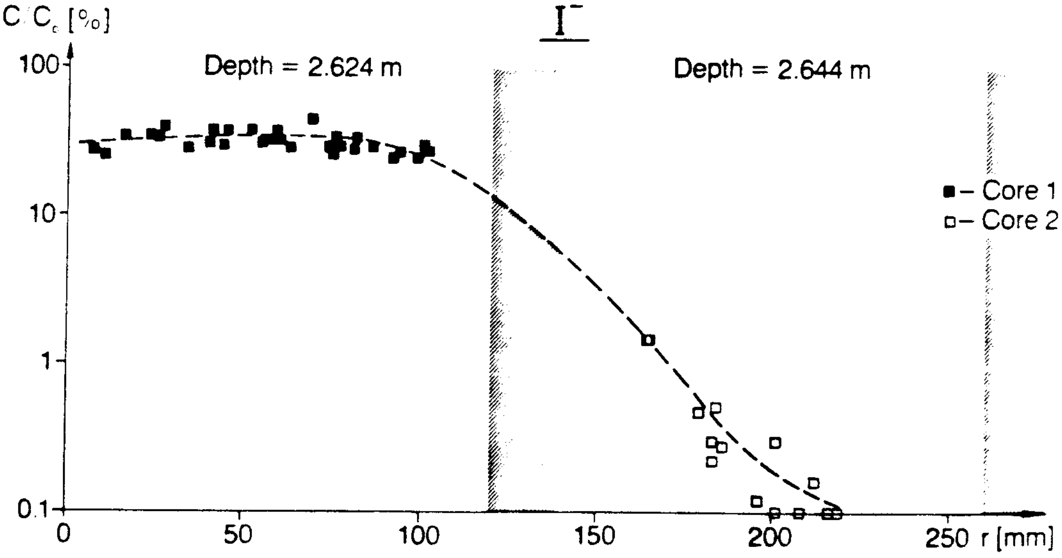

Figure 2. Concentration profile of iodide in rock under undisturbed lithostatic load

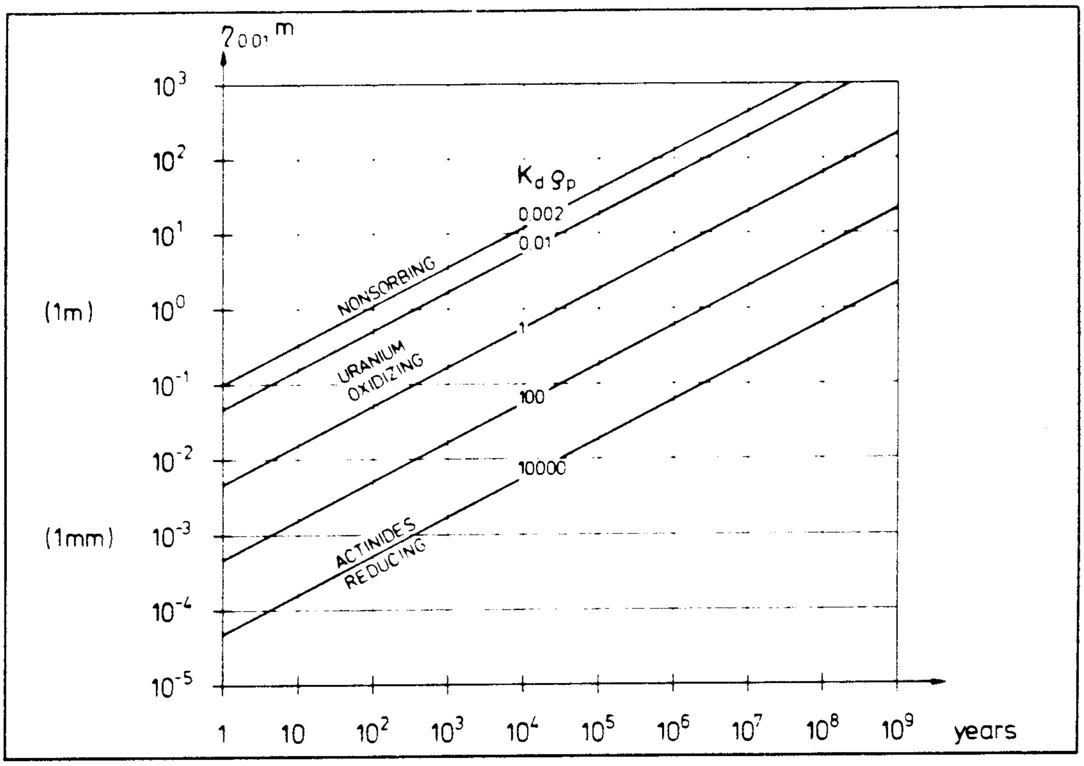

Figure 3. The penetration depth $\eta_{0,01}$ versus time for nonsorbing and sorbing species $D_p\varepsilon_p = 5 \cdot 10^{-14}$ m^2/s

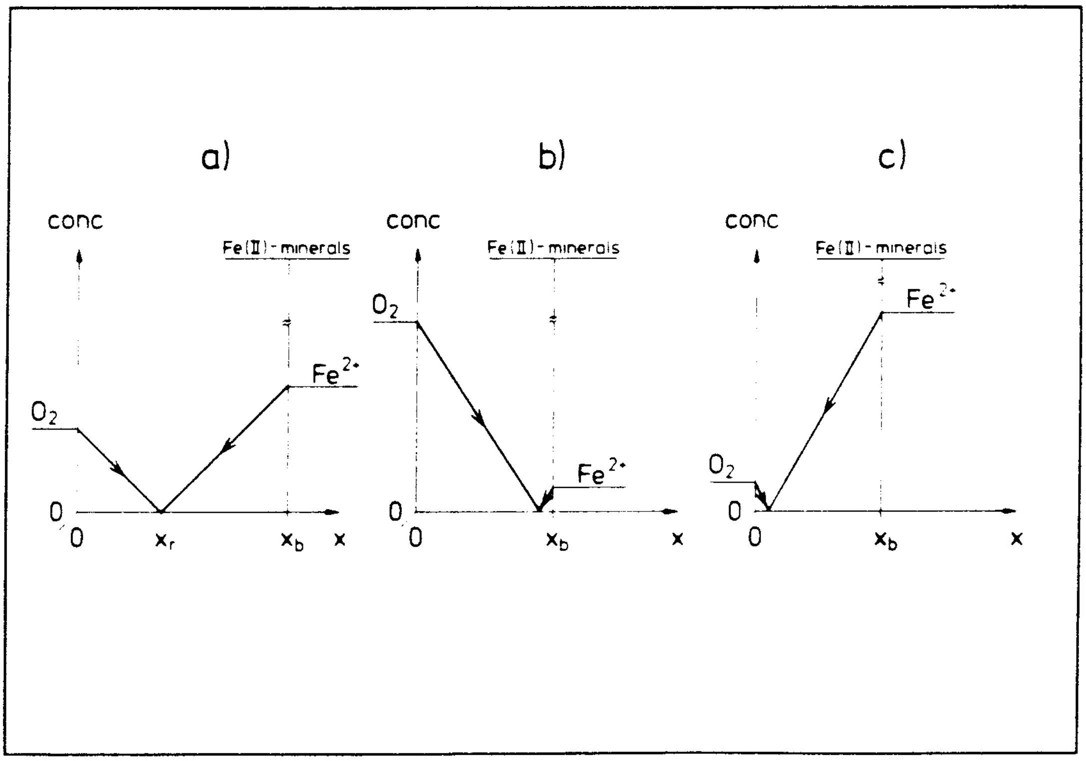

Figure 4. Oxygen moving into the rock matrix reacts with ferrous ions moving in opposite direction

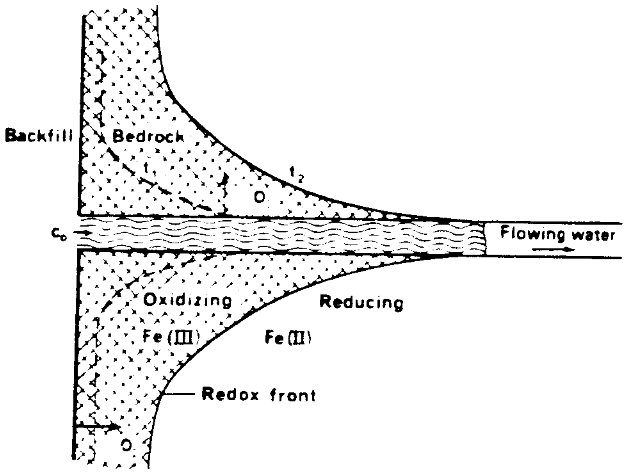

Figure 5. Infiltrating oxidizing waters in a fissure will eventually be depleted by reaction with ferrous iron minerals

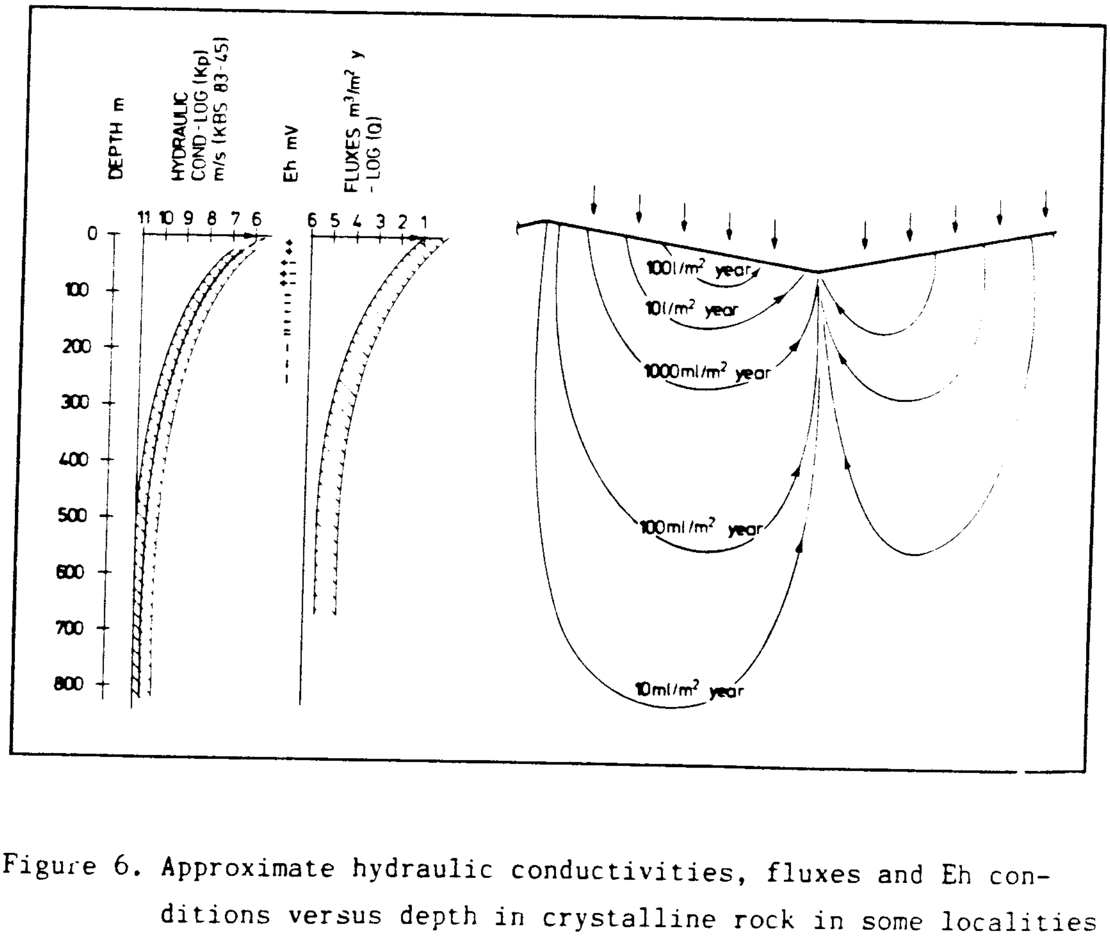

Figure 6. Approximate hydraulic conductivities, fluxes and Eh conditions versus depth in crystalline rock in some localities in Sweden and an idealized view of flow paths

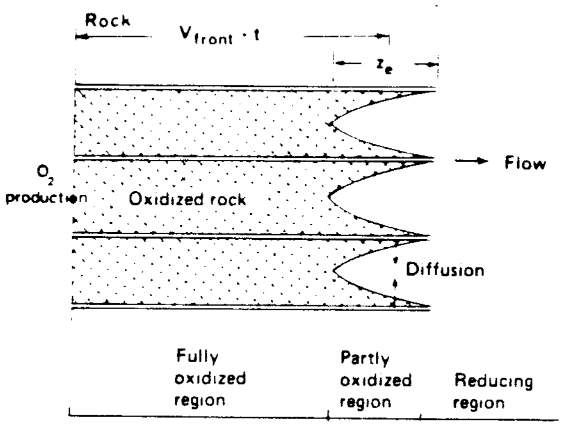

Figure 7. Eventually the rock between the fractures will be fully oxidized

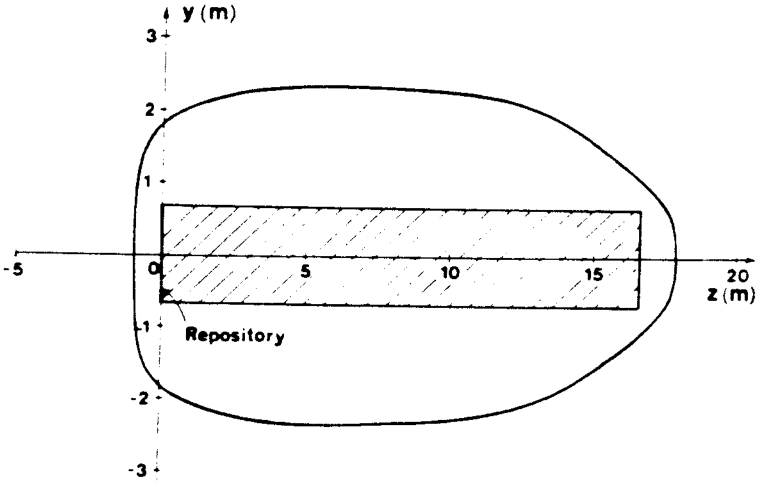

Figure 8. Sample calculation of the redox front downstream from a degraded canister for spent fuel

APPENDIX

A MODEL FOR THE MOVEMENT OF A REDOX FRONT IN A SYSTEM OF PARALLEL FISSURES

This appendix summarises and gives some special simplified forms of the model described by Neretnieks (1983a).

Diffusion from both sides into a slab of thickness S when the capacities of the pore liquid for holding the diffusing species are negligible compared to the reaction capacity of the solid, can be modelled as a semistationary case with a moving boundary.

For a flat surface the rate of transport of the species at the moving boundary is

$$\frac{dN}{dt} = - \left.\frac{dC}{dr}\right|_{r_b} \cdot D_p \varepsilon_p \cdot A \tag{1}$$

where r_b is the distance from the center of the slab, at which the redox front is at a given moment.

The redox front moves with a velocity that depends on the rate of transport of the oxidizing species and the concentration q_o of the stationary reducing agent. The reaction has a stoichiometric factor f. f indicates how many moles of the diffusing species react per mole of stationary species.

$$\frac{dN}{dt} = \frac{dr_b}{dt} \cdot A \cdot q_o \cdot f \tag{2}$$

Combining Eqs. (1) and (2) gives

$$\frac{dr_b}{dt} = \left.\frac{dC}{dr}\right|_{r_b} \cdot \frac{D_p \varepsilon_p}{q_o \cdot f} \tag{3}$$

The following initial conditions (IC) and boundary conditions (BC) are used:

$$\text{IC} \quad \left.\begin{array}{l} C = 0 \\ q = q_o \end{array}\right\} \text{ at } t = 0,\ r < S/2 \tag{4}$$

$$\text{BC 1} \quad C = C_s(t) \quad \text{at } r = S/2 \tag{5}$$

$$\text{BC 2} \quad C = 0 \quad r < r_b \tag{6}$$

If the capacity of the pores for holding the diffusing species is neglected $dC/dt = 0$, then the transport in the pore for $r_b < r < S/2$ is described by

$$\frac{\partial^2 C}{\partial r^2} = 0$$

This can be permitted if the capacity of the solid is much larger than that of the liquid in the pores. This gives

$$\frac{dC}{dr} = \left.\frac{dC}{dr}\right|_{r_b} = \frac{C_s(t) - 0}{S/2 - r_b} \tag{7}$$

Inserting Eq. (7) into Eq. (3) gives

$$\frac{dr_b}{dt} = \frac{C_s}{S/2 - r_b} \cdot \frac{D_p \varepsilon_p}{q_o \cdot f} \tag{8}$$

Integration of Eq. (8) from $r = S/2$ to $r = r_b$ and with $C = C_o$ = constant gives

$$\frac{D_p \varepsilon_p C_s}{(S/2 - r_b)^2 q_o \cdot f} \cdot t = \frac{1}{2} \tag{9}$$

for $0 < r_b < S/2$ and for times less than full penetration.

For penetration to the center of the slab $r_b = 0$, i.e., to a depth of $S/2$, we have

$$t = \frac{1}{2} \cdot \frac{(S/2)^2 \cdot q_o \cdot f}{D_p \varepsilon_p C_o} \tag{10}$$

Flow in a fissure

In the case of flow in a fissure the surface of the fissure is subject to a concentration that is dependent on the location along the fissure as well as on time. A differential mass balance along a fissure, neglecting dispersion is given by

$$\frac{\partial c}{\partial t} + v \frac{\partial c}{\partial z} + \frac{f}{m} \frac{\partial q}{\partial t} = 0 \tag{11}$$

Introducing

$$Z = \frac{D_p \varepsilon_p}{(S/2)^2} \frac{z}{mv} \tag{12}$$

and

$$Q = q/q_o = 1 - r_b/(S/2) \qquad (13)$$

Equation (8) transforms into

$$\frac{\partial Q}{\partial t} = D^* \cdot \frac{C_s}{C_o} \cdot \frac{1}{Q} \qquad (14)$$

where

$$D^* = D_p \varepsilon_p \; C_o/q_o \; f \; (S/2)^2 \qquad (15)$$

The solution of equations (11, 4, 5, 6) (after introducing equation (12) and equation (15)) is

$$Q(\Theta,Z) = (2D^*t)^{1/2} - Z \quad \text{for } \Theta < \frac{1}{2} \qquad (17)$$

and

$$Q(\Theta,Z) = \Theta - Z + \frac{1}{2} \quad \text{for } \Theta > \frac{1}{2} \qquad (18)$$

where

$$\Theta = (t - \frac{z}{v})\; D^* \qquad (19)$$

Equation (17) shows the constant pattern case, meaning that the shape of the breakthrough front does not change as it moves in the direction of the flow. The velocity of the front is directly obtained from Eq. (18) by following the movement of the midpoint of the break-through curve $Q(\Theta,Z) = \frac{1}{2}$.

We then obtain $\Theta = Z$, which after simplification gives

$$V_{front} = \frac{v}{1 + \frac{q_o \cdot f}{c_o m}} \qquad (20)$$

Equation (20) may also directly be obtained by a mass balance of the intruding oxidant and the reacted reductant.

GEOCHEMICAL ANALOGUES OF HIGH LEVEL RADIOACTIVE WASTE REPOSITORIES

P.L. Airey[1] and M. Ivanovich[2]

[1] Australian Atomic Energy Commission, Research Establishment, Private Mail Bag, PO, Sutherland NSW 2232, Australia.
[2] United Kingdom Atomic Energy Authority, AERE, Harwell, OX 11 ORA, United Kingdom.

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 operating 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.

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). In its Draft Regulation 19, the EPA has defined maximum recommended integrated dose to individuals over the next 10 000 y. The criteria under which

HLRW repositories performance conditions required by the US Nuclear Regulatory Commission are consistent with EPA requirements have recently been discussed (Chu, et al. 1983).

Deep burial of HLRW in geological formations relies on the multiple barrier concept. A number of engineered and natural barriers are combined to isolate wastes for sufficient time to permit radioactive decay to occur to appropriate levels. An integrated model must incorporate mathematical descriptions of time dependence of the components of the HLRW, the groundwater induced corrosion of the primary containment, the leaching of the immobilised waste, the transport through the primary containment and migration through the geological strata. This review will be restricted to the potential use of geochemical analogues in refining the scientific basis for the long-term prediction of the transport of radionuclides through geological media.

Extensive modelling of radionuclide transport following the breaching of a repository has been undertaken. As a result, a short list of critical radionuclides has been identified, including ^{237}Np, ^{239}Pu, ^{241}Am, ^{226}Ra, ^{99}Tc and ^{129}I (Croft and Alexander, 1980; Hill, 1979). The migration rate depends on the groundwater velocity and the radionuclide retardation factor, which in turn depends 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 (Birchard and Alexander, 1983). 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 the Morro do Ferro thorium mineralization.

The aims of the paper are as follows:

i) To define the essential characteristics 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.

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 (Birchard and Alexander, 1983) and cavities formed by underground nuclear explosions are also useful (Hoffman and Daniels, 1981).

No geochemical analogue can model all aspects of radionuclide migration. Those defined by mineral accumulations, igneous intrusives reflect the cumulative effect of transport over a very wide time span, but one which is determined by geological history. A much greater flexibility is possible by studying uranium and thorium series disequilibria. Uranium/lead and thorium/lead systems may be used to establish a chronology over the 10^9 year time frame; $^{234}U/^{238}U$, $^{230}Th/^{234}U$, $^{231}Pa/^{235}U$ fractionation effects reflect processes which have occurred over the past 10^4-10^6

years; ^{226}Ra/^{230}Th, ^{228}Ra/^{232}Th, ^{224}Ra/^{228}Th and ^{223}Ra/^{227}Th couples can be used to assess relative distribution coefficients over periods varying from days to about 5000 years. The last mentioned range of time-scales is particularly significant as it provides a basis of assessing the validity of laboratory adsorption data for prediction over the 10 000 year time-scale.

The value of the analogue is enhanced to the extent that the geochemistries of the indicator elements reflect those of the critical radionuclides defined for HLRW repositories. Uranium accumulations are particularly useful as they comprise a suite of actinides and radium isotopes. In addition, it may prove possible to measure the transuranics ^{237}Np and ^{239}Pu and the fission products ^{99}Tc and ^{129}I.

EXAMPLES OF GEOCHEMICAL ANALOGUES

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 geologic 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 (Walton and Cowan, 1975) 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 (Bryant et al., 1976; Curtis et al., 1981) have revealed that radionuclide products of the natural reactor operation were contained in crystalline uraninite which remained unaltered mechanically for some 2 x 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 (Lancelot et al., 1975; Gauthier-Lafaye et al., 1978). The average loss of about 50% was interpreted by Gancarz (1978) to indicate a primary age of 2.05 x 10^9y with Pb loss from uraninite by continuous volume diffusion. Further, lead isotope data reported by Gancarz and Curtis (1979) 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.

Geological Intrusives

Eldora Bryan stock intrusive into the Idaho Springs Formation

The Bryan-Eldora stock (Brookings et al., 1982) 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) (Hart et al., 1968). 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 2000 m from the contact. However, petrographic studies reveal that only in the 1 to 3 m 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 3 m of the contact zone. The authors conclude, that, based on this study, crystalline rocks may be suited as a host for HLRW repositories.

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) (Brookings et al., 1983). Based on oxygen isotope studies, Williams (1980) 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 quarz 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.

Thorium Deposits (Morro do Ferro)

Another example of geochemical analogues is that of Morro do Ferro thorium deposit situated on the Poços de Caldas plateau in the state of Minas Gerais, Brazil. The Poços 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 140 m above its immediate surroundings. The geology of the area has been described by many workers (Ellert, 1959; Frayha, 1962; Wedow, 1967; Bushee, 1971; Almeida, 1977). The age determinations (Bushee, 1971) 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 200 m (Frayha, 1962; Eisenbud, 1984). The reasons for the thorium and REE accumulation in this site are not understood. However, recent mineralogical study (Eisenbud et al., 1984) 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 coworkers (Eisenbud et al., 1982a,b; 1984) 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: "Mobility of Thorium from the Morro do Ferro in Proc. Int. Symp. on Migration in the Terrestrial Environment of Long-lived Radionuclides from the Nuclear Fuel Cycle", summarised below.

The chemical similarity between Pu^{4+} and Th^{4+} has been recognised (see for example Bondietti and Tamura, 1980). The principal difference between the two elements is that plutonium may exist in several oxidation states whereas thorium is restricted to 4+ state. Nevertheless, in the moderate range of Eh and pH characterising most natural environments including those acceptable for a repository, the behaviour is expected to be similar and the greater solubility of plutonium compounds for example would only be expected under extreme oxidising or reducing conditions. Thus, in spite of the uncertainty in the quality of some published data, the similarity in equilibrium constants for the two elements is striking (Eisenbud et al., 1982b; Allard et al., 1980; Rai et al., 1980a,b; Jacubick, 1979; Jensen, 1980). Where differences exist Pu^{4+} complexes appear more stable because of its slightly smaller ionic radius. Solubilities of both elements are markedly increased by the presence of organic material.

Weimer et al. (1980) have pointed out that neodynium should be an appropriate analogue for americium and curium. Like neodymium, these actinides are expected to exist in the 3+ oxidation state under environmental conditions. The ionic radii for Am^{3+} and Nd^{3+} (1.05A) are identical and nearly identical to Cm^{3+} (1.06A). Experimental evidence for the analogous behaviour of these elements has been provided both by laboratory and field work (Weimer et al., 1980). Although similar laboratory comparisons have not been made with lanthanum, its chemical properties are known to be similar to those of neodymium. Thus, because lanthanum is present in higher concentrations in the Morro do Ferro environment and is easier to analyse Eisenbud et al. (1982a,b; 1984) chose lanthanum as the analogue for curium and americium.

Eisenbud et al. (1982b) 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 x 10^8y compared to 3.4 x 10^4y 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 repositories (NRC, 1978) 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 (Eisenbud et al., 1982a,b; 1984) that the transuranic actinide elements are so extraordinarily immobile is consistent with findings at Oklo described in section "Oklo Uranium Deposits". So far only the first objective quoted for this project in Allard et al. (1980) 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.

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 (Airey et al., 1983a,b; Airey, this volume). 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 (Roman, 1984). 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.

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 is to examine whether there are mechanisms of retardation which occur over the long-term which are not manifest over laboratory timescales. 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.

(1) 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 (Airey et al., 1983; Zielinski et al., in press). 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 on to the amorphous iron and its subsequent incorporation by crystallisation retardation mechanism which applies over geological, but not over laboratory, timescales.

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 (Curtis et al., 1981; Jensen, 1982). Detailed insights will only be possible if the isotopic fractionation both in the groundwater and or 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 β 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 (Airey, this volume). 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, ie 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, ^{228}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 situation 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 precisely measured. More importantly, however, it may prove possible to measure directly the levels of certain transuranic elements (eg ^{239}Pu) and fission products (^{129}I and ^{99}Tc). In most geological settings, the levels of these indicator elements would be below the detecable limit.

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 50 W 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 30 m 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 5 my^{-1} (Curtis et al., 1981).

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) <u>They can be used to establish a scientific basis for the longterm prediction of the rate of transport of radionuclides.</u>

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 "Uranium Deposits (Alligator Rivers Uranium Province, Northern Territory, Australia)" 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) <u>In many circumstances the findings may be transferred from the setting of the geochemical analogue to that of the waste repository.</u>

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 (Allard et al., 1980). Thus, acceptable predictions of the transport of Pu^{3+}, Am^{3+} and Cm^{3+} can be drawn from studies of the lanthanide elements, eg 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 "Uranium Deposits ..." 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, ie, they would be allogenic. Attempts would be made to use information on the distribution of uranium and thorium series nuclides which was evolved over geological time, together with laboratory sorption and leaching studies to predict retardation factors over the next 10 000 years.

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NATURAL ANALOGS TO NUCLEAR FUEL WASTE DISPOSAL IN CRYSTALLINE ROCKS: AN OVERVIEW

J.J. Cramer
Atomic Energy of Canada Ltd., Whiteshell Nuclear Research Establishment, Pinawa, Manitoba ROE 1LO, Canada

ABSTRACT

The safety assessment of concepts for the disposal of nuclear fuel wastes deep underground in crystalline rock uses computer models to predict changes over-long periods of time. Yet by definition, data from the field and laboratory research, used in the computer models, detail only short-term phenomena. The use of such data can be justified by studying analogs for the physical, chemical and biological processes that will occur in the different zones of a disposal vault. This paper reviews in a general sense the important processes, and analogs for them.

INTRODUCTION

In several countries, including Canada, extensive research programs are being considered to assess the concept of safe disposal of nuclear fuel waste underground in crystalline rock formations. The concept consists of a combination of engineered and natural barriers to isolate the waste from the biosphere (KBS, 1983; Rummery and Rosinger, 1981). In the concept, the waste is placed in a durable container, which is then surrounded by a clay-based buffer material. Since transport of radionuclides by groundwater is the only credible migration mechanism, the function of the barriers is to prevent groundwater penetration to the waste on a short time-scale, and to retard the migration of radionuclides on a long time-scale. This time-scale is dictated by the radiation levels and the decay times of the radionuclides in the waste, and extends from tens to hundreds of thousands of years for most high-level wastes.

To assess the safety of the disposal concept over such a long period of time, mathematical models are required. These models use results obtained mainly from field and laboratory experiments, where extrapolation of these results is limited by the uncertainty of the short-term experimental data. The main restrictions to extrapolation are slow kinetics for chemical reactions at low temperatures ($\leq 150^{\circ}C$) and the complexity of the systems and processes. The level of confidence in this extrapolation can be greatly enhanced by the use of natural analogs for both the processes and the systems being considered. These processes include physical, chemical and biological processes, whereas the parameters of the systems depend on the selection of the natural and engineered barriers.

For the natural analog studies, the complete disposal system has been subdivided into three main zones: the nearfield, the farfield and the biosphere (see Fig. 1). The nearfield contains the waste disposal vault and will be the zone subjected to thermal and stress effects. It includes the waste, the engineered barriers and the host rock immediately surrounding the excavation. The farfield is the zone separating the nearfield from the biosphere. The boundary between the biosphere and farfield is determined by the extent of the downward circulation of the soil and surface waters. The biosphere includes the upper part of the host rock formation, the overburden, all biological life and the atmosphere. The biosphere is essentially the zone to which man has ready access through respiration and consumption of fauna, flora and water; however, from a geochemical viewpoint, the biosphere starts where ascending groundwater mixes with surface waters that contain live biota or biologically derived organic species.

The upper and lower farfield boundaries are both diffuse as well as variable with time. The boundary with the nearfield is initially determined by the extent of fracturing and microcracking that is caused by the excavation of the vault. However, the thermal effect of emplaced waste on host rock and groundwater will extend beyond the limit of the stress effects during part of the thermal transient from cooling of the waste. A result of the thermal effect may be a further microcracking of the host rock beyond the initial damage from excavation. The boundary between the farfield and the biosphere may also vary with time due to changes in hydraulic gradient, erosion level or climate. Furthermore, in some concepts (e.g., the Swedish Concept) the farfield may extend only over a short distance, or not exist, because of the shallow location of the waste vault.

PROCESSES

In this section, the main processes and their effects on the various components and parameters of a waste disposal vault are reviewed. These processes have been identified as the most important ones based on observations of both experimental and natural systems, and their perceived role in the performance of a disposal vault.

Although the physical, chemical and biological processes are discussed individually, they are invariably coupled and interactive. For example, the water is the single most important parameter in the mobilization and migration of radionuclides from the vault to the biosphere. In particular, almost all chemical processes occur only when water is part of the system, and the effect of many physical and biological processes also depends on the presence of water. Thus, the prevention of water access to the waste itself, and of dissolution of the waste upon contact with water, are primary objectives in engineering the composition and conditions of the nearfield. In an ideal nearfield, therefore, the physical processes resulting from newly emplaced waste will initially operate in a dry zone immediately surrounding the waste. The intensity and extent of some of the physical processes will subsequently change when water penetrates the host rock and the engineered barriers. Another example of the coupling of processes is the effect of a climatic change towards glaciation. Under moderate climatic conditions, upward migrating groundwater will be diluted and modified by mixing with surface and near-surface derived water. Upon glaciation, mixing of the groundwater will be reduced due to a limited supply of water from the frozen surface layer.

No attempt has been made here to rank the relative importance of each process, because of the coupling of the various processes and, at this time, the undertainty in the extent and duration of the coupling or interaction. However, some of the processes are relevant or important only in one system and not in another. For example, thermal processes will be restricted to the nearfield while some biological processes will obviously be restricted to the biosphere.

The following processes have been identified as potentially important in the long-term performance of the disposal vault, and natural analog studies must be used to determine their relative importance.

Physical Processes

(1) Heat-related processes. The radiogenic heat from the waste will have several effects on the surrounding engineered barriers and host rock. Dehydration or drying of the buffer will lead to a reduction in thermal conductivity and possibly to cracks in the buffer. Differential thermal expansion in the host rock may lead to microcracking of the minerals. The result in both cases will be an increase in the permeability of the buffer and host rock.

(2) Stress-related processes. Stress in the rock due to tectonic phenomena, or in response to glaciation or the excavation of the vault, may lead to fracturing of the host rock and the engineered barriers, including the waste container. As a result, new groundwater flow paths will form, and this may enhance the accessibility of water to both the waste and the newly exposed, fresh rock. Cracking and fracturing of mi-

nerals in the host rock will cause bursting of fluid inclusions in these minerals and this could change the composition of the groundwater.

(3) Radiation-related processes. Radiation is another form of energy emanating from the waste into the nearfield. The irradiation of solid materials generally causes structural damage. Structural damage in the form of devitrification is probably the most important effect of radiation on vitrified or glass-ceramic waste forms.

(4) Fluid flow. The flow of groundwater, under the influence of a hydraulic, thermal or density gradient, is the main transport mechanism for radionuclides. For example, mixing with surface water will modify the composition of ascending radionuclide-bearing groundwater.

(5) Creep. As a result of water uptake by the clay minerals, the buffer will swell and the internal pressure may cause deformation or creep of the clay into cracks and crevices of the surrounding host rock, thereby reducing its porosity and permeability. The backfill may also be subjected to creep.

(6) Evaporation. Evaporation can take place in the nearfield and the biosphere. As mentioned earlier, heat from the waste will dehydrate the buffer nearest the waste container. This drying process is a combination of evaporation and condensation along the thermal gradient. The result of this evaporation and of evaporation in the biosphere (i.e., through access to the atmosphere) is, in both cases, a concentration of dissolved salts.

(7) Erosion. Surface erosion can be caused by physical processes such as wind, thermal expansion and glaciation. Wind erosion will disperse the potential surface concentration of radionuclides. Rapid erosion (i.e., within the time frame required for safe disposal), due to processes such as glaciation, will result in decompression of the rock mass and a change in the hydrologic conditions.

Chemical Processes

(1) Dissolution. Interaction of water with minerals, the waste, the waste container or concrete seals will lead to dissolution or leaching, particularly in the higher temperature nearfield. The main factors influencing dissolution are water composition, temperature and radiation effects.

(2) Precipitation. Reaction and precipitation of dissolved species may occur due to changes in temperature, redox condition or composition of the water. This could lead to a reduc-

tion in the permeability (self-sealing) of the buffer, backfill and host rock, and to formation of new minerals with a sorption capacity for radionuclides. However, a significant amount of precipitation in the buffer could have an adverse effect on the desired long-term properties of the buffer, such as swelling and sorption capacity.

(3) Mineral reactions. Metamorphic mineral transformations will likely be restricted to the clay minerals in the buffer and backfill. Retrograde alteration of high-temperature minerals will occur in the host rock, depending on the amount and composition of the water.

(4) Solution chemistry. The composition of the groundwater plays a major role in many of the chemical processes, in particular in stable Precambrian Shield terrains where deeper groundwaters are saline. Changes in composition, due to vault emplacement or to mixing with shallower water, may have a strong effect on radionuclide migration.

(5) Radiolysis. Radiolysis of water produces free radicals and H_2O_2, which can have a strong effect on the pH and Eh of water, depending on its composition.

(6) Mass transport. Mass transport in static or flowing groundwater can occur through diffusion, complex formation and colloid formation. Matrix diffusion into the host rock alongside water-filled fractures may be an important retardation mechanism for dissolved radionuclides.

(7) Sorption. This general term describes any interaction between a dissolved radionuclide and a solid phase that could retard the migration of that radionuclide in groundwater. Dissolved radionuclides and colloids with attached radionuclides could be sorbed (reversible or irreversible) onto minerals along the water flow path.

(8) Redox reactions. Most of the chemical processes and the mobility of multivalent radionuclides in and around a waste vault will depend strongly on the redox conditions of the groundwater. In particular, the initial release of radionuclides from used fuel will depend on redox reactions that control the availability of any free oxidants.

Biological Processes

(1) Bacterial activity. The capacity of certain bacteria to change the redox conditions of groundwater and to produce organic complexants could affect the mobility of radionuclides. The presence of bacteria will not be restricted to the biosphere since they will be introduced underground to the

vault during excavation and waste emplacement. However, the extent of bacterial activity in the nearfield will also be determined by the availability of organic material.

(2) Production of organics. The formation of organic complexes in the biosphere could enhance the mobility of radionuclides upon mixing of biosphere water with ascending groundwater. Sediments in the biosphere invariably contain more organic material than igneous rocks.

(3) Element uptake. The uptake of dissolved radionuclides by flora and fauna can concentrate these elements into the atmosphere-geosphere interface, where they can enter the food chain or otherwise contribute to the exposure of man (e.g., through the inhalation of gaseous daughter products).

(4) Mesofaunal activity. Both fossil and modern records show that certain small and medium-size burrowing animals root up soil and unconsolidated sediment in large quantities. This activity could potentially lead to redistribution or concentration of radionuclide-containing soil and organic matter.

ANALOGS

This section describes some analogs for the processes mentioned above. Although several analogs cover more than one process, no one analog covers all the processes and aspects of a conceptual disposal vault. The uranium deposit at Oklo in Gabon is probably the most comprehensive analog, both in terms of the fossil-presence of fission products and transuranics in the system and in terms of the time over which the phenomenon took place. Analogs to several of the physical and chemical processes can be studied in the Oklo deposit, but some other important processes, such as glass dissolution, container corrosion and matrix diffusion into igneous rock, can not. Also, data from various analogs must be combined to give a more complete picture of the operation and extent of certain processes. For instance, the natural fission reaction in the Oklo deposit produced a chemical and physical "overprint" on the composition and conditions of the original ore zone. To obtain the net effects of the fission reaction and the subsequent radionuclide migration, baseline data must be obtained from unreacted ore zones in the Oklo deposit or from similar uranium deposits (e.g., sandstone-hosted deposits in northern Saskatchewan).

Furthermore, a natural analog is unlikely to be an exact equivalent of the process or aspect under investigation in the disposal concept, because there will always be some differences between the composition and conditions of the analog system and the disposal system. The main difficulty is the comparison of laboratory-derived kinetic data with kinetic data obtained from the analog, because of the uncertainty in the time factor for reactions in a geological system. For a chemical process the main value of an analog is the qualitative verification that the process does occur in that system, although the extent may not be known. On the other hand, analogs of physical processes can generally give both qualitative and quantitative information because, in natural systems, physical processes take place over a short time scale compared with chemical processes. But, since physical and chemical processes in natural systems are almost always coupled, care must be taken in extracting and interpreting quantitative data from any natural analog.

The analogs are arranged by the zone in which the particular process is most important, and they include both documented analogs and potential analogs.

Nearfield

(1) Waste form. The physical and chemical stability of the waste itself can be studied in different analogs, depending on the waste form. Good analogs for unreprocessed used fuel, which consists of a crystalline UO_2 matrix, are natural uranium deposits. The fission products in used fuel occur either inside the crystal structure, in pores within the matrix, or attached to the outside of the matrix, depending on the element. Thus, the release of both the uranium and the contained fission products will depend on the stability of the fuel matrix. The survival of natural uranium oxide minerals, after millions to billions of years of water interaction (Hoeve et al., 1980) and radiation effects (Haaker and Ewing, 1980; Curtis et al., 1981), provides information about the conditions of survival and the integrity of uranium oxides.

For fuel recycle waste, several waste forms are being considered: silicate-glass, glass-ceramic and SYNROC. Analogs for silicate-glass waste forms are volcanic glasses, (Zielinski, 1980) including their use in prehistoric products (Ericson, 1981) and tektites (Barkatt et al., 1984). These analogs are mostly aluminosilicate glasses. No natural analogs exist for the borosilicate glasses considered for the waste form in some countries.

In the absence of water, the structural and chemical stability of volcanic glasses is very high. In general, low temperatures and low water flow rates (such as in tight crystalline rocks) limit the hydration rate of glass, making the dissolution of glass too slow to be of concern for safe disposal (Allen, 1982; Stuart et al., 1983). In contact with low-temperature surface waters, volcanic glasses appear to survive intact for up to two million years (Malow and Ewing, 1981). Hydrothermal leaching of volcanic glass shows a higher stability for aluminosilicate glass compositions than for borosilicate glass (Dickin, 1981).

Glass-ceramic and SYNROC waste-form compositions are based on highly insoluble and stable natural minerals, mainly belonging to the group of titanium and zirconium oxides and spinels. The obvious analogs for these waste forms are their natural mineral counterparts set in systems similar to those anticipated in the disposal vault. For example, for a sphene-based glass-ceramic, a study on the alteration of sphenes from various granites (Vance and Gascoyne, 1984) shows that only when water is present (i.e., from the presence of alteration products in the sphene) is there some correlation between leaching of uranium and radiation-induced structural damage.

(2) Buffer/backfill. Buffer and backfill materials will be mixtures of smectite-clays and quartz, or crushed host rock. All the processes that adversely affect the design parameters of the buffer and backfill materials depend on the presence of water. After emplacement of the waste, heat from the waste will cause at least some partial drying of the buffer (Pusch et al., 1983). An analog to this process can be found in contact metamorphic aureoles in clay-rich sediments, caused by the intrusion of a relatively dry magma. Several studies on element migration in contact metamorphic aureoles show, in general, a positive correlation between extent of migration and the relative water content of the intrusive magma (e.g., Brookins, 1984). Although temperatures of intrusive magmas are much higher than for emplaced waste, important information on the drying mechanism, fluid flow and mineral transformations can be derived from appropriate sections of the thermal profile in the sediment.

With water present in the buffer and backfill, a reaction between the smectite-clay and water will occur. Many studies on this reaction in natural systems (e.g., Boles and Frank, 1979) show that illite forms at any temperature above ambient, although at a very slow rate below about 100°C. So far, no results have been reported on analogs of the reaction of highly saline waters (brines) with clays. One place where this reaction can be studied is in the Salton Sea geothermal field (Elders and Cohen, 1983).

Cementation is another process that could affect the properties of the buffer and backfill (e.g., self-sealing). This process could occur through the dissolution of quartz or host rock minerals in the buffer and backfill in the high-temperature zone, followed by precipitation of the same or new minerals in the clay matrix in the low-temperature zone. Alternatively, cementation would occur without a thermal gradient, either when saturated groundwater from the host rock enters the buffer or backfill and becomes supersaturated, or when a difference in pH or Eh between the host rock and the buffer or backfill causes certain dissolved phases to precipitate. Analogs of these cementation processes may be found in active systems such as the Salton Sea geothermal field or in fossil systems, e.g., the sandstone host rocks of the unconformity-type uranium deposits in northern Saskatchewan (Cramer, 1985).

Deformation or creep of clay minerals could occur due to water uptake and internal (swelling) or external (tectonic) pressure. This process may occur immediately after waste emplacement, when drying of the inner part of the buffer will cause saturation of the other part of the clay buffer, which will experience additional pressure from the excavation response of the host rock. Potential analogs of this process may be found in clayrich seams around diapirs and in reservoir traps in sedimentary oil basins.

(3) Host rock. The host rock in the nearfield may be altered by interaction with hydrothermal solutions. This alteration will affect both the fresh rock along the excavation and the existing altered rock along old flow paths. The degree and extent of alteration will depend largely on the temperature and the amount of water involved. Good analogs of hydrothermal alteration are found in geothermal systems (e.g., Tammemagi and Parrish, 1983), in porphyry copper systems such as at Butte, Montana (Sheppard and Taylor, 1974), and in altered rock along side fractures in model host rocks. These analogs in both active and fossil systems provide information on alteration over a range of temperatures, and water volumes and compositions.

Analogs are also required to determine water flow rates in crystalline rock under the influence of a thermal gradient. But it is difficult to find a natural system in which temperature and duration of the thermal episode similar to that of the disposal system have been imposed on a previously unaltered rock. The incipient stage in a young, or newly formed, geothermal system is probably the best analog to determine water flow rates.

Another process affecting water flow and radionuclide migration in the near-field host rock is self-sealing due to the infilling of fractures with secondary minerals. Good analogs are fracture mineralogies in model host rocks that show a history of hydrothermal fluid migration (e.g., Kamineni et al., 1982) or a low-temperature geothermal system in a model host rock (e.g., Tammemagi and Parrish, 1983, for granite).

(4) Radiolysis. Analogs of the effect of radiation on the composition of water are restricted to natural concentrations of radioactive minerals, such as high-grade uranium ores. Curtis and Gancarz (1983) report on the potential for, and the effects of, radiolysis in the reactor zones of the Oklo deposit. Indirect evidence on the distribution of various multivalent elements suggests that radiolysis may have produced locally oxidizing conditions in water in contact with the ore minerals. Another potential analog is found in some of the sandstone-hosted uranium deposits in northern Saskatchewan (Cramer, 1985). Here, thin hematite lenses occur in close spatial association with the high-grade mineralization in a strongly reduced system, which is characterized by the absence of iron oxides anywhere else in this system. Radiolysis of groundwater flowing through the mineralization may be responsible for this localized oxidation and precipitation of dissolved iron from the groundwater.

(5) Fission reaction products. Radionuclides produced during the fission reaction include fission products and actinides, which are extremely rare in nature. Analog data for these radionuclides are obtained either from studies on the fossil reactor zones in the Oklo deposit (e.g., Curtis et al., 1982) or indirectly from chemical analogs to other elements. For instance, some of the more abundant and better known lanthanides are used as chemical analogs for the actinides plutonium, americium and curium. However, the value of using such chemical analogs depends strongly on matching the critical properties (e.g., oxidation state, ionic radius etc.) of the analog element to those of the radionuclide. Thus, for neptunium and plutonium in the reduced IV form, it may be better to use the fellow actinides uranium (IV) and thorium as analogs, rather than one of the lanthanides, because the latter have generally larger ionic radii than the actinides.

Iodine is another radionuclide requiring special attention because of its high mobility under a wide variety of conditions. For the elevated temperature conditions of the near-field zone, retardation of iodine may be studied in analogs such as hydrothermal silver or copper deposits, where iodine enrichment has been reported. This enrichment of iodine can be explained by the low solubilities of silver iodide and copper iodide compared with those for the equivalent chlorides and sulfides. The silver-iodine compounds are also of interest because their formation is independent of redox conditions.

Farfield

(1) Water migration. The migration of groundwater through the farfield is the main transport mechanism for radionuclides released from the waste. The bulk of the groundwater will migrate along existing fractures, which are pathways already established during the preceding geological history of the host rock. Hydrological data from fracture-flow studies in model host rocks, complemented by mineralogic and isotopic data on fracture infillings, probably give the best analog for bulk flow around a sealed waste vault.

Even though the shaft(s) of the underground vault will be sealed after completion of the disposal operation, potential new flow paths will exist along the shaft(s). A good analog here may be the migration of groundwater through a diatreme. The forceful emplacement of a diatreme causes severe stress effects on the host rock; in addition the composition of the diatreme differs from that of the host rock. Both aspects are similar to those of a backfilled shaft, and the occurrence of secondary minerals in the diatremes indicates that water has migrated through these rocks.

(2) Matrix diffusion. The diffusion of dissolved radionuclides into the host rock matrix along fracture flow paths is potentially an important retardation mechanism, particularly in disposal concepts with relatively short pathways between the nearfield and the biosphere. Natural analogs of matrix diffusion are found mainly in alteration profiles along fractures (e.g., Cramer and Gascoyne, 1984), or hydrothermal quartz veins (e.g., Shea, 1984). Careful selection of these profiles is highly critical to observations on matrix diffusion because tectonic stress fractures cause secondary cracks in the rock matrix that allow infiltration, rather than diffusion, of dissolved species. In igneous rocks such as granite, good analogs are alteration profiles from a fracture formed due to shrinkage of the rock upon cooling.

(3) Radionuclide mobility. The mobility of radionuclides under farfield conditions is determined by the compositions of the groundwater and of the minerals in contact with this water. Good analogs in this case are the secondary dispersion halos around deposits of uranium ore or of other specific mineralizations (e.g., Cs). In these halos, uranium and other radionuclides, or their chemical analogs, have been transported and/or retarded in response to variable conditions and compositions. Examples of these types of analog are sandstone-hosted uranium deposits, hydrothermal vein deposits (for U and Th), pegmatite vein deposits (for Cs and lanthanides) and roll-front uranium deposits. However, these latter deposits often show evidence of bacterial activity and, therefore, this type of analog is not exclusive to

the farfield. In the absence of high iodine concentrations in the above-mentioned analogs, bromine can be studied as a chemical analog for iodine.

Biosphere

(1) Composition of overburden water. The evolution of the composition of overburden water is largely determined by interaction of this water with the surface water, soil and regolith. The composition of these latter materials can change due to changes in, for instance, climate or topography. A good analog here is the dynamic evolution of overburden waters in glacial sediments where changes in water composition can be modelled and dated from the last known glaciation event. The composition of overburden water can also be modified by mixing with ascending deep groundwaters, on either a short time scale or more permanently. Analogs to short-lived mixing of overburden water and deeper groundwater are "dirty-water" events in natural springs, where brief phenomena, such as heavy rainfall or an earthquake, disturb the normal spring discharge (Everdingen, 1984).

(2) Mineral stability. The stability of both primary and secondary minerals in the biosphere differs from that in the farfield or nearfield because of the difference in both the composition and in the volume of water interacting with the minerals. Good analogs for stability data for primary and secondary minerals are weathering profiles of bedrock, whereas soil profiles provide stability data for secondary minerals.

(3) Radionuclide mobility. The mobility of radionuclides in the biosphere depends to a large extent on the presence of organics, including both solid organic matter and dissolved organic substances, and of living organisms. Reaction with organic complexes can increase the mobility, and sorption onto solid organic matter can reduce the mobility of radionuclides, whereas uptake by organisms can concentrate radionuclides. Good analogs can be found in the fields of exploration geochemistry and soil science: dispersion halos in the overburden, biogeochemical surveys over uranium and thorium mineralizations (e.g., Levinson et al., 1984; Sheppard and Thibault, 1984; Eisenbud et al., 1984), and uraniferous peatbogs (e.g., Coker and DiLabio, 1979). Potential analogs for studying the long-term retention of radionuclides (particularly iodine) or their chemical analogs are paleosoils and fossils of specific organisms.

(4) Aerial dispersion. The ultimate dispersion of radionuclides in the biosphere can occur through the action of wind on surface concentrations of radionuclides in both inorganic

(soil) and organic (plant) materials. Analogs in this case are eolian deposits, for dispersion on a medium to long time scale, and mine and mill tailings, for recent dispersion on a short time scale.

CONCLUSIONS

This paper summarizes many of the established, as well as promising, analogs to selected processes identified as important in the concept of underground disposal of nuclear-fuel waste in crystalline rocks. It is obvious from the cited references that analog data are usually extracted from non-analog studies. Rather, useful information is often available from disciplines other than waste management, emphasizing the importance of communication between the concept assessors, the modellers, and the "field" specialists in the other disciplines. The "analogger" has the role of interpreter, trying to extract and synthesize the relevant and useful data.

The following are the conclusions from this overview:

(1) Most analogs are for the chemical processes where the availability and composition of water are the critical parameters.

(2) Most of the analog effort appears to be for nearfield processes, which have the highest degree of coupling of chemical and physical processes.

(3) Analogs are available for most of the processes that will affect the integrity and performance of the engineered package (waste, container, buffer and backfill) to be placed in the vault.

(4) Uranium deposits, including the Oklo deposit, provide analogs to many important aspects and processes of the disposal concept, and justify more concerted study.

Finally, natural analogs should not just be used to test observations from experimental work. Analogs also have an important value in an inverse mode where information from the natural system should be used to design or modify the engineered package.

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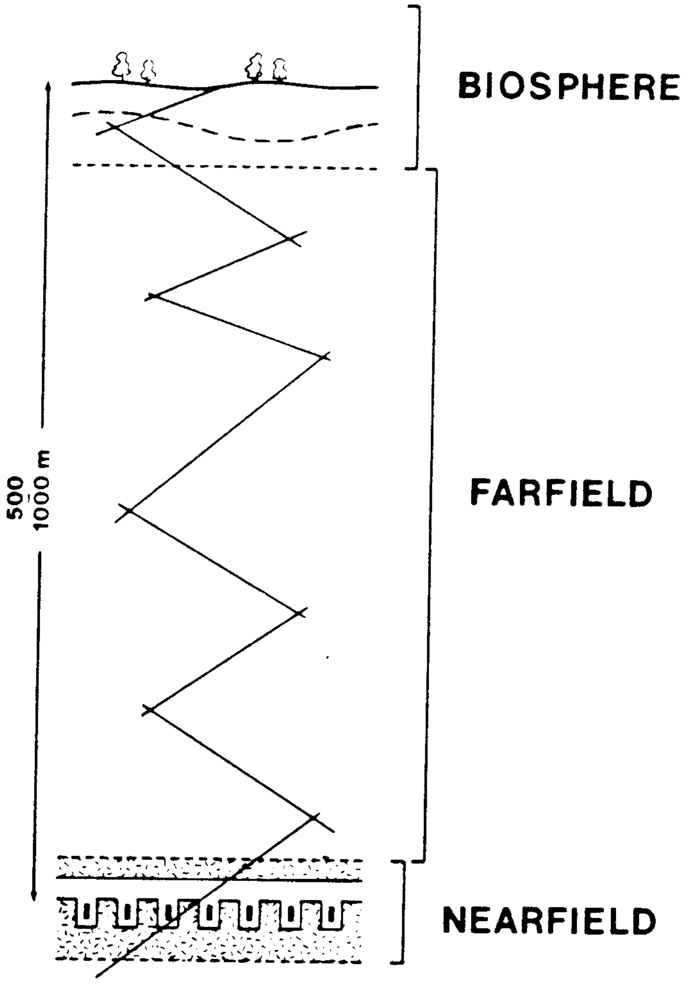

Figure 1:

The three main zones of a disposal vault in a massive body of crystalline rock (white) showing an interconnected fracture flow system. The dashed zone around the excavation defines the rock affected by thermal and stress effects. The stippled area in the biosphere is overburden.

NATURAL ANALOGUES AND VALIDATION OF PERFORMANCE ASSESSMENT MODELS

N.A. Eisenberg
Office of Nuclear Regulatory Research, U.S. Nuclear Regulatory Commission*

ABSTRACT

Most of the natural analogue research has been directed toward and successful in identifying and qualitatively describing the processes and phenomena that are important in natural analogues of components of the waste isolation system or the system as a whole. A few studies are more quantitative and have determined values of parameters used in models of component or system performance. Still fewer studies are sufficiently quantitative and complete to provide validation of performance assessment models. Since performance assessment uses quantitative models, validation of those models must proceed beyond qualitative to quantitative studies. Thus, with a few notable exceptions, the studies of natural analogues have not been as helpful in providing validation of performance assessment methods as the users of such models desire. It is believed that this dissappointment results from a number of technical difficulties, which include the following:

(1) Because naturally occurring events initiated long ago are used to replace the role of experiments in model validation, investigators cannot, as in laboratory or field studies, carefully control the experimental variables, the environmental conditions, the physical configuration, the timing, etc.

(2) The lack of control over variables and environmental conditions is often confounded by an inability to determine what conditions prevailed and what events occurred over geologic time spans in the natural system.

(3) The large heterogeneities inherent in many geological systems produces large uncertainties in the knowledge attainable for the system.

(4) Many, if not most, geologic systems are extremely complex, with numerous physical and chemical processes occurring simultaneously; this complexity generally precludes the use of natural analogues to validate a single aspect or regime of modelling at a time, as with laboratory validation.

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* The views expressed in this paper are not necessarily those of the U.S. Nuclear Regulatory Commission.

(5) Because of the complex nature of the interacting processes involved, the state-of-the-art of quantitative models for geologic systems is not as advanced as for certain other sciences and engineering.

(6) Natural analogues are often data poor in the sense that the same data must be used to specify model parameters and to validate the model; without a second independent data set only data matching is achievable.

INTRODUCTION

Performance assessment for the geologic disposal of nuclear waste, like many other safety assessment methods for large, complex technologic systems, is a vehicle to describe the safety-related aspects of the system and to evaluate whether the system, in part or in its entirety, meets a specified safety standard. As with many other safety assessments, reliance is placed on mathematical models (based on physicochemical theory, phenomenological data, or both) to predict system performance under a variety of conditions. This reliance on modeling is the usual practice for large, complex systems where proof testing would be too expensive, too difficult, or too dangerous to conduct. Nonetheless the models describing system performance for these complex systems need to be validated and usually are for large, technologic systems other than the geologic disposal of nuclear waste. Typically this is done in a piecemeal fashion by proof testing simple systems described by the submodels, which are used in the aggregate to describe the complex system. Given certain difficulties with simultaneity among different submodels and/or feedback among different submodels, this type of piecewise validation generally provides a substantial degree of confidence on the part of the users of the safety assessment, that effective decisions about safety can be made.

For geologic waste isolation systems, validation of system performance models is extremely difficult, both for the overall system performance models and for an individual submodel aimed at describing part of the overall system. The most potent obstacle to validation is that the performance of the system and of its various components takes place on a time scale of 10^3 to 10^6 years; clearly direct observation for the purpose of validation is precluded. For example, in the U.S. the proposed EPA standard (Environmental Protective Agency, 1981) requires consideration of overall system performance for a period of 10,000 years after repository closure. The NRC regulation 10 CFR Part 60 (U.S. Regulatory Commission, 1980) requires compliance with the EPA standard for the system as a whole and, in addition, places requirements on system components. Among other requirements the waste package is required to contain the waste for 300 to 1000 years and the site is required to have a groundwater travel time of at least 1000 years. In addition to these time scales set by regulatory requirements, some studies (e.g. Pigford, 1984) of the performance of geologic waste disposal systems, which have been used in part to study the effectiveness of requirements for safe disposal, consider time spans up to 10^7 years. Two other major problems impede the validation of performance assessment models for waste disposal. First, some of the multiple barriers that comprise the waste isolation system are natural and not man made; hence, it is usually not possible to obtain the type of controlled conditions desireable for a validation study. Second, it appears that the significance of various important phenomena changes as the scales of time and distance are varied; consequently, the range of validity of simple scaling laws and simple scaled experiments is limited.

One solution to these problems of direct validation is the use of natural analogues to the geologic waste isolation system. These geologic and archaeologic analogues are configurations similar to the waste isolation system or its components in situations similar to the expected development conditions of a repository. These analogues are essentially unplanned experiments that have been running for hundreds to thousands of years and in some cases longer than the time scales of interest for a repository. This paper discusses the relation of natural analogues to the validation of performance assessment methods. This is accomplished: (1) by describing performance assessment, including model validation needs, (2) by reviewing previous research on natural analogues and by evaluating the degree to which that work validates performance assessment methods, and (3) by describing the type of research and procedures that appear to have promise for improving the ability of future work on natural analogues to validate performance assessment methods for waste disposal.

PERFORMANCE ASSESSMENT

The term "performance assessment" was described from a regulatory perspective by the NRC staff in their Draft Site Characterization Analysis report (NUREG-0960, U.S. Regulatory Commission, 1983a) as "the process of quantitatively evaluating component and system behavior, relative to containment and isolation of radioactive wastes, to support development of a high level waste repository and to determine compliance with the numerical criteria associated with the regulation (10 CFR 60)." Other, less broad definitions of "performance assessment" have been proposed (Ross and Giuffre, 1981); however, this more inclusive meaning of performance assessment will be used in this paper.

A performance assessment can be considered to be a set of sequential steps:

(1) system description:	description of the repository and its setting as a waste isolation system
(2) scenario specification:	specification, either externally or as part of the assessment procedure, of a set of states of nature (including static and dynamic conditions), usually termed scenarios
(3) consequence estimation:	estimation of the response of the waste isolation system to the set of scenarios specified; this always involves estimating one and often several measures of system and/or subsystem performance
(4) uncertainty evaluation:	evaluation of the type and extent (qualitatively, if not quantitatively) of the uncertainties inherent in the estimates of system response (consequences)
(5) acceptance evaluation:	the estimated measures of system performance of the various scenarios are evaluated individually or collectively, against established safety criteria, considering fully the significance of the uncertainties inherent in these estimates.

Clearly, the performance assessment procedure outlined above culminates in the final step wherein the "bottom-line" question of "Is it safe enough?" is answered, given that additional safety issues beyond the scope of the performance assessment may also need resolution. The inclusion of the fourth step, uncertainty evaluation, may surprise some readers familar with waste management and performance assessment; however, it is included as a separate step to stress its importance and also to express the belief that such an evaluation is always part of the performance assessment, whether recognized and stated explicitly or not. The NRC staff has specifically required that an evaluation of uncertainty be included in the licensing submittal for a repository (U.S. Regulatory Commission, 1984).

This listing of procedural steps is sufficiently inclusive for virtually all types of performance assessment methods, e.g. design basis standard, probabilistic risk assessments, geosphere simulation. For some of these methods, especially risk assessments (Cranwell et al. 1982; U.S. DOE, 1979; Girardi et al. 1980a,b;

Dove et al. 1982; Dormuth and Sherman, 1981), considerable attention is paid to quantifying the probabilities of scenarios and using probability values to estimate performance measures. This is brought up, since the listing of steps above is not explicit about these additional steps. In order to keep the focus of this paper on applying natural analogue research to validation of performance assessment methods, the description of performance assessment has been intentionally truncated.

Although several performance assessment methodologies (Cranwell et al. 1982; Girardi et al. 1980a; Dove et al. 1982) incorporate a full suite of consequences models, depending upon the application, or more particularly the performance measure, the consequence modeling may be truncated at any step. For example, assessment of compliance with certain provisions of the NRC high-level waste standard (10 CFR 60) requires, among other things, estimation of the waste form leach rate, the container life, and the groundwater travel time. Assessment of compliance with the proposed EPA standard for high-level waste (40 CFR 191) would require estimation of radionuclide transport to the accessible environment. In neither case would the use of biosphere transport or health effects models be required. However, a set of consequence models more complete than required to measure compliance with a particular standard have been employed to help formulate and assess those requirements (U.S. Regularoty Commission, 1983b; Chu et al. 1983; Ortiz et al. 1983).

Validation Needs in Performance Assessment

A safety evaluation performed on an engineered system (e.g., a nuclear power plant, a space shuttle) would include most of the broad features of the performance assessment discussed above. For these systems, however, field or laboratory testing could be used to validate the consequence models; furthermore, the key scenarios and failure rates could be observed by life testing the system. For the geologic waste disposal system such validation tests are not possible because: (1) the time span of interest is large and (2) the systems involved are natural systems, for which controlled experiments are difficult. Nevertheless, because natural and man-caused events occurring long ago have observable manifestations now, natural and archaeological analogues may provide a degree of validation for performance assessment. The degree of validation is not expected to be perfect or exact, but these analogues appear to have a significant potential in satisfying the scientific community, regulators, and the general public that the performance assessments are adequate. The degree of validation will depend upon how well the operative process are identified and how well the natural analogue matches the model to be validated. Challenge to the adequacy of performance assessments are likely to be on the basis of completeness, accuracy, or counter-examples. Studies of natural analogues may help to assure that the quantitative models used in performance assessment include all the significant phenomena and that all significant disruptive events or other states-of-nature are included in the analysis. The scientific community is likely to be most concerned about the accuracy, completeness, and appropriate use of the quantitative models. Validation of models using natural analogues, presuming that some quantitative models can be so validated, can demonstrate that the models have sufficient accuracy and completeness for their intended use, when applied over time periods and distances similar to those encountered in waste isolation. Prudent study of natural analogues should be able to equip the users of performance assessment with sufficient knowledge so that counter examples will not cast doubt upon a safety assessment, because the counter examples will have either been included in the analysis or omitted, based on substantiated grounds that the example is unimportant.

It is anticipated that the validation provided by natural analogues would apply to either consequence modeling or system-related behavior. The discussion of natural analogue research that follows is therefore subdivided into the following categories:

A. Component Studies

1. Waste Form
2. Engineered Barriers
3. Geological Site

B. System Studies

1. Scenarios
2. Sensitivity and Uncertainty
3. Overall System Performance

Most current and past research on natural analogues appears to fall into the component studies category.

Natural Analogue Research and Performance Assessment Validation

In the following, research on natural analogues is reviewed to determine the degree to which past and current research may be used to validate performance assessment methods. This review is not intended to be comprehensive or exhaustive, but rather representative. This discussion is subdivided into the categories of component and system studies presented above. For convenience the degree of validation provided by a given research effort may be placed into four broad categories:

Process/phenomena identification. The research identifies, for a given set of circumstances, the processes or phenomena which appear to influence the behavior of one or more components of the waste isolation system. The behavior of the component may be qualitatively or semiquantitatively described and the importance of the processes or phenomena in affecting component behavior may be described qualitatively or semiquantitatively. The use of natural analogues for this purpose has been suggested by others (Birchard and Alexander, 1983).

Parametric quantification. The research quantifies the values of parameters used in performance assessment models. Generally in these natural analogue studies parametric values for use under a certain set of conditions are deduced by adjusting model parameters until the model predictions match observed behavior. Clearly some means other than data matching must be used to attempt to deduce the conditions under which these parametric values are operative. This can be an alternative or adjunct to direct measurement of parametric values.

Component submodel validation. The study of behavior of a component of the waste isolation system is sufficient to validate the performance assessment submodel describing the behavior of that component given that the regime of validation may be limited and the uncertainties of validation may be large. The data demands required for submodel validation are considerably greater than those required for parametric quantification. If one set of data is used to fix parametric values used in performance assessment models, then another set of data, applicable to the same field conditions must be used to determine whether the model predictions agree with field observations. If there is not one more set of data than that required to fix parametric values, then the degrees of freedom in the model equal that of the data and validation is not possible. Additional data sets may be required if the analogue is to (1) fix parametric values, (2) compare model predictions with field data, (3) determine the conditions under which these parametric values apply.

System model validation. A repository-like configuration is studied in sufficient depth so that either (a) the coupled behavior of two or more surrogate components of a waste isolation system validates (as for components) the performance models for those components or (b) behavior of a component, a coupled set of components, or the entire waste management system surrogate validates the probabilistic predictions of the performance assessment methodology. Clearly for the second type of validation a sufficient number of similar structures or events must be observed of a variety of evolving states of nature, so that a comparison to behavior under the various scenarios generated by the performance assessment can be made. An example of the first type would be validation of waste form leaching and radionuclide migration models by studying leaching and migration from ancient glasses or ceramics containing actinides. An example of the second type would be validation of radionuclide migration models by studying transport of species away from a number of similar plutons intruding into the same type of country rock, but at a variety of sites experiencing different climatic, geologic, and hydrologic histories.

Component Studies

Most of the natural analogue studies to date focus on one of the waste isolation barriers, rather than on the entire waste isolation system or partial system comprised of two or more components. Most of these studies appear to be concerned with the identification of the significant phenomena and processes. A few estimate parametric values used in performance assessment modelling.

Waste Form

Most natural analogue research directed toward the waste form component of the waste isolation system appears to be concerned primarily with understanding the phenomena and processes that may be important in waste isolation and with obtaining a qualitative ordering of the importance of various processes. Thus, for example, a study of ancient glass artifacts (Kaplan, 1980) defines five categories of observed weathering: weeping, crizzling, layer formation, pitting, and crust formation. The type of weathering observed, which appears to depend on the chemical composition of the glass, seems to proceed by leaching of alkalis rather than dissolution of the silica matrix. An important observation is that the same physical mechanism is able to produce more than one type of weathering.

By studying the occurrence and alteration of minerals similar to proposed waste forms, other investigators (Haaker and Ewing, 1980, 1981) have identified compatibility of the waste form with the host rock as an important influence on waste form stability. Although these studies are highly suggestive, without thermodynamic and kinetic data, which are currently largely unavailable, the bridge to predictive, quantitative methods is not clear. Another study (Malow and Ewing, 1981) compares the thermal and chemical stability of waste glasses and naturally occurring volcanic glasses. The study concludes that volcanic glass is more stable because of a higher silica content, yielding a higher formation temperature. Some of the evidence supporting this conclusion was that high temperature caused a phase change in the waste glass, but essentially none in the volcanic glass. Since most volcanic glasses are less than 2 million years old, this age is tentatively adopted as an upper age limit of stable glass.

One study (Ericson, 1981), that attempts to quantify the process rates relevant to waste form stability, discusses the hydration of obsidian glass. This study points out that a dating method based on obsidian hydration has been employed in archaeological and geological studies for decades. The hydration rates for obsidian samples from a variety of sources are given for both natural hydration and laboratory tests. The discrepancies between the natural and laboratory rates are not explained (natural rates are usually higher). External variables affecting the hydration process are time and temperature; intrinsic variables most important in determining hydration rate appears to be CaO, TiO_2, and H_2O concentrations in the obsidian.

Engineered Facility

Natural analogue studies of components of the engineered facility include studies related to the waste canister, backfill materials, and shaft sealing materials. A rather comprehensive compendium (Johnson and Francis, 1980) of the behavior of archaeological objects, metal meteorites, and native metals subject to corrosive environments of varying intensities provides evidence for metal durability over hundreds to thousand of years. Early human uses of metals included gold, silver, copper, lead, iron, tin, and mercury. Some of these early metallic artifacts have survived to the present. Earliest uses of metal probably began 8000 to 9000 years ago with gold and copper. Clearly gold is the most durable. Metal meteorites are iron-nickel alloys. Weathering of metallic meteorites is variable, depending on the conditions where they fell; but some meteorites estimated to be 5,000 to 20,000 years on earth show little weathering. Deposits of native metals such as copper, gold, silver, and mercury, indicate that conditions existed at some time permitting the formation of such deposits. Some deposits appear to have persisted in an unaltered state for at least several millenia. For all three cases (meteorites, native metals, and ancient artifacts) dry or mildly moist environments generally promote greater metal durability. In addition to determining general trends for durability and factors affecting it, this study also discusses the details of corrosion processes obtained by metallographic examination of the objects under study. Also from data obtained from archaelogical specimens, linear corrosion rates over long time spans are estimated for iron and copper based alloys.

A different perspective on naturally occurring metals is used to investigate the use of a backfill in a repository. A study (Apps et al. 1981) on the formation of natural iron-nickel alloys finds empirical support for the chemical thermodynamic concepts advanced to explain the formation process. From this base of understanding the authors propose that altered ultrabasic rocks, e.g. serpentinite, might provide a superior backfill material for waste cannisters made on iron-nickel alloys, because the formation of such alloys in these rocks demonstrates the thermodynamic stability of the alloys in that environment. A different type of potential backfill material, clay, was studied (Register et al. 1980) for possible use in a salt medium. The chemical composition of clay minerals found in evaporite sequences was studied. Rare earth elements are found to remain in the clay minerals, rather than migrating into the surrounding evaporite. It is proposed that clay minerals used as backfill in a salt repository would retard both lanthanides and actinides. In another clay backfill study Brookins (1981) considers data from uranium deposits near Grants, New Mexico. This study concludes that clay minerals appear to be a useful overpack material, based on the preferential retention of actinides and lanthanides by these minerals in uranium deposits. These minerals also appear to have the capacity to retain Cs and other fission products.

Samples of ancient (4,400 to 3,000 year old) cement containing building materials are studied (Langton and Roy, 1984) in an attempt to identify common factors related to the longevity of the cement. A key factor appears to be low porosity of the hydraulic cement, usually achieved by low water to cement ratios, which reduce workability. Clean, well graded, inert aggregates also appear to promote longevity. These same factors are projected as influencing the longevity of borehole seals.

Site

Natural analogue studies of the repository site have succeeded in identifying certain phenomena influencing the ability of the site to isolate waste as well as determining the numerical values for parameters of models used to describe the site behavior. Thus a study (Laul et al. 1984) of the migration of elements from igneous intrusions (pegmatite) into country rocks (amphibolite and quartz-mica schist) shows that some elements (K, Li, Rb, Cs, As, Sb, Zn, Pb) migrated over 40 m during contact metamorphism. Other elements (rare earths, Al, Sc, Cr, Hf, U, and Th) did not migrate appreciably. The authors proposed that the behavior of these igneous intrusions are analogues of the behavior of a repository over a time scale of thousands to millions of years. A similar study (Levy, 1984) in a different geologic medium considers the alteration of a vitrophyre at Yucca Mt. as a natural analogue of changes anticipated to result from waste emplacement in welded tuff. Anticipated changes include crystallization of glassy rock to zeolites and smectite. Although secondary porosity would increase as glass dissolved, countering this effect would be the partial filling of fractures by newly precipitated minerals. Extensive studies have been conducted of the fossil natural reactor at Oklo, Gabon (IAEA, 1975, 1977). This is considered to be an important natural analogue, because certain actinides (including transuranics) and other fission products, which are important constituents of reactor waste, have not been discovered in significant quantities elsewhere in the earths crust. One study (Brookins, 1981) of the migration behavior of alkali and alkaline earth elements at Oklo concludes that post reaction migration of Rb and Sr from the reactor zones occurs, while Cs appears to be retained for at least 26 million years after cessation of the reaction. A study by Curtis and Gancarz (1983) of the mineralogy at Oklo shows that rocks in the reactor zones are significantly altered and that nearby rocks are mineralogically modified compared to normal uranium bearing rocks. The authors attribute these changes to the production of oxidizing and reducing species by the radiolysis of water. Among the study´s conclusions are: (1) iron was chemically reduced and accumulated in the reactor zones; (2) U and multivalent fission products were oxidized and transported from the reactor zone; (3) about 10 percent of these mobilized species moved as far as a few meters from the reactor zones; (4) an effective radiation yield of 0.06 molecules of hydrogen per 100 ev of energy imparted to the fluid phase is deduced. For an active reactor this study indicates that radiolysis produces significant geochemical, thermal, and groundwater flow effects.

Other natural analogue studies related to site behavior have succeeded not only in determining important processes and phenomena, but also in quantifying parametric values for use in performance assessment models. One study (Hubbard et al. 1984) of the migration of naturally occurring radionuclides (^{238}U and ^{232}Th chains) in brine aquifers concludes: (1) Ra does not appear to be retarded by sorption, (2) Th is strongly sorbed, (3) the retardation factor for Th is estimated to be greater than or equal to 40 for these aquifers, and (4) for similar half lives, isotopes of Th and U behave similarly suggesting that uranium remains in the quadravalent oxidation state. Shea (1984) studied radionuclide migration, viz. migration of uranium-235 from veins and veinlets, microcracks, secondary minerals sealing microcracks, etc., and concludes that migration over short distance (1-5 cm) yields apparent diffusivities of 10^{-19} to 10^{-16} m^2/sec in the rock matrix (several orders of magnitude less than laboratory measurements) and K_D values of 1 to 100 m^3/Kg (several orders of magnitude greater than laboratory measurements). Postulated causes for these discrepancies include: (1) more microfracturing in the field, (2) secondary mineral formation in microcracks in the field, (3) differences in temperature and nuclide oxidation state, (4) time dependence of the system process. Another study (McKinley et al. 1984) of elemental (including uranium) migration considered movement of elements from a thin layer deposited during a period of seawater intrusion into lacustrine sediments. Certain elements deposited during the intrusion were remobilized at rates different from other elements so deposited, during a period of about 10^4 years. Uranium effective dispersivity was estimated to be 1.2 x 10^{-4} m^2/s and K_D was estimated to be 0.4 m^3/Kg. By conducting a series of laboratory experiments on these sediments these investigators found that in most cases it appears that sorption is poorly reversible. Also they conclude, "Simple sorption measurements show little qualitative agreement and no quantitative correlation with the observed profiles (of element concentration vs. distance)". An extensive study by Airey et al. (1983; 1984) of radionuclide migration around ore bodies in the Alligator Rivers region of Australia has succeeded in shedding light on the physicochemical processes important to radionuclide migration and in determining values for some parameters used in quantitative models. Some of the significant qualitative findings include: (1) U and Th are associated with iron minerals in the weathered surface of the ore body; (2) Ra concentrates on clay; (3) Ra formed by α-recoil on clay particles has a higher K_D than Ra adsorbed from solution; (4) U appears to migrate mainly in solution, while ^{230}Th appears to migrate significantly through groundwater colloids. The retardation factor for uranium was estimated to be 250, downgradient from an ore deposit.

System Studies

Because only a few systems studies using natural analogues have been conducted, this discussion is not subdivided as was the previous discussion of component studies. Most of these studies consider the coupled behavior of two or more components of the waste isolation system. For example, one study (Brookins, 1983) of an igneous dike intruding into evaporite rocks near the WIPP site is proposed as an analogue to migration from the waste form (a source term model) into a salt host rock (a groundwater transport model). Studies of the chemical composition of the halite and lamprophyre (dike rock) indicate that little migration of heavy metals from the dike into the halite occurred. A rather comprehensive study by Wollenberg et al. (1982) investigated element migration from intrusive rocks into a variety of country rocks. Contact zones between quartz monzonite intruding into Precambrian gneiss and Tertiary monzonite intruding into tuff were studied in depth· less detailed study was given to contact zones between a rhyodacite dike cutting into basalt and Kimberlitic dike cutting into bedded salt. Actinides, rare earths, and alkaline earths showed little movement from contact zones in gneiss and tuff. Work on the monzonite intrusion into tuff, reported elsewhere (Brookins et al. 1983), showed that only limited migration (~10 m) of the most mobile elements (Cs, Cr, Co) occurred, even in the presence of convective flow. Actinides appear to migrate very little from contact zones in salt and basalt. A similar analogue was proposed based on the study (Gancarz et al. 1980) of the migration of Tc, Pb, and Ru around the Oklo natural reactor. All three elements were shown to migrate from the reactor zones into rocks about 10 m away. ^{99}Tc was fractionated from Rn within one million years after the reactor ceased operating. Pb/U fractionation has been occuring throughout the history of the deposit, about two billion years. Lead loss appears to be due to diffusion followed by groundwater transport.

As an analogue of groundwater flow and transport of radionuclides, one study (Andrews and Pearson, 1984) compares field measurements on the migration of naturally occurring ^{14}C, ^{234}U, and ^{238}U to model predictions. This is one of a few studies in which the predictions of an advanced quantitative model (SWENT in this case) are compared to field data. Because these field data were used to fix model parametric values, satisfactory model validation was not achieved. Nevertheless the ability of the model to match a broad range of data is encouraging. Simulation distance was approximately 100 km and time was 10^5 to 10^6 years. For ^{14}C, $K_D = 0$, while for U, $K_D = 0.006\ m^3/Kg$.

Studies (Mickeley, 1982; Eisenbud et al. 1982) of radionuclide migration from the soil through the biosphere at the Moro do Ferro in Brazil have succeeded in identifying significant phenomena and in determing some parametric values used in models. Mobilization rates for Th (considered to be an analogue for quadravalent plutonium) from the ore body into the biosphere is estimated to be 5.9×10^{-7} per year for erosion and 7.5×10^{-10} per year for groundwater solubilization. Apparently organic acids, especially humic acid, complex with the thorium and help to mobilize it. The presence of naturally occurring radioisotopes in humans was used in another study as a natural analogue to the uptake of radionuclides from waste disposal (Gilbert, 1984). The overall transfer factors for the processes dispersing radionuclides from a source to human receptors, as obtained from quantitative models of biosphere transport, are compared to natural occurrences. In general these models are more optimistic than field measurements would indicate. Discrepancies as high as approximately 10^2 have been observed.

Conclusions and Recommendations

In reviewing these four categories of natural analogue studies, the following conclusions are reached. Most of the natural analogue research has been directed toward and successful in identifying and qualitatively describing the processes and phenomena that are important in natural analogues of components of the waste isolation system or the system as a whole. A few studies are more quantitative and have determined values of parameters used in models of component or system performance. Still fewer studies are sufficiently quantitative and complete to provide validation of performance assessment models. Since performance assessment uses quantitative models, validation of those models must proceed beyond qualitative to quantitative studies. Thus, with a few notable exceptions, the studies of natural analogues have not been as helpful in providing validation of performance assessment methods as the users of such models desire. It is believed that this dissappointment results from a number of technical difficulties, which include the following:

(1) Because naturally occurring events initiated long ago are used to replace the role of experiments in model validation, investigators cannot, as in laboratory or field studies, carefully control the experimental variables, the environmental conditions, the physical configuration, the timing, etc.

(2) The lack of control over variables and environmental conditions is often confounded by an inability to determine what conditions prevailed and what events occurred over geologic time spans in the natural system.

(3) The large heterogeneities inherent in many geological systems produces large uncertainties in the knowledge attainable for the system.

(4) Many, if not most, geologic systems are extremely complex, with numerous physical and chemical processes occurring simultaneously; this complexity generally precludes the use of natural analogues to validate a single aspect or regime of modelling at a time, as with laboratory validation.

(5) Because of the complex nature of the interacting processes involved, the state-of-the-art of quantitative models for geologic systems is not as advanced as for certain other sciences and engineering.

(6) Natural analogues are often data poor in the sense that the same data must be used to specify model parameters and to validate the model; without a second independent data set only data matching is achievable.

These problems are formidable, but perhaps are not insurmountable. Although no easy solution appears to be at hand, some of the following suggestions may provide some avenues of relief: (1) natural analogues, that are simpler systems, may provide more useful quantitative data for comparison to predictive models, than more useful quantitative data for comparison to predictive models, than more complex systems that are closer to a repository component or configuration; (2) to answer some of the fundamental issues of groundwater flow and transport and how best to model these processes, natural analogues involving species other than those found in nuclear waste may provide very valuable information; (3) for all analogue studies, greater pains taken to attempt to determine the environmental conditions (thermal, chemical, hydraulic, etc.) operative during the period studied would be helpful; the behavior of species unrelated to the waste analogue may provide valuable clues to these conditions, (4) some consideration might be given to collecting data to validate (or not) the scenario formulation and probability determinations inherent in many performance assessments; (5) Natural analogue studies that yield more quantitative data better coordinated with modeling efforts would serve the purpose of validation better.

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SESSION B

SOME APPLICATIONS OF ISOTOPIC METHODS TO HIGH-LEVEL RADIOACTIVE WASTE

Chairman: David B. Curtis

EVALUATION OF LONG-TERM AND SHORT-TERM INTEGRITY OF CRYSTALLINE ROCKS BASED PRIMARILY ON URANIUM SYSTEMATICS

J.N. Rosholt, R.A. Zielinski and Z.E. Peterman

U.S. Geological Survey, Box 25046, Federal Center, Denver, CO 80226, USA

ABSTRACT

The abundance of uranium and of its long-lived and stable decay products can be used in conjunction with radiographic and other isotopic data to assess the history and depth of fluid circulation in plutonic rocks. Such information is critical for the evaluation of crystalline rocks for containment of radioactive waste. The long-term chemical and isotopic integrity of Precambrian rocks are assessed by U-Th-Pb and Rb-Sr systematics. Fission-track radiography is used to investigate the spatial association of redistributed uranium and secondary alteration products (timing unspecified). The ^{238}U-^{234}U-^{230}Th system is used as a sensitive indicator of geologically recent (last 0.5 m.y.) uranium mobility and rock/water interaction in matrix rock and fracture zones.

INTRODUCTION

Evaluation of crystalline rock bodies for possible containment of nucler waste would be incomplete without a thorough understanding of the timing and effects of various geologic events that have occurred since emplacement and crystallization. The number of isotopic decay schemes (U-Pb, Rb-Sr, $^{40}K/^{40}Ar$) in whole-rocks and in constituent minerals are useful tools in identifying thermal or tectonic events that may have left no clear mineralogic or textural imprints on the rocks. Perturbation of these isotopic decay schemes can occur through recrystallization or alteration of the rock minerals, commonly facilitated by a fluid phase, and by diffusion. To the extent that parent-daughter disequilibrium is a product of rock/water interaction, isotopic data can be used to assess the history and depth of fluid circulating in plutonic rocks.

A common approach in establishing a time framework for the crustal history of granitic rocks involves U-Pb analysis of zircon and Rb-Sr analysis of whole-rock samples to establish an emplacement or crystallization age. Other isotopic decay systems that are more susceptible to disturbance are then checked for the extent of concordance (agreement) with the crystallization age; internal isochrons developed from Rb-Sr analyses of minerals commonly provide important information on post-crystallization events, and K-Ar and whole-rock U-Pb systematics also yield information. In favorable situations the data on disturbed isotopic systems yield discrete ages that can be related to past thermotectonic events (see J.S. Stuckless article in this volume). Depth related measurements may also be used to investigate zones of rock that are more isotopically disturbed than others. Because of the time required for daughter-product buildup, Precambrian crystalline rocks are most amenable to study by a number of isotopic clocks, and measurements by several isotopic decay schemes permit detection of disturbances as recent as late Cenozoic time. Fission-track ages of apatite can be used to investigate the later cooling history of the rock (time at which the rocks passed through the 100°C isotherm). Detection of even more recent isotopic disturbance (less than 0.5 m.y.) is possible through measurement of disequilibrium between ^{238}U and its long lived daughters ^{234}U ($t_{1/2}$ = 247,000 years) and ^{230}Th ($t_{1/2}$ = 75,200 years) Ivanovich and Harmon (1982). It is not always possible to estimate the timing of redistribution of uranium via rock-water interactions, however, the spatial association of uranium with secondary alteration products is another important area of investigation for evaluating crystalline rocks (Zielinski and others, 1981).

In many ancient granites studied by isotopic methods, the data indicate that uranium has been mobilized at least twice; (1) at least one episode related to dilatancy and thermotectonic events of pre-Quaternary ages, as measured by U-Pb systematics, and (2) a much more recent mobilization as indicated by radioactive disequilibrium in the uranium decay series (Rosholt, 1983). Evidence for mobility of uranium and its daughter products is particularly pertinent for evaluation of potential waste disposal sites because the behavior of uranium in the natural system is a probable analog to the behavior of chemically similar actinides that could be introduced from the waste package. For example, the ^{238}U daughters ^{234}U and ^{230}Th are good natural analogs for predicting the behavior of ^{237}Np daughters, ^{233}U and ^{229}Th, that are contained in the waste package (Rosholt, 1980).

This paper presents a summary of uranium-based techniques that are currently employed by the U.S. Geological Survey for evaluating the chemical and isotopic integrity of crystalline rocks. We believe such methodology should become a routine part of any detailed evaluation of this geologic media for waste repositories.

DEPTH RELATED INVESTIGATIONS

The uranium contents of plutonic rocks may not be the original values because of secondary redistribution of loosely bound (labile) uranium. Labile uranium in part is the same as intergranular uranium prior to secondary redistribution. Evidence that post--emplacement redistribution of uranium has occurred in ancient rocks is based on the radiogenic imbalance that exists between parent ^{238}U and stable decay product ^{206}Pb (Zielinski and others, 1981; Stuckless and Nkomo, 1978; Stuckless and Ferreira, 1976; Rosholt and others, 1973). For example, if the whole-rock age is known from independent measurements and if ^{206}Pb is in excess of that which could be generated by the amount of ^{238}U present, the rock has lost some of its original ^{238}U or gained radiogenic ^{206}Pb. In cases where Pb immobility can be documented, these results substantiate that labile U once existed. Plutonic rocks, with biotite and high Si, Th, and alkalis, appear especially vulnerable to uranium redistribution. In one study (Stuckless and Nkomo, 1978) radiogenic Pb excesses indicated removal of as much as 70% of the U from Archean granite, whereas little or no Th was removed. The U-Th-Pb systematics are described in detail by J.S. Stuckless (this volume).

Some post-emplacement mobilization of uranium in crystalline rocks occurs at surface and near surface conditions. During uplift and unloading, subhorizonthal sheeting fractures form within a few tens or hundreds of meters of the surface, and older, steeply dipping fractures may be reactivated and opened. Water may be released during such dilation events (Goldich and Mudrey, 1971), and the fracturing allows ingress and circulation of groundwater. Deep saline groundwaters, recently investigated in the Canadian Shield (Fritz and Frape, 1982), may play an important role in uranium and other element mobilization in crystalline rocks. These saline waters are found in deep mines and drill holes commonly at depths in excess of 1 km. Their existence places limits on the depth of circulation of shallow, relatively fresh groundwater. In detailed studies of fractures and fracture fillings in the Eye-Dashwa Lakes pluton in western Ontario, Kamineni and Stone (1983) and Stone and Kamineni (1982) observed that fractures within about 400 m of the surface commonly are open and show evidence of groundwater movement, whereas deeper fractures are commonly filled with secondary minerals. In drill holes in this pluton, saline waters are encountered at depths of about 1 km (Fritz and Frape, 1982). Frape and others (1984) reported additional data on the chemical and isotopic compositions of groundwaters to depths of 1.6 km in the crystalline rocks of the Canadian Shield. They found that, due to the intense rock/water interaction which had taken place at each site, it was impossible to say what the exact origin of these brines could have been.

RADIOGRAPHIC AND CHEMICAL MEASUREMENTS

The abundance and distribution of uranium in whole-rock can indicate past interaction with oxidizing water. Of particular interest are apparent changes in uranium content as a function of crystallinity, alteration, fracturing, etc., that are not coupled to parallel changes in thorium content. Because uranium and thorium have similar geochemical properties in silicate magmas, any apparent postcrystallization fractionation of the two is assumed to result from the preferential solubility of uranium (as uranyl) in an oxidizing aqueous phase. In the absence of firm estimates of primary magmatic abundances of uranium and thorium, preferential mobility of uranium is indicated by greater sample-to-sample variability. Variability results fm rock/water interactions and may cause both leaching and enrichment of uranium, the latter by adsorption on secondary minerals.

Direct observation of the spatial association of redistributed uranium with secondary alteration products is provided by fission-track radiography. Secondary minerals that commonly are observed hosts of uranium include secondary silica (opal), calcite, and especially Fe-Mn oxides. The latter occur as dendritic stains on mineral surfaces, as fracture and void fillings, and as alteration rims on ferromagnesium silicates or primary Fe-Ti oxides (Figs. 1 and 2). Such observations indicate possible sites of fixation of dissolved uranium and other actinides that may be introduced from a waste package (Means and others, 1978), and also help to identify ancient pathways of solution flow on a microscale. In favorable situations, the abundance of uranium-scavenging phases and their contribution to whole-rock uranium abundances can be estimated by selective dissolution techniques. For example, Fe-Mn oxides and calcite can be selectively dissolved by a mildly-reducing, acetic acid-based solvent (Chester and Hughes, 1967; Zielinski and others, 1984).

The above chemical and radiographic methods give no indication of the timing of uranium movement, but measured uranium concentrations in whole-rocks can be usefully compared with radium-equivalent concentrations determined by gamma spectrometry. Although limited by the analytical precision of about ± 10 percent, apparent discrepancies between chemical and radiometric uranium contents indicate major open-system mobility of uranium or its long-lived daughters within approximately the last 300,000 y (Zielinski and others, 1984). Samples screened on this basis may be subdivided for further study by more precise and sensitive isotopic measurements as described herein.

URANIUM-DECAY SERIES MEASUREMENTS

The ^{238}U-^{234}U-^{230}Th system can reveal geochemical and physiochemical processes that cause open system behavior of U and its daughter products in crystalline rocks, provided the disturbance occurred within the last 0.5 m.y. To the extent that U series disequilibrium is a product of rock/water interaction, these measurements may help evaluate the effective permeability of unfractured and macroscopically fresh rocks, and they can be used to assess geologically recent U mobility in "sealed" fracture zones. Expanded ternary diagrams (Figure 3) whose apexes are ^{238}U, ^{234}U, and ^{230}Th, expressed in percent of the combined activity, are used to display the results. Various representative activity ratios of $^{234}U/^{238}U$ and $^{230}Th/^{238}U$ are shown by dashed lines in Figure 4. Rocks that are in radioactive equilibrium plot in the center of the triangle, and areas that represent commonly encountered types of isotopic fractionation are noted.

The data for 82 granitic rock samples described by Rosholt (1983) are shown in Figure 5. These have been divided into (1) core samples that have abundant microfractures, (2) unfractured core samples, and (3) surface and near-surface samples. The location of a data point on the diagram can be used to infer which process affected the rock. Data for twenty-two core samples of unfractured rock cluster about the radioactive equilibrium point indicating no disturbance of the abundances of U and its long-lived daughter products during the past 0.5 m.y. The five most important geochemical processes that contributed to uranium-series disequilibrium in the remaining samples are outlined in Figure 6. These are (1) uranium leaching in which ^{238}U and ^{234}U are removed with little or no fractionation, (2) preferential ^{234}U leaching following alpha recoil displacement processes (^{234}U recoil loss) with lesser ^{238}U loss, (3) ^{234}U recoil loss with little or no ^{238}U loss, (4) U assimilation in which both ^{238}U and ^{234}U recoil loss with little or no ^{238}U loss, (4) U assimilation in which both ^{238}U and ^{234}U were added with present-day $^{234}U/^{238}U$ activity ratios varying from 0.8 to 1.2, and (5) addition of ^{234}U and ^{230}Th by daughter emplacement processes (^{234}U + ^{230}Th recoil gain). The ^{234}U displacement mechanism (3 above) operates when ^{234}U, produced by decay of structurally incorporated ^{238}U, is selectively displaced from mineral surfaces in response to the alpha-recoiled decay product ^{234}Th. This mechanism has been extensively documented in natural samples (Osmond and Cowart, 1976) and in laboratory experiments (Kigoshi, 1971; Fleischer and Raabe, 1978). Fleischer (1980) reported on experiments which indicate direct recoil ejection into a liquid interface augmented by ejection directly from one mineral grain to another, producing alpha recoil tracks. Subsequent track etching by natural solutions releases some of the recoil nuclei. Less attention has been given to the complimentary process (5) of daughter emplacement in which dissolved ^{238}U and ^{234}U atoms decay by alpha disintegration, and recoiling daughter nuclides of ^{230}Th,

^{234}Th, ^{234}Pa, and ^{234}U are absorbed or embedded in particulate matter at the solid-liquid interface. After sufficient geologic time, this mechanism (^{234}U + ^{230}Th recoil gain) results in solids in which ^{234}U/^{238}U activity ratios are greater than unity. It is the only process described that invokes the transport of ^{230}Th. All other disequilibrium processes involve the decay of ^{230}Th excess unsupported by ^{234}U; this type of excess ^{230}Th is a result of leaching of uranium (1), preferential leaching of ^{234}U (2), or ^{234}U recoil loss processes (3).

The predominant processes affecting silicic igneous rocks are U assimilation (4) and ^{234}U + ^{230}Th recoil gain (5) in core samples that have microfractures; bulk U loss (1) occurs in highly altered rocks; preferential ^{234}U leaching (2) and ^{234}U recoil loss (3) predominate in unfractured core samples, but several samples cluster about radioactive equilibrium; in surface and near-surface samples, preferential ^{234}U leaching (2) predominates. As expected, ^{234}U recoil loss predominates over preferential ^{234}U leaching in petrographically fresh granites which have experienced minimal interaction with solutions. Nevertheless, ^{234}U/^{238}U ratios near unity may be found in some significantly weathered rocks, not because of undisturbed radioactive equilibrium but rather representing only a transitional state in the weathering profile. Incipient weathering generally produces a relative deficiency of ^{234}U, but as weathering progresses, there is also a tendency for recoil gain incorporation of ^{234}U, ultimately to produce an excess of ^{234}U in intensively weathered rocks and surficial deposits.

CONCLUSIONS

In Precambrian granitic rocks, ages derived from the ^{207}Pb/^{206}Pb relations commonly agree with U-Pb zircon ages or ages determined by other methods. In sharp contrast, the U-Pb ages on a whole-rock scale are discordant and commonly anomalously old indicating loss of uranium during Cenozoic time. These results suggest that deep fluid circulation does not penetrate crystalline terranes below some critical depth (usually less than 0.5 km). The whole-rock U-Pb systems are not perturbed until these terranes are uplifted and exposed to groundwater circulation. Establishing the depth of fluid circulation in different geologic environments could be an important consideration in selecting repository depths. Fluid circulation commonly causes a redistribution of uranium in the rock. Direct observation of the association of redistributed uranium with secondary alteration products is provided by fission-track radiography. Secondary minerals that are commonly hosts of uranium include Fe-Mn oxides, opal, and calcite. These observations indicate phases that are capable of scavenging dissolved uranium and indicate ancient pathways of solution flow on a microscale.

Uranium-series disequilibrium indicates several geochemical processes that are related to solution flow and subsequent mobilization of uranium. Five processes - (1) bulk uranium leaching, (2) preferential ^{234}U leaching, (3) ^{234}U recoil loss, (4) uranium assimilation, and (5) ^{234}U + ^{230}Th recoil gain - cause the data to plot in discrete regions of a ternary diagram which has apexes of ^{238}U, ^{234}U, and ^{230}Th. The data indicate that (1) only unfractured rock from drill cores is in radioactive equilibrium, (2) ^{234}U recoil loss and preferential ^{234}U leach predominates in surface and near-surface rocks, and (3) ^{234}U + ^{230}Th recoil gain and U assimilation occur predominantly in drill core samples of fractured rocks. Uranium leach, preferential ^{234}U leach or ^{234}U recoil loss also occur in some unfractured rocks from drill holes. Ternary diagrams are especially useful to distinguish between processes 2 and 3, and between processes 4 and 5, both of which are more difficult to visualize from isotopic ratios only. The most important findings indicate that ^{234}U recoil loss is diagnostic of incipient weathering, whereas U assimilation and ^{234}U + ^{230}Th recoil gain accompany substantial penetration of water into fractures and weathered zones. During the last 0.5 m.y., bulk uranium loss occurred primarily in weathered or highly altered zones.

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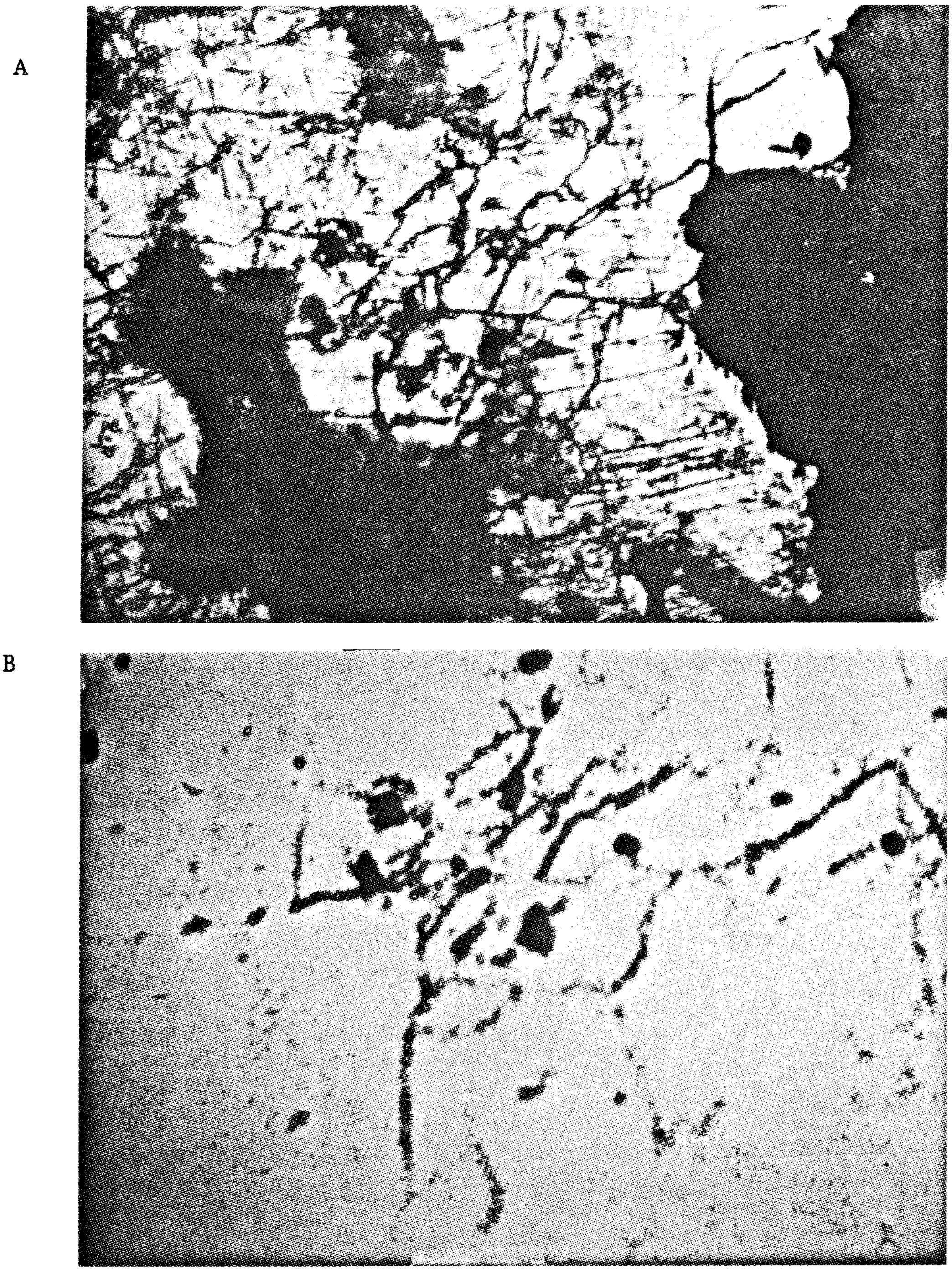

Figure 1. Photomicrograph (A) of sample of Proterozoic Sherman Granite and corresponding fission-track image (B) of the uranium distributions; dark areas on the fission-track image corresponds to areas of high uranium concentration. A network of uraniferous fractures in plagioclase; fine grained fracture filling is probably a mixture of hematite and clay (scale of view = 1.5 x 1.0 mm).

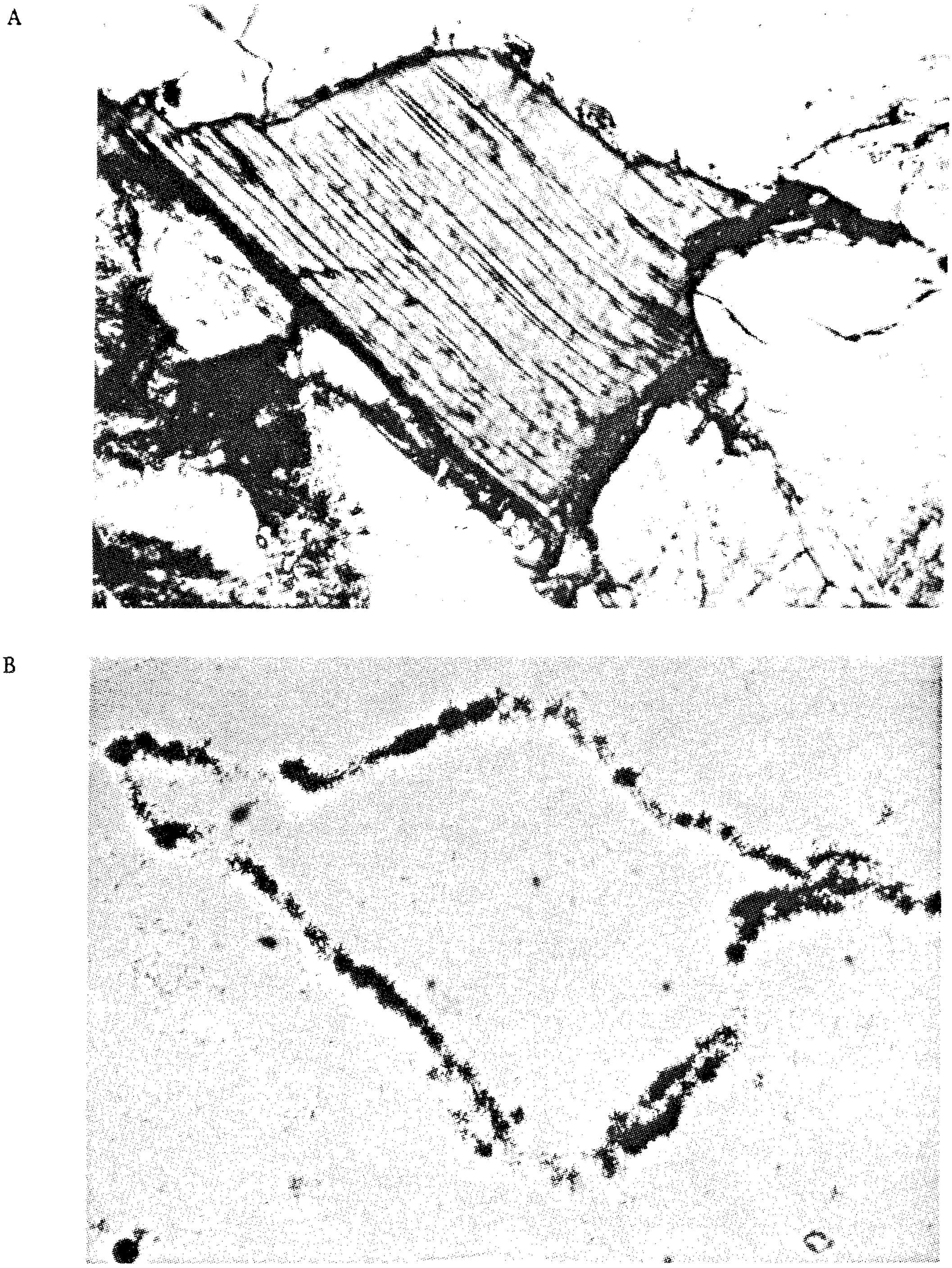

Figure 2. Photomicrograph (A) of sample of Precambrian granite basement rock from Illinois Deep Hole Project and corresponding fission-track image (B) of the uranium distribution. Partially altered biotite where uranium is associated with hematitic stain along altered grain edges (scale = 1.5 x 1.0 mm).

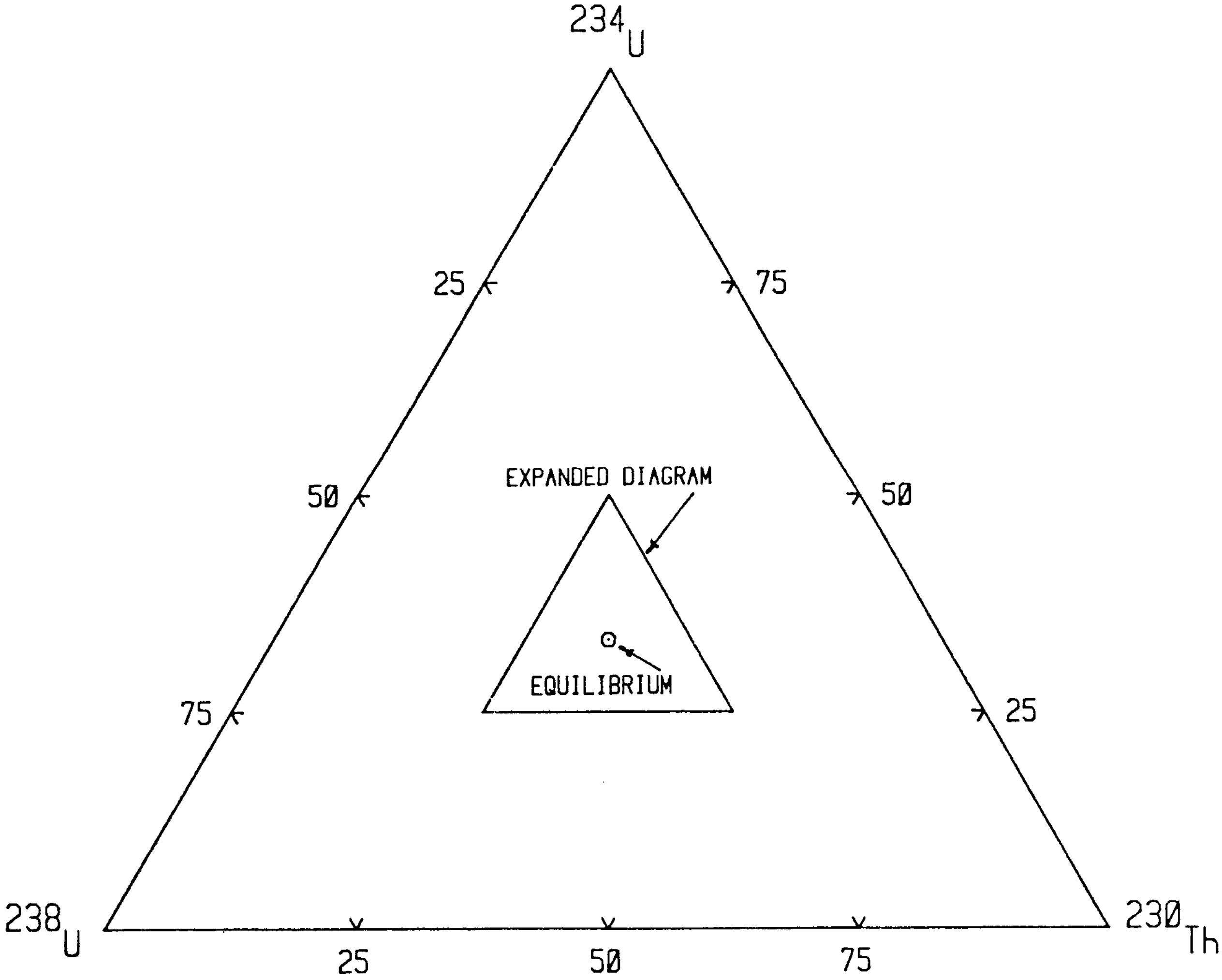

Figure 3. Area of the expanded ternary diagram used to show the ^{238}U-^{234}U-^{230}Th data.

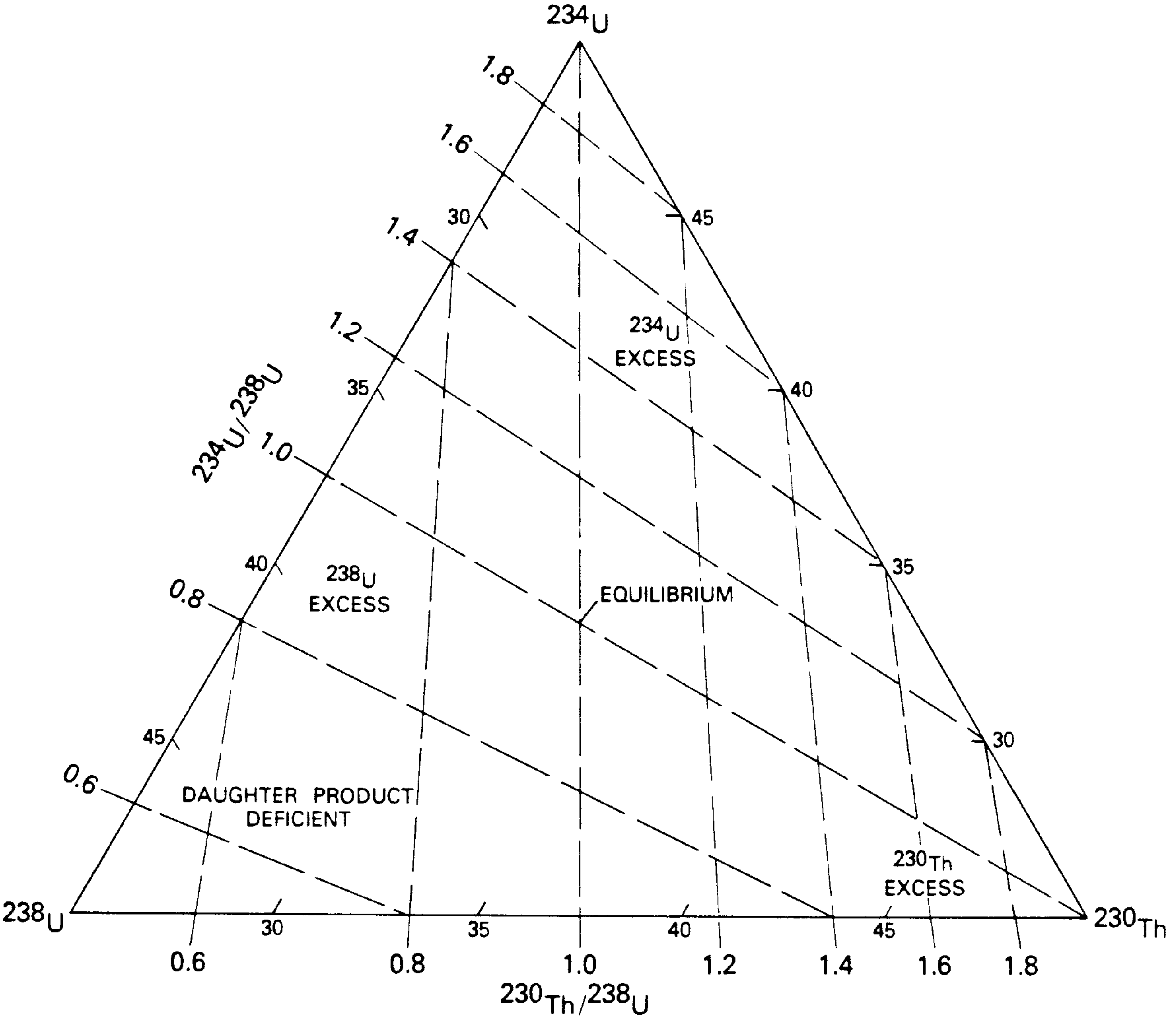

Figure 4. Ternary diagram of percent relative activities of ^{238}U, ^{234}U and ^{230}Th showing selected (dashed) lines of activity ratios of $^{234}U/^{238}U$ and $^{230}Th/^{238}U$, and areas of specific variations in isotopic fractionations.

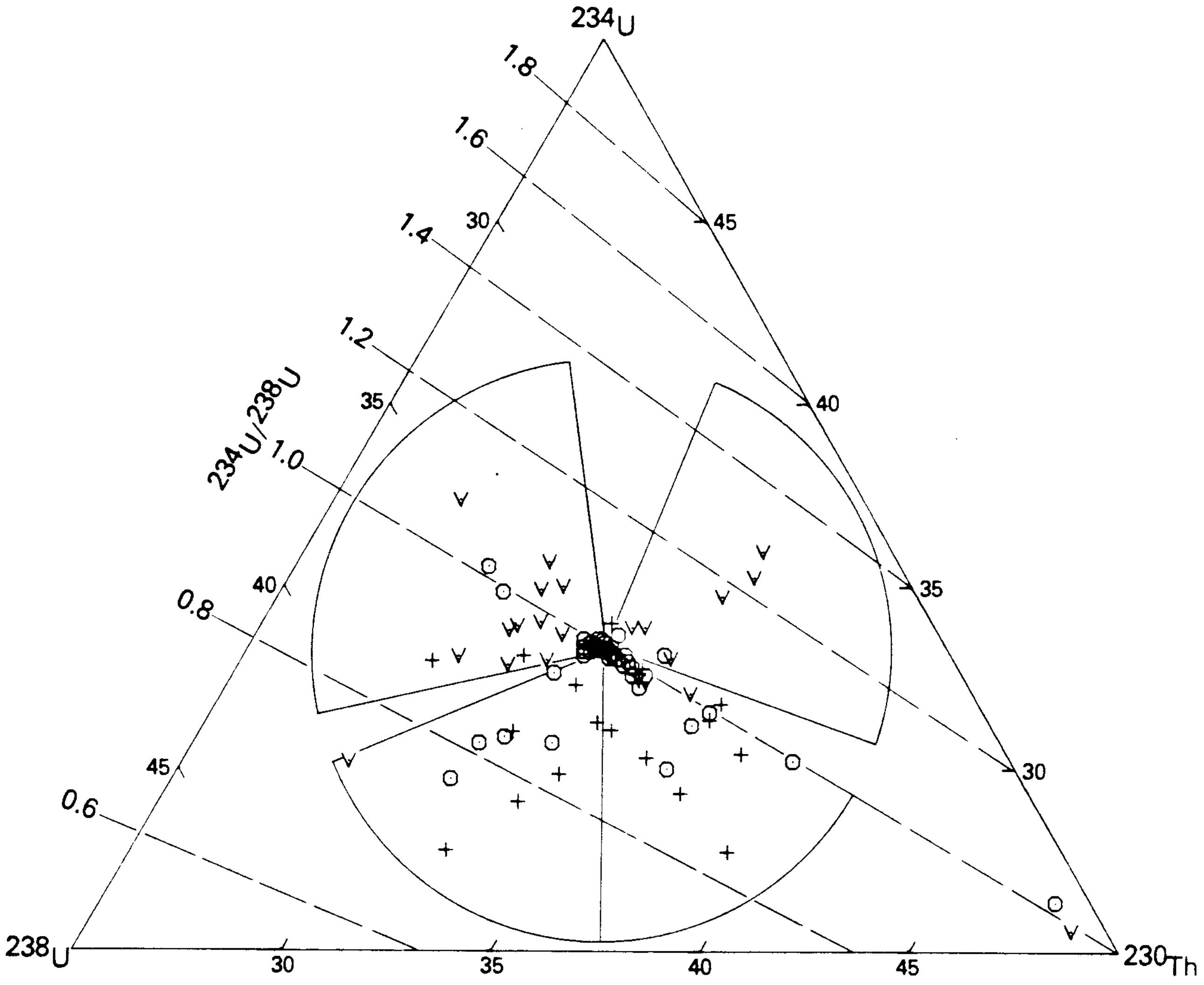

Figure 5. Ternary diagram of relative activities of ^{238}U, ^{234}U, and ^{230}Th in 84 granitic rocks from western United States; "vee" indicates core sample with abundant microfractures, circle indicates unfractured core sample, and plus sign indicates surface or near-surface sample.

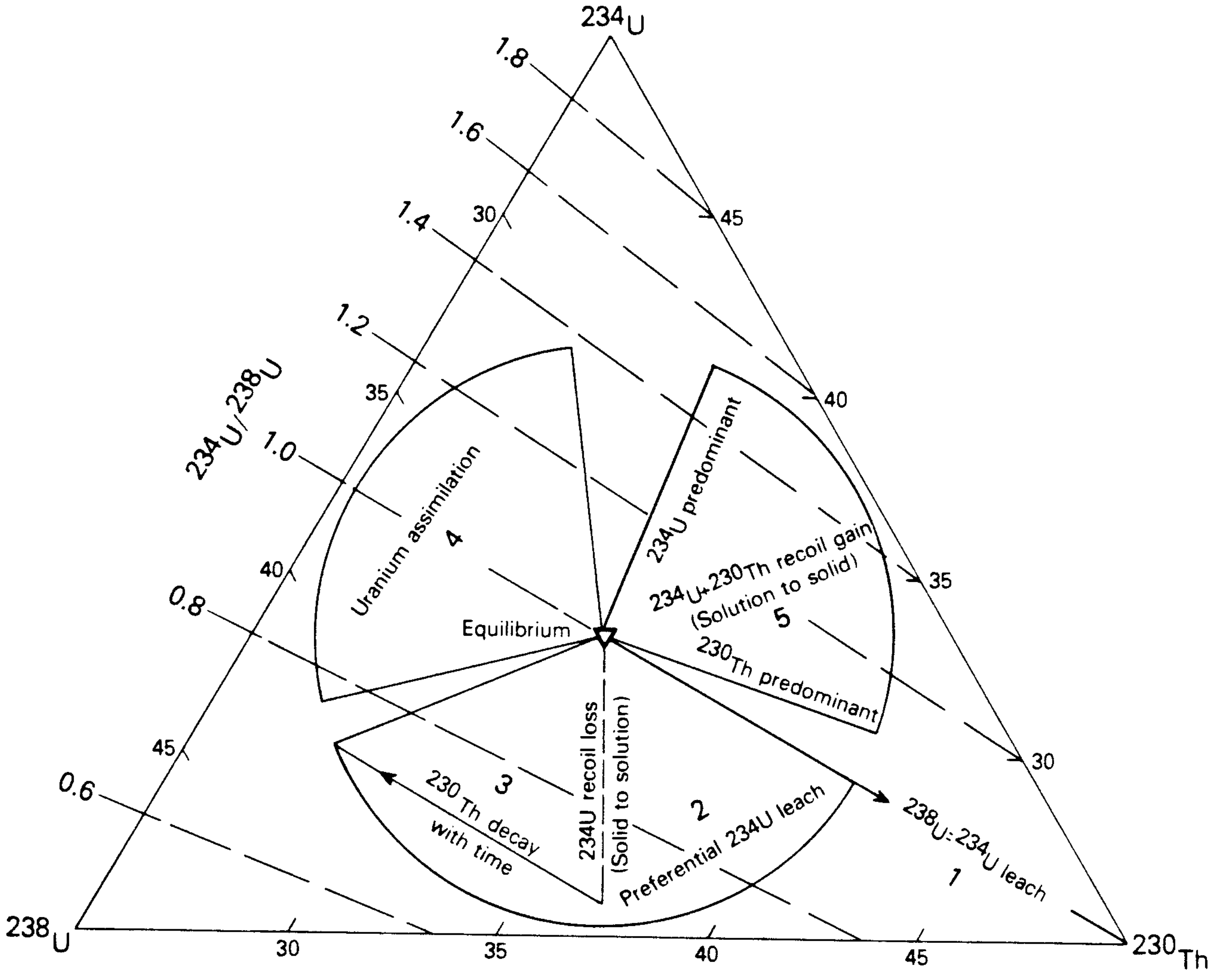

Figure 6. Ternary diagram which includes description of processes (large numerals) that affect the rocks and the areas where sample data plot as a result of these processes. Dashed lines indicate ^{234}U/^{238}U activity ratios.

APPLICATIONS OF U-Th-Pb ISOTOPE SYSTEMATICS TO THE PROBLEMS OF RADIOACTIVE WASTE DISPOSAL

J.S. Stuckless

U.S. Geological Survey, Box 25046, Federal Center, Denver, CO
80226, USA

ABSTRACT

Concentrations of uranium, thorium, and lead, and the isotopic composition of lead for whole-rock samples of granitoids show (1) that open-system behavior is nearly universal in the surface and near-surface environment, and (2) that elemental mobility is possible to depths of several hundred meters. Several identified or at least postulated factors that control uranium and/or lead mobility include (1) the mineralogic sites for uranium and its daughter products, (2) access of ground water to these sites, (3) the volume of circulating water, and (4) the chemistry of the ground water.

Studies of granitic samples from peralkaline complexes in the Arabian Shield have shown that most samples lost less than 20% of their uranium during recent exposure to the near-surface environment. Most of the uranium in these samples appears to be firmly bound in zircons. In contrast, most surface and shallow drillcore samples of the granite of Lankin Dome (Granite Mountains Wyoming) have lost about 70% of their uranium. Most of the uranium in these samples is weakly bound in biotite and epidote-family minerals. The granite recovered during the Illinois Deep Drill Hole Project (Stephenson County, Illinois) is mineralogically similar to the granite of Lankin Dome, but this granite lost radiogenic lead rather than uranium, probably as a result of exposure to ground water that had a markedly different chemistry from that in the Granite Mountains.

Studies of the Sherman Granite (Wyoming) and the Götemar granite (southern Sweden) have shown that uranium and/or lead mobility is greatest in and near fractured rock. The greater mobility is interpreted to be the result of both a larger water to rock ratio in the fractured rock and exposure to water over an increased surface area (and consequently a greater number of uranium sites).

Several types of geochemical and mineralogic data can be used to identify rock-water interaction in granites; however, if rock samples have favorable radiogenic to common lead ratios, both the amount and timing of uranium or lead mobility can be obtai-

ned through the use of isotopic studies. Such information can be extremely important in the search for favorable hosts for containment of radioactive waste. Rocks such as the Götemar granite have undergone considerable rock-water interaction, most of which occurred about 400 m.y. ago and little in recent times. Thus a search for zones that have experienced only a little interaction with water may provide a misleading prediction as to the ability of such zones to shield radioactive wastes from the modern biosphere.

From an isotopic point of view, an ideal candidate for evaluation as a host rock for radioactive wastes would have the following characteristics: (1) a high ratio (>2) of radiogenic to common lead in order to optimize precision of the results, (2) a simple two-stage geologic history so that results could be interpreted without multiple working hypotheses, and (3) an originally high percentage (>50%) of labile uranium so that the results would be highly sensitive to even small amount of rock-water interaction. These characteristics should produce rocks with marked radioactive disequilibrium in surface samples. The disequilibrium should grade to radioactive equilibrium with increasing depth until zones in which water has not circulated are found. Extensive regions of such zones must exist because U-Th-Pb systematics of most analyzed granitoids demonstrate closed-system behavior for almost all of their history except for their recent history in the near-surface environment.

INTRODUCTION

The problem of safe disposal of high-level radioactive wastes differs from most other modern scientific problems in terms of the span of time over which the technological solution must be effective. The tens of thousands to hundreds of thousands of years required for effective isolation of radioactive wastes from the biosphere has caused skeptics to question models and solutions developed from data collected over a period of a few years. Studies of natural analogues can provide valuable data about long-term, natural systems. Such data can be used to test some conclusions of theoretical models. Analogue data, in conjunction with other data may even provide a means of identifying repository sites that can be expected to remain isolated from the biosphere for periods of millions of years.

Early studies of U-Th-Pb systematics in whole-rock samples of crystalline rocks showed the method to be of little value as a geochronologic tool because uranium appeared to have been lost from samples which exhibited no discernible effects of alteration (Rosholt and Bartel, 1969; Moorbath et al., 1969; Manton, 1973; Rosholt et al., 1973). Manton (1973) even suggested that the leaching of uranium from surficial rocks might be a universal phenomenon. Studies of drill-core samples (Oversby, 1975; Stuckless and Nkomo, 1978; Smellie and Stuckless, in press) have shown that uranium mobility may exist to a few hundred meters depth below the surface of the earth. Whole-rock samples recovered from depths in excess of 400 m have been shown to contain equilibrium amounts of uranium and radiogenic lead even though some mineral constituents within the samples exhibit radioactive disequilibrium (Oversby, 1975; Zartman, 1979; Stuckless and Nkomo, 1980).

The abundant U-Th-Pb data that have become available in recent years together with the interpretive capabilities that have been developed suggest that natural-analogue studies can be enhanced by incorporation of U-Th-Pb data, especially in the study of Precambrian Shield areas for which the technique has its greatest sensitivity. This paper presents some of the general theory of applying U-Th-Pb systematics to geologic studies and reviews results obtained during the past 15 years.

THEORETICAL BACKGROUND

This section presents a brief summary of graphical techniques used to present isotopic results in the U-Th-Pb system as well as the underlying principles and assumptions of the technique. Detailed discussions of the mathematics and theory of U-Th-Pb systematics can be found in several published works (e.g. Doe, 1970; Gale and Mussett, 1973; Rosholt et al., 1973; and Stuckless and Nkomo, 1978).

The U-Th-Pb isotopic system differes from other geologically important and useful isotopic systems in that two isotopes of one element (U) decay to two isotopes of another element (Pb), and thus the two radioactive parents (^{235}U and ^{238}U) or the two radiogenic daughters (^{207}Pb and ^{206}Pb, respectively) can be expected to behave identically in response to geologic events. In addition, uranium is almost always associated with thorium, which is generally immobile in the geologic environment (Zielinski et al., 1981), and the radioactive parent (^{232}Th) also decays to a radiogenic lead (^{208}Pb). Therefore, if radioactive disequilibrium is noted between uranium and lead, it is generally possible to assess whether uranium or lead has been mobilized by checking for equilibrium between ^{232}Th and ^{208}Pb. If equilibrium exists within the Th-Pb system, or if the amount of disequilibrium can be estimated quantitatively, the timing of disturbance of the U-Pb system can be calculated with a fair degree of certainty because of the order of magnitude difference in the decay constants for the two isotopes of uranium.

For geologic purposes, the Th-Pb system can be thought of as a simple parent-daughter system even though the stable daughter product is reached only after a series of ten decays. The simple parent daughter relationships are typically shown graphically on an evolution diagram (e.g. Doe, 1970) in which both parent and daughter isotopes are indexed to a non-radiogenic isotope of the daughter element (e.g. ^{204}Pb, Fig. 1). The indexing is used because mass spectrometers record ratios more accurately than absolute amounts, and therefore changes in accumulated radiogenic isotopes relative to an originally present isotope can be measured with great accuracy (typically $\pm$ 0.1% at the 95% confidence level).

The three radiogenic isotopes of lead can occur in geologic materials as a result of two processes in a closed-system: (1) decay of parent isotopes which were incorporated in the material at the time the material formed or (2) as primary or existing lead that was incorporated when the material formed. The latter lead is referred to as "common" or "initial" lead, and the isotopic composition of that lead (e.g. $^{208}Pb/^{204}Pb$) is represented on Figure 1 by the intercept of a line through data points (for samples from a closed system) with the $^{208}Pb/^{204}Pb$ axis. This intercept is also the lead composition for samples that have a Th/Pb value of zero, and therefore contemporaneously formed minerals such as galena (PbS) provide a means of measuring the initial isotopic composition of lead.

Implicit in the interpretation of isotopic data is the assumptions that all analyzed material in a given sample suite had the same isotopic composition at the time the material formed. This means that all samples would have plotted initially along a horizontal line and that samples differed only in their parent-isotope to daughter-isotope ratio (Fig. 1).

In a simple parent-daughter system, one atom of parent decays to one atom of daughter as a function of time, and therefore, each initial data point migrates towards the $^{208}Pb/^{204}Pb$ axis along a pathway for which the slope is -45°. Thus, if the system remains closed, analytical data will form a linear array (called an isochron) the slope of which is proportional to age of the system. Scatter about a line regressed through the data points in excess of that attributable to analytical error indicates open-system behavior (or an initially inhomogeneous isotopic system). If the age of the system is known by independent means, the calculated age can be used to assess open-system behavior. In the Th-Pb system, open-system behavior is generally due to gain or loss of lead.

Data for the two uranogenic-lead isotopes are usually displayed relative to one another by one of two methods. One diagram uses only isotopic compositions and shows ^{206}Pb versus ^{207}Pb with both isotopes indexed to ^{204}Pb (Fig. 2). On this diagram the lead in each sample evolves from a single point (represented by the triangle on Fig. 2) along a curved path (because of the difference in decay constants for ^{235}U and ^{238}U). At any time after formation of a closed system, analytical data for all samples will lie along a straight line for which the slope is proportional to age of the samples. The distance of displacement of data points from the common-lead composition is a function of the U/Pb ratio; however, the ratio which is normally given is μ (which is defined as the present-day $^{238}U/^{204}Pb$ and assumes $^{238}U/^{235}U = 137.88$). Note that the linearity of data plotted on this diagram is uneffected by uranium gain or loss either very early or very late in the history of the system. Early or late lead loss will also have little or no effect on linearity and lead gain will only have a noticeable effect if the composition of the lead gained plots away from the line regressed through the final data array. Maximum scatter due to open-system behavior will result if the disturbance occurs during the time period when the lead growth curves lie farthest from the line of the final data array (which is roughly the middle third of the history of the system).

The other commonly used plot for display of uranogenic lead data is a concordia diagram (Fig. 3). This diagram contains a curve called concordia (Wetherall, 1956). The curve is the locus of equilibrium values for $^{207}Pb/^{235}U$ and $^{206}Pb/^{238}U$ as a function of time. Thus data points for samples from a closed systems will always plot exactly on the curve within the limits of experimental error (i.e. the ages calculated from the ^{235}U - ^{207}Pb and ^{238}U - ^{206}Pb systems are equal or concordant). The solid square on Figure 3 is an example of concordant analyses for a 2,500 m.y. old sample.

Only the radiogenic component of the lead is used for a concordia diagram, and thus the common lead must be subtracted from the analytical data if a concordia treatment is to be used to evaluate isotopic equilibrium. Unfortunately, the intercept of an isochron in either U-Pb system with the ordinate will yield an initial lead composition for closed-systems only, and closed U-Pb systems are geologically rare. Hence, initial-lead compositions must either be measured in minerals with very low U/Pb ratios or calculated from lead-evolution models such as the one proposed by Stacey and Kramers (1975). A method for using this model and the Pb-Pb isochron is described by Stuckless et al., (1981a).

The subtraction of common lead from the total analysis introduces error, the size of which is dependent on how accurately the common-lead composition is known and how large a fraction of the total lead is common lead. These error considerations mean that a concordia treatment of data is useful only if the uranium to lead ratio is large relative to the age of the system. For most granitoids, the U/Pb ratio and age conditions are not favorable for rocks younger than Precambrian.

The great value of a concordia treatment is that it provides simultaneously an age of formation of the system, information as to whether the system has been open one or more times, and, in the event of a single period of open-system behavior, the timing and amount of isotope movement. These types of information are shown schematically on Figure 3 for a 2,500 m.y. system. If the system remained closed from 2,500 m.y. until 1 m.y. ago and then gained or lost uranium or uranoenic lead, data points will plot on a line that extends from the 1 m.y. concordant point through the 2,500 m.y. concordant point. Examples of points in the same age system are shown for a 50% lead-loss (star below concordia) and a 50% uranium-loss (circle above concordia). Gains of uranium or lead produce opposite senses of movement (relative to concordia) as losses.

Multiple periods of open-system behavior will not generally produce linear arrays on a concordia diagram. If the 2,500 m.y. system is first open at 1,200 m.y., data points would form a linear array along the light line on Figure 3. A second period of open system behavior could then produce data points that might plot almost anywhere to the right of the dotted line on Figure 3. Thus only an exact proportionally among samples (such as 20% uranium loss for all samples) in all but the last period of open-system behavior will produce a linear array for a system that experienced multiple periods of element mobility.

MOBILITY OF URANIUM AND LEAD

Isotopic studies, in conjunction with other geologic techniques, have identified several factors that control uranium and uranium-daughter-product mobility in granitic whole-rock systems. Controlling factors that can be documented with some certainty include: (1) the physical sites of uranium, thorium, and their decay products, (2) the access of circulating fluids to these sites, and (3) the chemistry of the circulating fluids. By inference, the total volume of circulating fluids must also be important. Other factors that may exert some control on the behavior of whole-rock systems in the near-surface environment are mineralogy, rock alteration by hydrothermal solutions, and metamictimization of radio-element-bearing silicates.

The original locations of uranium and thorium (and consequently their radiogenic daughter products) exerts a major control on the degree of uranium and/or lead mobility that can develop in response to circulation of fluids in the near-surface environment. The late Precambrian peralkaline granites of the Arabian Shield are generally enriched in uranium by a factor of two relative to an average granite, and although most analyzed samples have lost uranium relative to radiogenic lead, the amount of uranium loss in the near-surface environment is generally less than

20% (Fig. 4) and averages about 10% (Stuckless and others, 1984). Most of the uranium in these rocks is located in zircon, and studies of both experimental and natural systems have shown that both uranium and thorium are very firmly fixed in this mineral (Silver et al., 1982). The zirconium saturation limit (i.e. the concentration above which zirconium must precipitate in a solidus phase) is higher in peralkaline magma than any other type of crystalline rocks (Watson, 1979), and consequently zircon is an abundant and late-crystallizing mineral in this family of rocks. Therefore, low degrees of uranium or lead mobility, as observed in the Arabian granites, is probably a general case for peralkaline rock, and a waste repository chosen in zircon-rich rocks would be difficult to test by use of a natural-analogue analysis.

Surface and shallow drill-core (<30 m) samples of the granite of Lankin Dome (Granite Mountains, Wyoming) have lost approximately 70% of their uranium (Fig. 5) as a result of exposure to the near-surface environment following early Tertiary uplift and erosion (Stuckless and Nkomo, 1978). Analysis of minerals separated from uranium-depleted whole-rock samples shows an excess of radiogenic lead in biotite and epidote-family minerals (Fig. 6). Analysis of these minerals separated from a non-depleted drill-core sample (recovered from a depth of 472 m) shows that epidote and biotite contain more than 60% of the total uranium and thorium in the whole-rock sample which is nearly twice the percentage noted for the uranium-depleted sample. Thus these minerals and their micro-inclusions of uraniferous phases appear to control much of the radioactive disequilibrium noted for the granite of Lankin Dome. However, even though the deep whole-rock sample contains near-equilibrium amounts of uranium and radiogenic lead, biotite and epidote lost much of their radiogenic lead during the Tertiary (Fig. 6), and thus other minerals must have gained lead.

Ludwig and Silver (1977) noted that many potassium-feldspars separated from Precambrian rocks contained unsupported radiogenic lead (i.e. no parent isotope in the mineral) and that the composition of the unsupported lead was compatible with the age of the host rock. Therefore the lead must have been gained very late in the history of the feldspar. Thus, like the uranium loss noted for so many different whole-rock samples, lead gain by potassium feldspar seems to occur when the rocks are exposed to the near-surface environment. Lead gain by potassium feldspars may account for apparent closed-system behavior of lead in many granites. In the Granite Mountains, the Th-Pb system is closed, and the U-Pb system is open on a whole-rock scale for samples that contain potassium feldspar (Stuckless and Nkomo, 1978), but rocks that lack potassium feldspar exhibit open-system behavior in both the Th-Pb and U-Pb systems (Stuckless et al., 1981a).

The control of ground-water chemistry in the mobility of uranium and lead in granitic rocks can be demonstrated, although quantitative data that can be compared directly with isotopic results are lacking. Granite recovered during the Illinois deep drill hole project (Stevenson County) is mineralogically similar to the granite of Lankin Dome, and has similar radioelement sites, but neither the Th-Pb (Fig. 7a) nor U-Pb (Fig. 7b) is closed at depths less than about 1000 m below the current surface (Doe et al., 1983). The degree of open-system behavior in both parent-daughter systems can be explained by approximately equal amounts of lead mobility. The concordia treatment indicates that open-system behavior occurred about 260 m.y. ago (Fig. 7b) but the isotopic composition of potassium feldspars shows no apparent gain of radiogenic lead (the data for feldspars plot at the intercept of the Th-Pb isochron (Fig. 7a) rather than above it. Thus, all data indicate that lead rather than uranium was lost from the system. Doe et al. (1983) postulated that the difference in element mobility was due to circulation of chloride brine through the Illinois granite as opposed to the more typical circulating fluid of oxidizing meteoric water.

Studies of the Götemar granite (southeastern Sweden) also show a preferential loss of radiogenic lead but in this case petrologic data suggest the loss was in response to hydrothermal alteration. Investigations of the granite of Lawler Peak (west-central Arizona) demonstrate two episodes of uranium and lead mobilization in response to circulating hydrothermal solutions (Silver et al., 1982). The compositions of hydrothermal solutions were not specified in either of the above studies, but two different compositions must be inferred for the granite of Lawler Peak because some minerals responded to an alteration at 228 m.y. ago and others responded to an alteration at 76 m.y. ago.

Different types of hydrothermal alteration also seem to have an effect on the response to the near-surface environment at some time after the hydrothermal event. Both the granite of Lawler Peak and the Götemar granite crystallized with three to five times the amounts of uranium typically found in granites. Samples of the granite of Lawler Peak show a recent loss of uranium that varies from 25% to more than 80%, and Silver et al. (1982) attribute these losses to preparation of the rock by hydrothermal alteration. In contrast, even shallow samples (<50 m depth) of the Götemar granite show only minor mobilization of uranium in response to exposure to the modern near-surface environment; this suggests that uranium may have been more firmly fixed by hydrothermal alteration.

The effects of metamorphism on the mobility of uranium and lead in crystalline rock and the subsequent mobility of these elements in response to exposure to the near-surface environment are more predictable than the effects of hydrothermal alteration. Several studies have shown that uranium is lost from rocks as a result of high-grade metamorphism (Lambert and Heier, 1968; Moorbath et al., 1969; Gray and Oversby, 1972; Dostal and Capedri, 1978; Montgomery, 1979). Although some of these studies also document some mobility of uranium from metamorphosed rocks as a result of near-surface processes, the amounts are generally small and difficult to measure accurately. In addition, metamorphism causes a three-stage history such that results are no longer linear on a concordia plot which further complicates interpretation of the data.

The mobility of uranium and lead within granitoids is strongly controlled by circulating fluids. This statement is based on the fact that many lead-isotope studies have shown that uranium and its daughter products have remained fixed within the volume of a relatively small whole-rock sample (1 to 10 kg) for periods of hundreds of millions of years and that whole-rock radioactive equilibrium was disturbed only during the geologically brief period of exposure to the near-surface environment (Manton, 1973; Oversby, 1975; Doe and Delevaux, 1980; Stuckless et al., 1981b; Zielinski et al., 1981; Silver et al., 1982). Other studies have demonstrated that data are compatible with discrete periods of radioactive disequilibrium in response to known geologic events (Moorbath et al., 1969; Gale and Mussett, 1973; Stuckless and Nkomo, 1980; Montgomery, 1979; Doe et al., 1983; Stuckless and Troeng, 1984). In all of the above studies, the agent that appears to have disturbed equilibrium was circulating fluids. In some, if not all cases, the circulating fluid communicated with the biosphere and deposited uranium in mineable quantities (Rosholt et al., 1973; Stuckless et al., 1981b).

Few published data exist on highly sheared and permeable rock because the expected open-system behavior would interfere with the objective of most isotopic studies; however data reported by Stuckless and Nkomo (1978) do show such rocks to be very susceptible to migration of uranium and lead. Other studies show that several elements in addition to uranium and lead are easily mobilized in fracture zones (Zielinski et al., 1981; Smellie and Stuckless, in press). Such results are predictable because shearing greatly increases the mineral surface area (and therefore uraniferous sites) that are in contact with circulating fluids. In addition, fracturing drastically increases permebility of crystalline rocks and thereby permits a large volume of water to come into contact with uranium sites.

A last variable with probable effect on open-system behavior is the presence of metamict (internal crystal structure destroyed by radiation damage) silicates. Metamict zircon is extremely easy to dissolve relative to non-metamict zircon (Krogh, 1975). A similar relationship presumably exists for other silicate minerals that become metamict, and thus rocks for which uranium is sited in metamict minerals may develop open-system behavior more readily.

SUMMARY

The study of U-Th-Pb systematics can add valuable data to the investigations of proposed repositories for high-level radioactive wastes. Although the technique is not well suited to the study of all natural materials, recent studies of granitic rocks show that the technique can, in favorable circumstances, be used to identify isopically undisturbed zones within the earth´s crust that have remained isolated from circulating fluids (and therefore the biosphere) for the last several hundred million years. Unless other data suggest that a change in geologic conditions is possible during the next million years, such undisturbed zones should be excellent candidates for repository sites.

Zones of isotopic equilibrium can be identified with the greatest level of confidence when favorable circumstances optimize the precision of analytical results. Interpretation of very recent open-system behavior requires correction for a common-lead component which introduces uncertainty. The amount of uncertainty introduced is minimized by a high radiogenic to common lead ratio and increase accuracy in the values used for the isotopic composition of common lead. The ratio of radiogenic to common lead is optimized by the passage of time and an initially high uranium to lead ratio. These features are most common in Precambrian granites. If such rocks contain a mineral that crystallized with a high percentage of lead, the common lead composition can be obtained with great accuracy, and error introduced in the calculation of radiogenic lead is small.

Disturbance of the natural U-Th-Pb system is most readily recognized for rocks that contain a large amount of labile uranium. Measureable radioactive disequilibrium in such rocks can apparently be caused by very small amounts of circulating fluid. Quantitative recognition criteria for such rocks have not been established, but high-thorium granites (>30 ppm) that contain epidote-family minerals and biotite (Stuckless and Nkomo, 1978; 1980) are possible candidates. Conversely, rocks with a high zirconium content (>500 ppm) such as the peralkaline suites, are probably poor candidates.

A complex geologic history following formation of the rocks results in non-linear patterns for the various isotopic systems measured in U-Th-Pb studies, and consequent ambiguities in interpretation. High-grade metamorphism removes much labile uranium from rocks, and thus in addition to introducing ambiguities to interpretations of the results, sensitivity to recent rock-water interaction is decreased. The least equivocal results can be expected for anorogenic granites that have not been subjected to post-intrusive disturbances. However, even results that require multiple, working hypotheses can be useful if combined with results from other types of studies.

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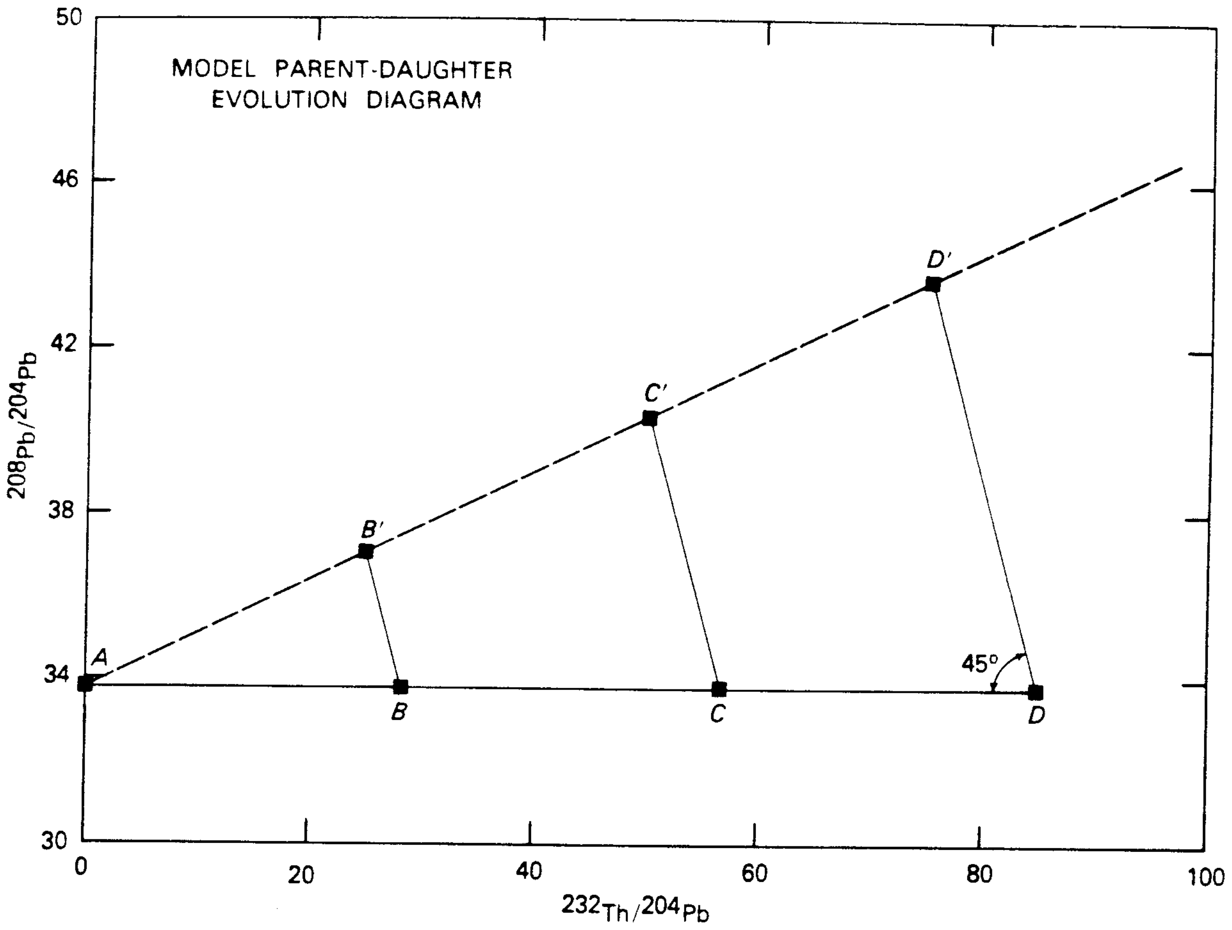

Figure 1. Parent-daughter evolution diagram for the Th-Pb system. The horizontal solid line shows four hypothetical samples (A through D) as they would plot if analyzed when the system first formed. The position of the data points along an isochron (dashed line) is shown assuming evolution is a closed system for 2,500 m.y. Note that the isotopic composition for sample A (a sample with no thorium) is unchanged during the 2,500 m.y. history. Growth lines (light solid lines) that connect original and current compositions for each sample have an actual slope of -45°, but appear to be steeper because of unequal scales used on the two axes.

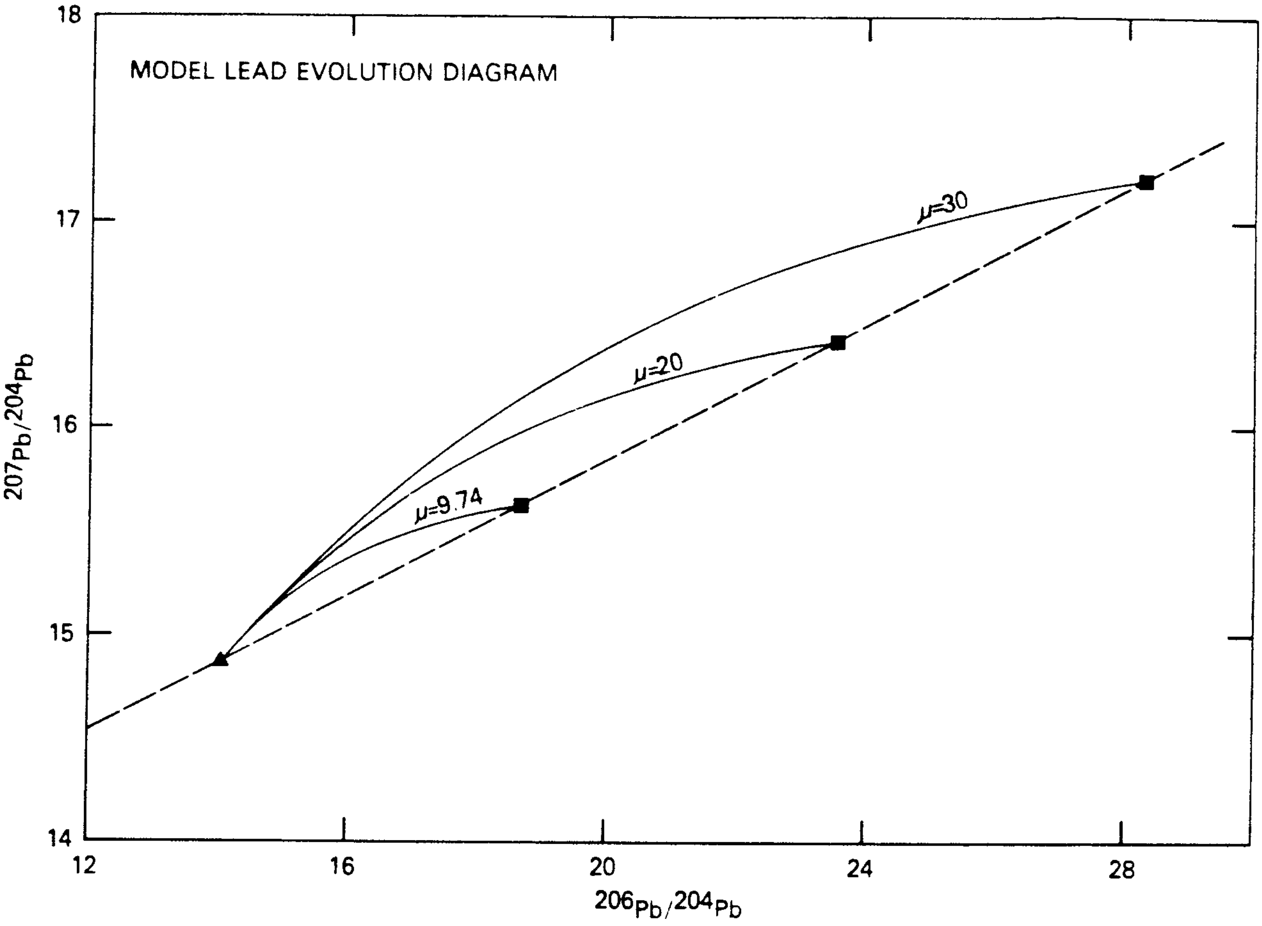

Figure 2. Lead-lead evolution diagram for a system that formed 2,500 m.y. ago and remained closed to the present. All samples started with a common lead composition of $^{206}Pb/^{204}Pb$ = 14.087 and $^{207}Pb/^{204}Pb$ = 14.870 represented by the triangle. Samples then evolved along different growth curves the position of which is dependent upon the $^{238}U/^{204}Pb$ ratio for each sample. The dashed line is an isochron from which an age for the system can be calculated. However, note that if all uranium were removed from each sample at some time during evolution of the system, the samples would still form a linear array, but the slope of this line would be dependent on both the age of the system and the time of uranium loss.

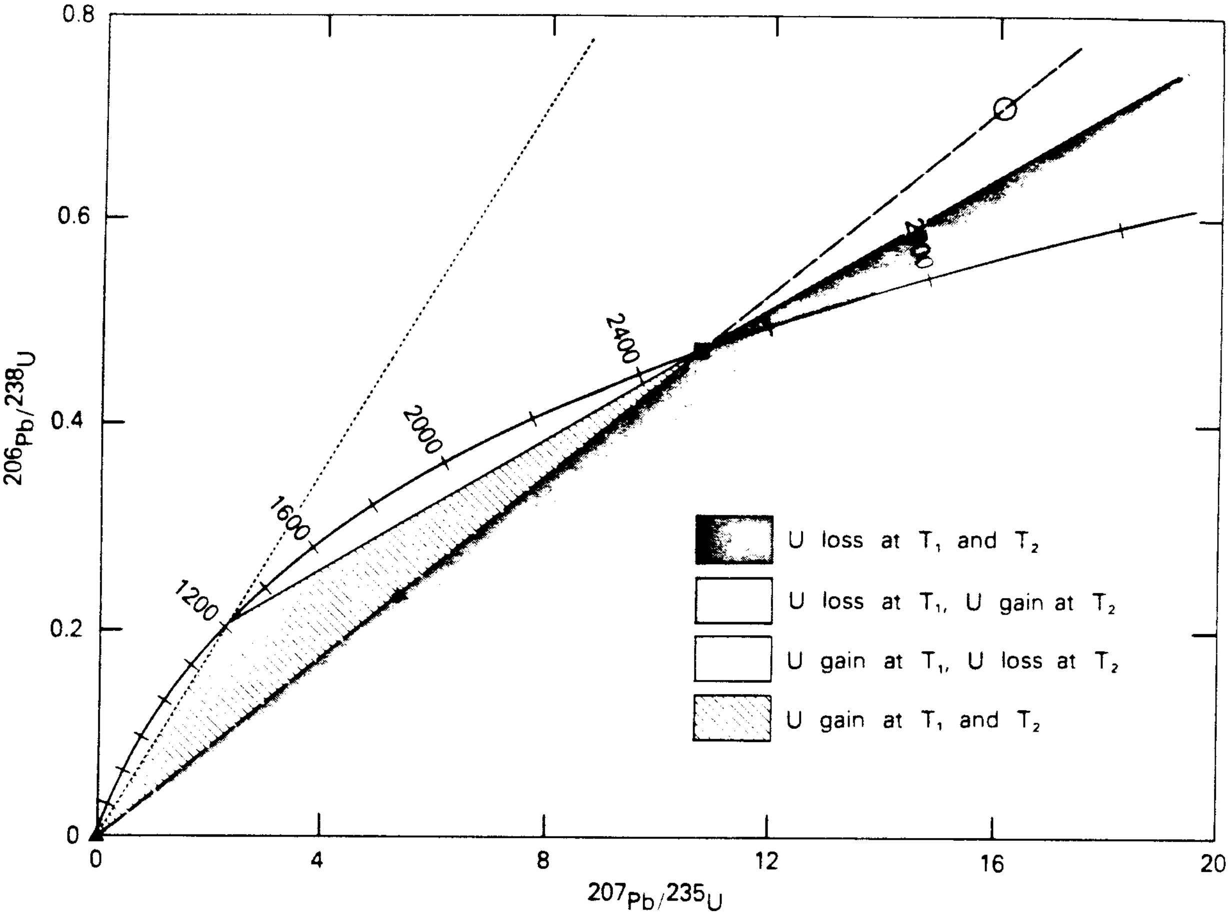

Figure 3. Concordia diagram for a hypothetical system that formed 2,500 m.y. ago and remained closed until 1 m.y. ago. Had the system remained closed through to the present, all samples would plot at the point shown by the solid square. A complete loss of radiogenic lead 1 m.y. ago would cause data to plot at the point shown by the triangle. Data with a 50% lead loss or 100% uranium gain would plot at a point shown by the star. Data with a 50% uranium loss would plot at a point shown by the circle. The position for data points that represent lead gain can not be predicted unless the isotopic composition of the lead gained is known. For lead gained from elsewhere in the same system, the effect on displacement of data points is the same as uranium loss. The light line shows the possible locus of data points as a result of uranium and/or lead mobility at 1,200 m.y. ago followed by closed-system behavior through the present. The dotted line shows that left-most limit of data points for samples that formed 2,500 m.y. ago, were open at 1,200 m.y. ago, and were open again 1 m.y. ago, because points on the dotted line would have lost all radiogenic lead at 1,200 m.y. ago. A complete loss of uranium at 1,200 m.y. ago and subsequent open-system behavior at 1 m.y. ago would form a data arry between 0 and infinite value on the light solid line. Thus a two-stage system tends to create considerable scatter on a concordia diagram.

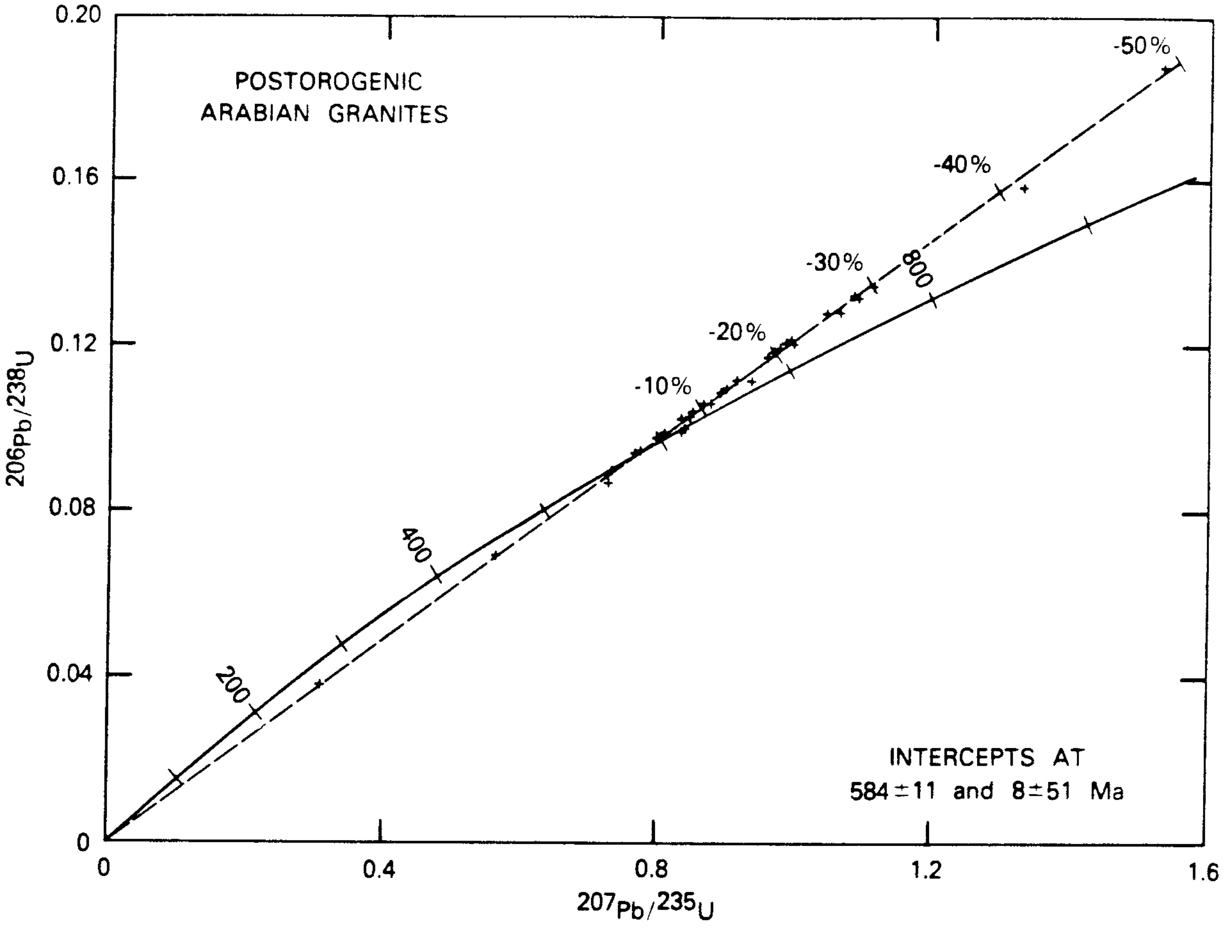

Figure 4. Concordia diagram for samples of the Late Precambrian, postorogenic granites of the Arabian Shield (Stuckless and others, 1984). Scatter about the isochron represents the real variation in age of the plutons of 570 to 628 m.y.; however, the errors for individual data points, are actually very large (~20%) due to the loss percentage of radiogenic lead and poorly known composition of common lead. For purposes of illustrating uranium mobility, ideal common-lead compositions have been calculated for each sample. The regressed line through the data points is marked with relative percentages of uranium loss assuming closed system behavior from 584 to 8 m.y. ago.

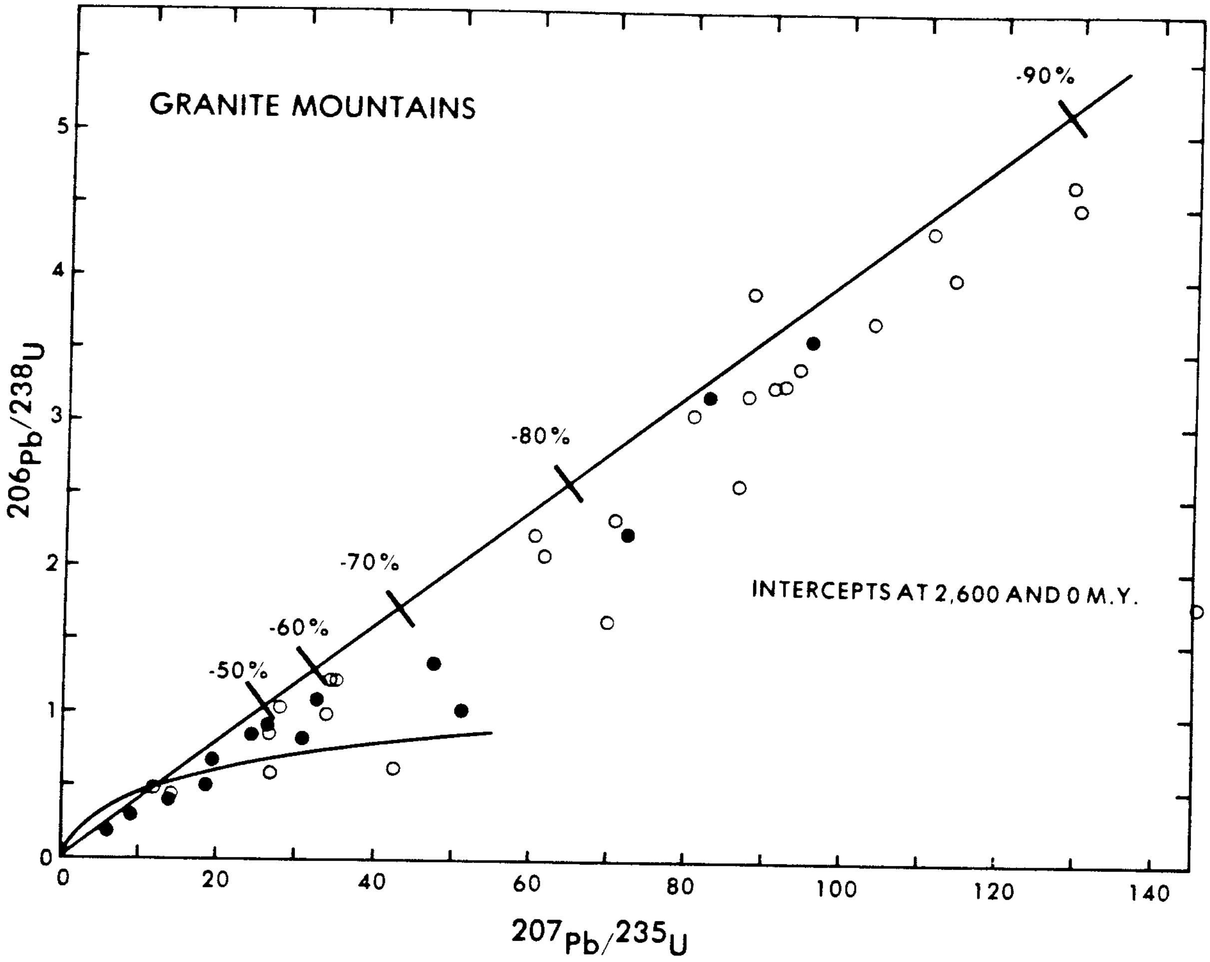

Figure 5. Concordia diagram for samples of the granite of Lankin Dome, Granite Mountains, Wyoming (data from Rosholt et al., 1973 and Stuckless and Nkomo, 1978). Circles represent samples from less than 30 m depth and dots represent samples from greater than 30 m depth. A reference cord from 0 through the 2,600 m.y. equilibrium point on concordia is marked with relative percentages of uranium loss assuming closed system behavior from 2,600 m.y. ago until 30 m.y. ago. Scatter about the line is due to an average uranium loss of 20% about 1,700 m.y. ago (Stuckless and Nkomo, 1978). The combined Proterozoic and recent uranium losses have left most surface and shallow drill-core samples with an apparent loss of greater than 80%. For most of these samples the recent uranium loss averages about 70%.

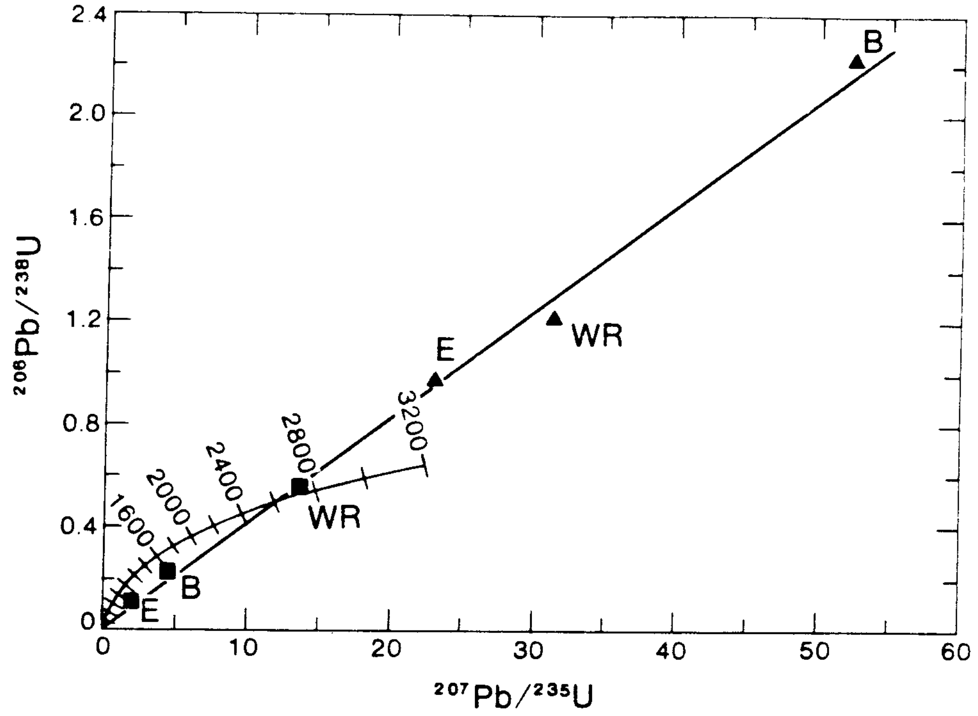

Figure 6. Concordia plot for whole-rock samples (WR), biotite separates (B), and epidote separates (E) from Stuckless and Nkomo (1980). Triangles represent data for a surface sample that has lost about 60% of its uranium, and squares represent a drill-core sample from 469 to 475 m depth that has had no recent uranium loss within the limits of experimental error. Apparent uranium loss for epidote and biotite from the surface sample are probably much greater than indicated in this plot because both minerals have also lost a large amount of radiogenic lead relative to current thorium contents.

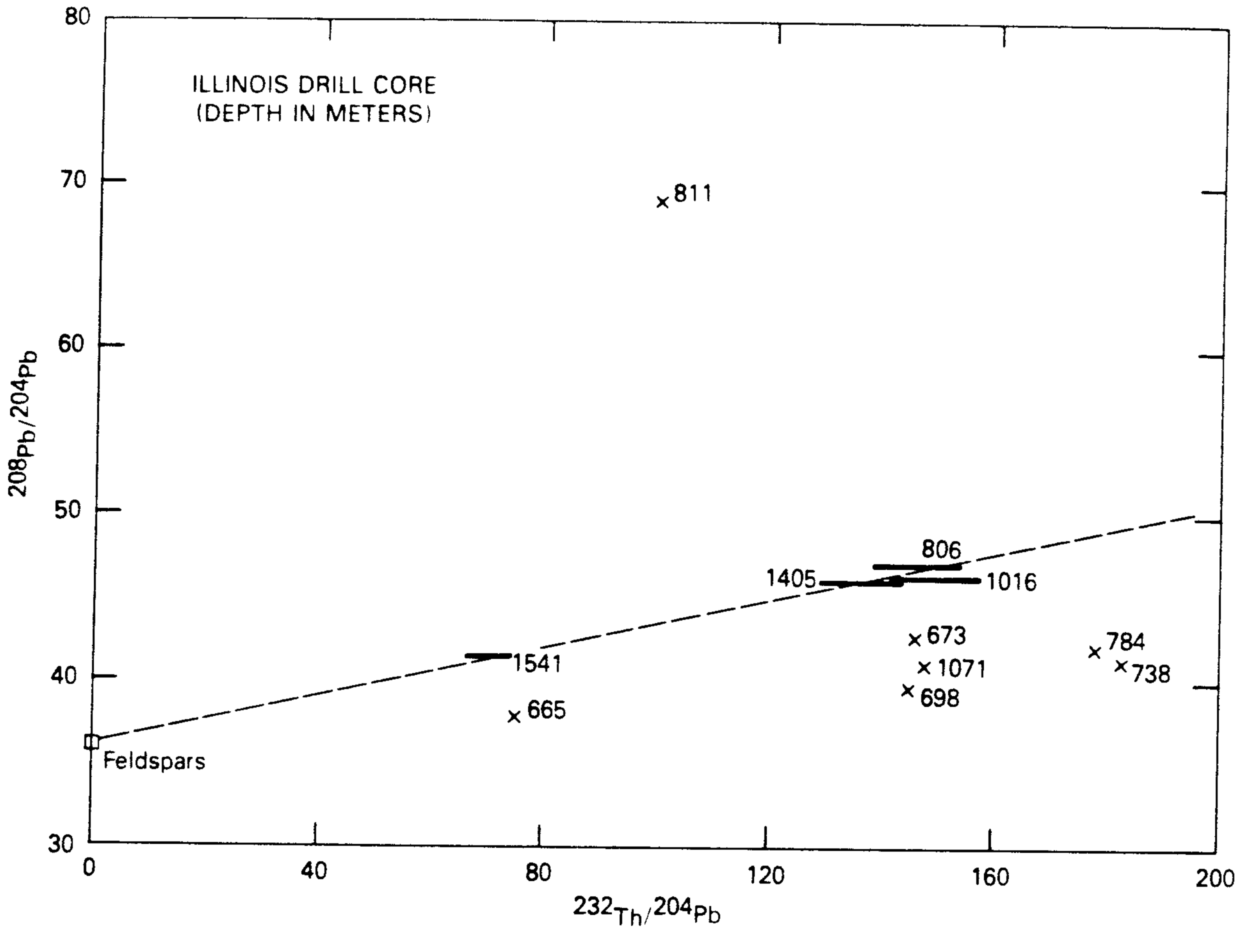

Figure 7a. Th-Pb evolution plot for granite samples recovered during the Illinois deep drilling project (after Doe et al., 1983). Samples are marked by depth (in meters) from the current surface. Samples used for regression of isochrons are shown by symbols that are proportional to analytical error at the 95% confidence level. Analyses of feldspars all plot within the square on the $^{208}Pb/^{204}Pb$ axis and are not distinguishable from the intercept of the isochron. Had the feldspars gained radiogenic lead at the time of system disturbance (261 m.y. ago), data points would plot on the $^{208}Pb/^{204}Pb$ axis, but above the isochron intercept. Most discordant data points plot below the Th-Pb isochron and below the concordia curve (see Figure 7b) which indicates that open-system behavior was largely due to loss of radiogenic lead at 261 m.y. ago.

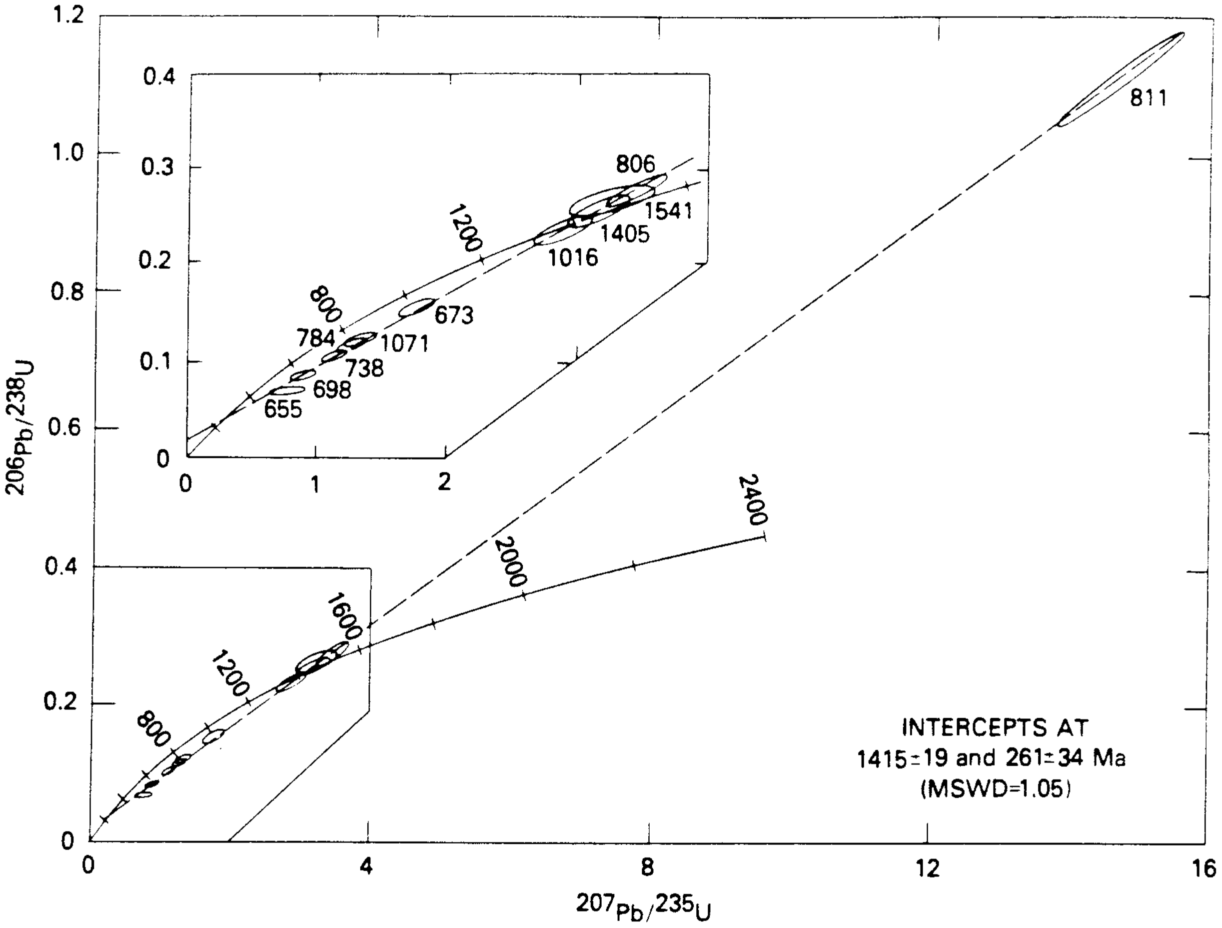

Figure 7b. Concordia plot for granite samples recovered during the Illinois deep drilling project (after Doe et al., 1983). Variation in the size of error elypses on the concordia plot results from different percentages of common lead and error magnification of uncertainty in the common-lead composition.

SESSION C

MORRO DO FERRO ANALOGUE

Chairman: Peter L. Airey

NATURAL ANALOGUES FOR THE TRANSURANIC ACTINIDE ELEMENTS: AN INVESTIGATION IN MINAS GERAIS, BRAZIL

M. Eisenbud[1], K. Krauskopf[2], E. Penna Franca[3], W. Lei, R. Ballad, P. Linsalata[4] and K. Fujimori[5]

[1] Department of Environmental Medicine, New York University Medical Center, Long Meadow Road, Tuxedo, New York 10987, USA
[2] Stanford University, Stanford, California 94305, USA
[3] Federal University of Rio de Janeiro, Rio de Janeiro, Brazil
[4] Department of Environmental Medicine, New York University Medical Center, Long Meadow Road, Tuxedo, New York 10987, USA
[5] University of Sao Paulo, Sao Paulo, Brazil

ABSTRACT

A highly weathered deposit of thorium and rare earth elements located near the summit of a hill in the state of Minas Gerais, Brazil, is being studied as an analogue for a radioactive waste repository that sometime in the distant future may be eroded to the surface or intruded by groundwater. Thorium serves as an analogue for Pu^{4+}, and La^{3+} as an analogue for Cm^{3+} and Am^{3+}. The mobilization rate constants of the analogue elements by groundwater are so slow (of the order of 10^{-9} per year) as to suggest that essentially complete radioactive decay of the transuranic actinides would occur in place even under the relatively unfavorable conditions that exist at a site such as this.

This paper, presented to the Workshop by M. Eisenbud, is already published in: Environ. Geol. Water Sci. Vol. 6, No. 1, 1-9, 1984.

INTRODUCTION

Because the transuranic actinide elements do not occur naturally in appreciable quantities, their behavior in a repository environment cannot be predicted from evidence of their movement in groundwater in the geologic past. Predictions about their long-time future behavior have therefore been made by extrapolation from short-time observations of their chemical properties in experiments conducted in the laboratory or in the field, and such extrapolation is fraught with uncertainty. A useful means of reducing the uncertainty is to observe the behavior, both past and present, of naturally-occurring elements with similar properties. Elements often suggested as naturally-occurring analogs include the rare-earth metals as analogs for the trivalent actinides and thorium as an analog for actinides in their quadrivalent form.

LANTHANIDE ELEMENTS AS ANALOGS FOR TRIVALENT ACTINIDES

For americium and curium, which in repository environments would exist only in their trivalent states, the analogy with rare-earth elements is particularly convincing. The light lanthanides (La - Sm) have ionic radii very close to those of americium and curium (Table 1), and solubilities of expected compounds are correspondingly similar. Scanty data on sorption and complex formation also show marked resemblances. For example, field and laboratory experiments reported by Weimer et al. (1980) show values of K_d for Nd nearly identical to those for Am and Cm over a wide range of pH and contact times; furthermore, concentration factors for all three elements in plants grown in laboratory experiments were very similar. There seems little question that much may be learned about the behavior of trivalent actinides from laboratory and field observations of the rare-earth elements. Thus the demonstrated very slight mobility of lanthanum at Morro do Ferro (Eisenbud et al. 1984) is good evidence that americium and curium will not escape in hazardous amounts from a breached water repository.

CHEMICAL RELATIONS OF THORIUM AND PLUTONIUM

The suitability of thorium as an analog for quadrivalent actinides is much less clear, because the heavier actinides that have stable quadrivalent states may also exist in other valence states that thorium can never assume. How good the analogy is for a particular actinide element depends on the stability of its quadrivalent compounds and complexes relative to the stability of other oxidation states, under the conditions of pH and redox potentials to be expected in the groundwater that may invade a waste repository and dissolve some of its constituents. The use of thorium as an analog for plutonium has often been suggested, and it is the principal purpose of this paper to look critically at the theoretical and experimental evidence bearing on the validity of this analogy.

The qualitative chemistry of the two elements in the quadrivalent state is closely similar. For both, the stable solid under a wide range of Eh and pH is the dioxide. The crystalline solids ThO_2 and PuO_2 are extremely insoluble, but finely divided and amorphous varieties may have solubilities several orders of magnitude higher than well-formed crystals. For both elements a series of hydroxy complexes from $MeOH^{3+}$ to $Me(OH)_5^-$ has been reported, and for both the uncharged complex $Me(OH)_4^0$ is the principal species in equilibrium with the dioxide in neutral and slightly alkaline solutions. Poly-nuclear hydroxy complexes are known but do not contribute importantly to solubilities under repository conditions. Both elements form complexes with most of the common anions in natural waters.

A comparison of solubility products and formation constants from the recent literature is given in Table 2; unfortunately data are poor for the carbonate complexes, which are the ones most likely to influence solubility in and near a repository. Because the ionic radius of Pu^{4+} is smaller than that of Th^{4+} (Table 1), plutonium compounds would be expected in general to be somewhat less soluble, and plutonium complexes somewhat more stable, than those of thorium. The expected difference is apparent in the solubilities of the dioxides and in the stabilities of the hydroxy complexes shown in Table 2, but stabilities of most other complexes show values more nearly alike than the empirical rule would suggest.

SOLUBILITY OF PUO_2

The outstanding difference between the two elements is the ability of plutonium to assume several oxidation states (+3, +4, +5, +6) whereas thorium is limited to the single value +4. Redox potentials for transitions between the oxidation states of plutonium are remarkably similar, which means, as Cleveland (1979) has pointed out, that different valence states can exist together in appreciable amounts in the same solution over considerable ranges of pH and Eh. The dissolved species that predominates in a given solution at equilibrium with solid PuO_2 depends on the Eh and pH and on the stability of the complexes formed by the element in its various oxidation states with the anions present. To show that thorium is a valid analog for plutonium requires a demonstration that the complexes of plutonium in oxidation states other than +4 are not stable enough to greatly influence solubility over the expectable Eh and pH ranges in a repository environment.

The solubility of PuO_2 as influenced by the acidity and redox potential of groundwater is conveniently displayed on a conventional Eh-pH diagram (Figure 1). The diagram is constructed from the free-energy data given in Table 3, which are in part taken from a compilation in Duda et al. (1982) and in part calculated from stability constants listed in Allard (1983). Uncertainties in the free-energy values are not given by Duda et al.; uncertainties reported for the stability constants would translate into uncertainties on the order of 1 kcal in the free energies, and overall uncertainties may well be somewhat higher. Parentheses indicate values that seem particularly questionable.

To interpret the diagram, consider first the heavy solid lines. Several of these lines enclose a large area in the middle of the diagram, marked PuO_2^s, within which the solubility of crystalline PuO_2 is less than 10^{-12} M (less than 2 x 10^{-4} ppb). On the left-hand side of the PuO_2 area the chief species in solution is Pu^{3+}, on the right side $Pu(OH)_5^-$, and at the top of the diagram PuO_2^+ and two hydroxy complexes of PuO_2^{2+}. Within the enclosed area the solubility is ultimately limited by the equilibrium concentration of undissociated $Pu(OH)_4^o$, 10^{-17} M. The total concentration of dissolved plutonium increases in all directions outward from the central area, as indicated by the heavy dashed lines drawn through points where the concentration is 10^{-9} M (ca 0.2 ppb). Heavy solid lines elsewhere in the figure separate fields of dominance of various dissolved species. The diagram shows clearly that in a solution without complexing agents other than OH^-, the concentration of dissolved plutonium in equilibrium with PuO_2 is very low over a wide range of pH and Eh, lower than the maximum permissible concentration (MPC) in drinking water (0.08 ppb = $10^{-9.5}$ M). Only under extremely oxidizing conditions (where Pu would assume one of its higher valences), or under reducing conditions at low pH (where the trivalent ion Pu^{3+} is stable), would the concentration become appreciable.

The solubility can be higher if a complexing agent is present. Of the possible agents, the one most likely to be present in substantial quantity under natural conditions is carbonate. For the carbonate complexes of quadrivalent plutonium, reliable stability constants are unfortunately not available. Such complexes might increase the solubility considerably, especially in the high-pH part of the diagram, but would not invalidate the thorium analogy because the corresponding thorium complexes would be expected to have similar stabilities. The most likely carbonate complexes of plutonium in other valences are $PuCO_3^+$ and $PuO_2CO_3OH^-$, and the possible effects of these two, with an assumed carbonate concentration near the maximum reported in deep groundwaters (0.01 M), are shown by light lines on the diagram. Again the solid lines represent total dissolved concentrations of 10^{-12} M, and the dashed lines 10^{-9} M. The stability fields of the oxidized and reduced forms of plutonium have obviously expanded, although the expansion due to $PuCO_3^+$ is very slight. A large part of the central PuO_2^s field still shows very low solubilities, and it is in this part of the field that Eh-pH conditions in the groundwater of most explored candidate sites for repositories in crystalline rocks are located.

For example, measurements of Eh and pH in deep groundwaters in Sweden, probably the best of such measurements yet obtained, are all included in the triangle on Figure 1 (Wikberg et al., 1983). Another example is provided by a compilation of analyses of groundwater from basalt underlying the Hanford reservation in Washington (Draft Site Characterization Report, 1982): these cannot be displayed easily on the diagram because they are given as summaries of many analyses, but the extreme ranges (pH 7.6 to 10.6, Eh -0.22 to +0.21 volt, alkalinity as HCO_3^- 70 to 298 ppm or about 10^{-3} to $10^{-2.4}$ M) fit within the PuO^s_2 field except for a slight overlap on the right.

Other recent estimates of the solubility of plutonium do not all agree in detail with solubilities shown in Figure 1, because of differences in thermochemical data used for the calculations. Duda et al. (1982) suggest solubilities of $10^{-8.8}$ M at Eh = +0.55 volt and $10^{-17.3}$ M at Eh = -0.40 volt, for water at pH = 9 and with total carbonate about 10^{-3} M; these numbers are close to those that can be estimated from Figure 1 - as might be expected, since these authors supplied many of the free-energy values used in constructing the Figure. Allard (1983) chooses a much higher solubility product for PuO_2^s (10^{-57} rather than $10^{-62.5}$), which leads to a solubility of $10^{-10.5}$ M for a pH range from 7 to 9.5 and Eh from about -0.06 to + 0.34 volt, with total carbonate equal to 0.76 pH - 10.83 (log of molality). Early et al. (1982) calculate expected solubilities in many samples of water from the Columbia River basalt; for a sort of average "reference" water (with pH = 9.7, Eh = -0.3 volt, and total carbonate about 10^{-3} M) they find $10^{-9.4}$ M, and for 29 samples an extreme range from $10^{-11.2}$ to $10^{-6.2}$ M. Characteristics of samples showing the high values are not given, so reasons for the apparent discrepancy are not clear. These various estimates show much uncertainty about the minimum solubility over the field of PuO_2^s in Figure 1; the value of 10^{-17} M that follows from the free-energy values may well be too low. The figure adopted for bounding concentrations of species other than $Pu(OH)_4^o$ (10^{-12} M - the solid lines on the diagram) may also be somewhat low. In any event, most estimates show agreement with the conclusion from Figure 1 that solubilities in the PuO_2^s field at Eh values under +0.4 volt are very small, near to or below the generally accepted MPC for drinking water.

Because thorium solubility is not affected by Eh, a diagram for thorium like Figure 1 would consist simply of two vertical lines bounding an area where the solubility of ThO_2 is very low and the principal dissolved species is $Th(OH)_4^0$. The left-hand line would mark the pH below which cationic hydroxy complexes (chiefly $ThOH^{3+}$ and $Th(OH)_2^{2+}$) would give total thorium concentrations greater than some specified figure, say 10^{-12} M, and the right-hand line would limit the area where anionic complexes would give concentrations exceeding the same number. The position of the two lines is highly uncertain. The free-energy data of Duda et al. (1982) suggest a pH of about 3.5 for the left-hand line, and a very questionable 12.3 for the right-hand line; it is quite possible that no anionic hydroxy complexes exist, so that very low solubilities would persist through the high-pH range. Allard (1983) suggests $10^{-9.6}$ M (ca 0.1 ppb) for the solubility of ThO_2 over the pH range 4.5 to 10; Duda et al. (1982) give 10^{-15} M at pH 9, and Early et al. (1982) propose $10^{-14.9}$ M at pH 9.7. Measured concentrations in natural waters (e.g. Eisenbud et al. 1984) are on the order of a few tenths of a ppb (ca 10^{-9} M), but this is mostly in the form of particulates; amounts in true solution (particles <0.45 nm) are at least a hundred times smaller. Precise values are uncertain, but assuredly solubilities at the pH´s to be expected in and near a repository are very small.

CRITIQUE OF THE CALCULATED SOLUBILITIES

The above review of calculated values indicates that PuO_2 and ThO_2 have comparably low solubilities in the groundwater that might leach them from a waste repository. This is the theoretical argument for the assertion that thorium is a useful natural analog of plutonium. Like any such theoretical argument, this one can be challenged on many grounds with regard to its applicability in the real world. Several possible challenges are explored in the following paragraphs.

ASSUMPTION OF EQUILIBRIUM

One reasonable challenge is the objection that the calculations are made for equilibrium conditions which are never closely duplicated in nature. The lines delineating stability fields on Figure 1 are drawn for strict thermodynamic equilibrium among solutes in a dilute solution in contact with crystalline PuO_2. No account is taken of possible supersaturation, sluggish reactions, or formation of colloids. Probably the most vulnerable of the assumptions is the crystallinity of the solid: plutonium dioxide can exist in a variety of forms, from finely crystalline through semi-amorphous to the hydrated and completely amorphous $Pu(OH)_4$, and solubilities range up to a million times greater than that of coarsely crystalline PuO_2. Lack of equilibrium with the crystalline solid would not require changes in the positions of lines on Figure 1, but minimum solubilities in the PuO_2^s field could be much larger.

The solubility product $(Pu^{4+})(OH^-)^4$ for the reaction

$$PuO_2^s + 2H_2O = Pu^{4+} + 4OH^-$$

as calculated from the free energies in Table 1 is $10^{-63.5}$, which gives for the minimum solubility of the crystalline solid in equilibrium with $Pu(OH)_4^o$ a value of 10^{-17} M. A common figure in the literature for the solubility product (see references cited by Allard (1983) is $10^{-62.5}$, which leads to a minimum solubility of 10^{-16} M. Allard himself, as noted above, uses a higher value, 10^{-57}, giving a minimum solubility of $10^{-10.5}$ M; this is close to the figure for the amorphous oxide ($Pu(OH)_4^s$), $10^{-55.2}$. Any of these numbers can be justified, depending on the state assumed for the solid dioxide.

The analogy between plutonium and thorium, however, is not jeopardized by deviation from equlibrium, because the general chemistry of the two elements is so similar that the effects of deviation should be parallel - as long as the dissolved plutonium remains quadrivalent. If lack of equilibrium should influence plutonium compounds in which the element has higher or lower valences, the behavior of the two metals might conceivably be very different. One can imagine, for example, that $PuCO_3^+$ might be capable of existing in highly supersaturated solutions in contact with PuO_2, so that the field of $PuCO_3^+$ in Figure 1 would be expanded and plutonium would thus be more soluble than thorium at low and intermediate values of Eh. Such a possibility cannot be completely discounted, but there is no evidence to suggest it and prolonged supersaturation of an ion in contact with a solid is most unlikely.

ACCURACY OF DATA

Figure 1 is based on a reasonably self-consistent set of thermodynamic data, and many of the numbers have been independently checked by several investigators. Nevertheless, considerable uncertainty remains about some of the numbers, and the diagram can be plausibly challenged on this basis. It is hard to assign specific degrees of uncertainty to the various lines, but probably for all of them an error bar would represent at least half a pH unit and/or 0.05 volt. For some the uncertainty is greater, particularly for the lines bounding the fields of $Pu(OH)_5^-$ and $PuCO_3^+$. The free energies of both ions are only estimates, and may well be in error by a few kilocalories. Allard (1983), for example, uses 10^{-51} as the stability constant for the reaction

$$Pu^{4+} + 5OH^- = Pu(OH)_5^-$$

rather than the commoner 10^{-55} (which is given by the majority of references that he himself cites); this corresponds to a free energy of formation of the ion of -372.7 rather than -378.1

kcal. If this number is used together with Allard's high value for the solubility product of PuO_2^s, the lines bounding the PuO_2^s field on the right would move 2.6 pH units to the left. This would make the solid more soluble at high pH's, but still a solubility as high as 10^{-9} M would be reached only at a pH near 11. As noted above, the existence of the ion $Th(OH)_5^-$ is questionable, so that plutonium may be more soluble than thorium if the pH is sufficiently high; but the necessary pH is so very high that it would have no relevance to a repository environment.

More serious would be a large error in the free energy of $PuCO_3^+$, for which there is no analogous Th compound. It can be urged, however, that the carbonate concentration used in locating the $PuCO_3^+$ boundary is near the maximum reported for deep groundwater (10^{-2} M), and that a 10-fold lower carbonate concentration would lower the $PuCO_3^+$ lines by 0.06 volt, hence below the lines for the uncomplexed ion. Certainly an imaginable combination of circumstances - say an underestimation of the free energy of $PuCO_3^+$ by 3 or 4 kcal, coupled with groundwater in a repository that is unusually acidic, unusually reducing, and unusually rich in carbonate - could so restrict the area of low solubility on Figure 1 that the analogy with thorium would break down. But such a combination is not very likely.

An excellent review of the quality of available thermodynamic data for the actinide elements is given by Allard (1984).

COMPLEXES WITH LIGANDS OTHER THAN OH^- and $CO_3^=$.

All the quadrivalent actinide ions form complexes with many ligands, but there is general agreement that the important ones in most deep groundwater are the hydroxy and carbonate complexes (Allard 1983, Duda et al. 1982, Early et al. 1982). Groundwaters of unusual composition might contain enough sulfate, fluoride, or phosphate for complexes of these ligands to affect solubilities appreciably, but stability constants for quadrivalent plutonium and thorium are so similar (Table 2) that effects on solubilities of the two elements would be much alike. The same would probably be true for complexes with organic ligands, but not enough of these have been studied to make the generalization completely safe. Of the complexes formed by plutonium in valences other than 4, those with fluoride seem most likely to influence solubility appreciably. But a sample calculation for the ion PuF^{2+} shows that with fluoride concentrations equal to the relatively high $10^{-2.8}$ M in the "reference basalt groundwater" of Early et al. (1982) mentioned above, the lines on the left-hand side of Figure 1 would be shifted upward by only 0.06 volt, and the size of the central low-solubility area would be only slightly diminished.

EFFECTS OF RADIOLYSIS

Because plutonium is more radioactive than thorium, one might expect its radiolytic effects to be greater. Two kinds of effect could be important: damage to the crystal structure of PuO_2, and production of a local oxidizing environment by radiolysis of water in the immediate vicinity of the solid followed by escape of some of the hydrogen produced. Both effects would make plutonium more soluble, and comparable effects on thorium would be negligible. The effects would be only local, however, and if moving groundwater carries the released plutonium a short distance into the prevailing more reducing repository environment, PuO_2 or $Pu(OH)_4$ would presumably precipitate and would thereafter control its movement.

TEMPERATURE AND PRESSURE

The thermochemical data used in constructing Figure 1 apply strictly only to standard conditions, 25°C and 1 atm pressure. Solubilities would presumably be somewhat greater at higher temperatures, and possibly at higher pressures also. The effects would probably be minor, however, since solubilities of most substances are not raised by more than a factor of 3 or 4 with a temperature increase of 100°C and even less with a modest pressure increase. Furthermore, the effects should be comparable for the two elements. Only if temperature or pressure should have an abnormally large effect on compounds in which plutonium has an oxidation state other than 4 might a significant difference appear, but this hardly seems likely.

NEGLECT OF ACTIVITY CORRECTIONS

In constructing the diagram in Figure 1 concentrations were assumed equal to activities, probably a reasonable assumption in view of the low solute content of most groundwaters and the greater errors introduced by uncertainties in the thermochemical data. Application of the diagram to more concentrated waters, for example brines near a repository in salt, would of course require activity corrections to make the solubilities realistic. Here again, however, the required corrections for plutonium and thorium should be comparable, except for possible effects of the corrections on concentrations of dissolved substances that contain plutonium in oxidation states different from +4.

In summary, the conclusion that plutonium and thorium would have similarly low solubilities in groundwater in a waste-repository environment, and hence that thorium is a valid analog for plutonium, can be challenged in many ways, of which the most serious is a possible underestimation of the stability of $PuCO_3^+$.

The estimated datum for this stability is reasonably conservative, however, and successful challenges on other grounds require improbable assumptions about the behavior of plutonium in its 3-valent, 5-valent, and 6-valent forms.

THORIUM AS AN ANALOG FOR NEPTUNIUM

Because the actinide elements in a given oxidation state all show much chemical similarity, it seems worthwhile to explore a possible analogy of thorium with neptunium as well as plutonium. Thermochemical data for neptunium are less reliable than those for plutonium, but are adequate to show similarities in stability constants (Table 2) and to construct an Eh-pH diagram (Figure 2) analogous to Figure 1. Again the lines on the diagram are located from free-energy data, and again the values are in part taken from Duda et al. (1982) and in part calculated from Allard's (1983) stability constants. Uncertainties in locations of the lines are probably greater than in Figure 1, but a precise comparison is not feasible. As in Figure 1, heavy solid lines around the central field (marked NpO_2^s) indicate concentrations of 10^{-12} M of dissolved neptunium in equilibrium with crystalline NpO_2; heavy solid lines outside this field are boundaries of fields of dominance of various ions and molecules of dissolved neptunium; heavy dashed lines show concentrations of 10^{-9} M of neptunium in equilibrium with NpO_2; light lines within the central field show similar concentrations of neptunium-carbonate ions (chiefly $NpO_2(CO_3)_3^{5-}$, with minor amounts of $NpO_2CO_3^-$ and $NpO_2(CO_3)_2^{3-}$ between pH's of 6 and 8) when total dissolved carbonate is 0.01 M. The vertical light dashed line at pH 6.35 separates the dominance fields of NpO_2^+ and the carbonate complexes. The central field, as in Figure 1, represents neptunium solubilities less than 10^{-12} M, presumably chiefly as undissociated $Np(OH)_4^o$; Allard (1983) gives a minimum solubility of 10^{-10} M over this pH-Eh range for the undissociated hydroxide in equilibrium with amorphous $Np(OH)_4^s$, but for the crystalline dioxide the solubility would be orders of magnitude smaller.

Outstanding differences between Figures 1 and 2 are (1) the much larger fields for the quinquevalent actinide in Figure 2 (NpO_2^+ and NpO_2OH^o); (2) the smaller field for the trivalent actinide (Np^{3+}); (3) the larger field for the negative hydroxide ion $Np(OH)_5^-$; (4) the lack of a field for a stable carbonate complex of trivalent Np, and a much larger field for carbonate complexes of the actinide in a higher oxidation state (chiefly $NpO_2(CO_3)^{5-}$). These differences mean that the central field for very low concentrations in equilibrium with crystalline dioxide is markedly smaller for neptunium than for plutonium, hence that the analogy with thorium is less close.

It is true that in a substantial part of the Eh and pH ranges to be expected in a repository, neptunium concentrations would be as low as those of thorium. It is true also that neptunium would be less vulnerable than plutonium to increased solubility at very low Eh and pH, where Pu^{3+} and its complexes become stable. Nevertheless, the greater ease of oxidation of neptunium, especially if carbonate is abundant, makes a comparison with the behavior of thorium more questionable than a similar comparison for plutonium. Repository conditions with Eh´s between +0.1 and +0.2 volt and pH´s from 8 to 9 would certainly not be abnormal, and under these conditions the solubility of neptunium is orders of magnitude higher than that of either plutonium or thorium.

APPLICATION TO MORRO DO FERRO

The thorium in near-surface material of the ore deposit at Morro do Ferro is probably in large part sorbed on surfaces of clay and iron-oxide particles (Eisenbud et al. 1984). It is being leached by surface water and shallow groundwater, under conditions of high oxidation potential, near-neutral pH, and low temperature. The situation is obviously very different from that to be expected in and near a breached subsurface waste repository, where plutonium as a minor constituent of spent UO_2 fuel or borosilicate glass will be exposed to warm, slightly alkaline groundwater at low Eh. Nevertheless, a good argument can be made that the behavior of thorium in its near-surface environment is analogous to that of plutonium underground.

In the theoretical discussion above, the two elements are assumed to be present as crystalline oxides, and a question is reasonable as to the applicability of such a discussion to the very different forms of the elements at Morro do Ferro and in a hypothetical repository. If the plutonium in a repository is contained in spent fuel it would be part of crystalline UO_2 (with which PuO_2 is isomorphous) in the fuel pellets, and its properties should closely match those of the assumed crystalline PuO_2. If it is incorporated in borosilicate glass its properties are more difficult to estimate, but would probably be more similar to those of an amorphous form of the oxide. Thorium sorbed on clay and iron oxide is certainly in a form very different from crystalline ThO_2, but presumably would have a solubility at least as great as that of amorphous ThO_2 or $Th(OH)_4^s$. Thus the mobility of thorium at Morro do Ferro should be greater than that calculated from theory, and the mobility of plutonium should be comparable to or somewhat greater than the calculated estimate. In any event, the mobility of thorium should not be less than that of plutonium. and a comparison of the two should be valid despite the differences from the solid forms considered theoretically.

If plutonium were exposed at Morro do Ferro as is thorium, it would clearly be dissolved more readily because of oxidation to higher valence states. But a breached repository underground would not be exposed to air, so that plutonium could not be oxidized, and thorium is not affected by oxidation; hence the movement of thorium near the surface is directly comparable to that of plutonium underground, despite the difference in the two environments. Furthermore, even if an extreme breaching event is postulated so that a little air does reach the repository, Figure 1 shows that plutonium remains very insoluble up to oxidation potentials of 0.4 or 0.5 volt. Unless the repository is actually exposed at the ground surface, where abundant oxygen and carbon dioxide are directly available, the similarity in mobility of the two elements should persist.

One other factor might give thorium greater mobility than plutonium: some of the water at Morro do Ferro contains enough dissolved organic matter to turn its color brown, and formation of organic complexes could increase the solubility of thorium. No organic matter, or at least a much smaller amount, would be available to plutonium in a repository. The concentrations of thorium at Morro do Ferro, therefore, should be at least as high and probably higher than those to be expected for plutonium in a repository environment.

One caution is needed about the general applicability of the analogy. It holds for all environments in which groundwater can be expected to remain reasonably dilute, for example repository sites in crystalline rock, but its validity is less certain for the concentrated brines that can be imagined to invade a breached repository in salt. As long as plutonium remains quadrivalent, the complexes it might form in a concentrated solution should be similar to those of thorium, and the analogy would hold. But plutonium has the ability, which thorium lacks, of forming stable complexes in its higher and lower oxidation states, and if the appropriate ligands are present at high concentrations such complexes could make it more soluble than thorium. Cleveland (1983), for example, has demonstrated that plutonium added to the alkaline water (pH 10) of Mono Lake distributes itself among oxidation states from +3 to +6, with 3 and 4 especially prominent despite exposure of the water to air. This water has high fluoride and very high carbonate (26,300 ppm, expressed as $CaCO_3$ alkalinity), and Cleveland suggests that complexes of these ligands are largely responsible for the solubility of plutonium. Most waters associated with salt deposits have lower pH and much lower concentrations of carbonate and fluoride, so that normal brines in and near a salt repository may not show a similar enhanced solubility. Without further experimental evidence, however, the validity of the thorium analogy in brines must remain to some extent questionable.

The low thorium concentrations of groundwater and surface water in contact with thorium ore at Morro do Ferro are good grounds for concluding that leaching of plutonium from an underground repository will be very slow, with the possible exception of a repository invaded by concentrated brine.

SUMMARY

Many aspects of the chemical behavior of the trans-uranium actinides in and near a waste repository can be inferred from the geochemistry of similar naturally-occurring elements. The rare-earth elements are particularly good analogs for the actinides that are most stable in their trivalent state, americium and curium. Analogs of quadrivalent actinides are less easy to find, because actinides that are stable in this oxidation state also form stable complexes in higher and lower states. With some qualifications, thorium is a good analog for plutonium, since over a wide range of Eh and pH common in repository environments plutonium is not easily altered from its quadrivalent state. The two elements are most stable in the form of the nearly insoluble dioxides, and in their quadrivalent states in solution they form many complexes with similar stability constants. In oxidizing environments plutonium forms soluble ions and complexes of its higher oxidation states, and in acid reducing environments it forms complexes of its trivalent state, but the conditions necessary are well outside the Eh and pH ranges of most groundwater at candidate repository sites. Thus the mobility of plutonium from a projected repository site can be inferred from observation of the mobility of thorium from an ore deposit, as at Morro do Ferro. The difference in oxidizing conditions between the ore deposit and the repository is not important, because thorium is not affected by oxidation and reduction. The analogy is most convincing for projected repository sites in crystalline rock, where groundwater is fairly dilute. Some question remains about sites in salt, where the high ionic strength and possible (but unlikely) high concentrations of complexforming ligands in brine that might invade a repository may be sufficient to make plutonium more soluble than thorium.

Thorium is also a satisfactory analog for neptunium under conditions to be expected in many repositories, but the range of oxidizing conditions under which the analogy holds is more restricted than for plutonium.

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Table 1. Ionic radii of lanthanide and actinide elements in 6-fold coordination, in ångströms (Shannon, 1976).

La^{3+}	1.03	Eu^{3+}	0.95	Cm^{3+}	0.97
Ce^{3+}	1.01	Np^{3+}	1.01	Th^{4+}	0.94
Nd^{3+}	0.98	Pu^{3+}	1.00	Pu^{4+}	0.86
Sm^{3+}	0.96	Am^{3+}	0.98		

Table 2. Comparison of stability constants for compounds and complexes of quadrivalent thorium, neptunium and plutonium.

Solubility products	Th	Np	Pu
$(Me^{4+})(OH^-)^4$ for MeO_2^s	-49.7	-58.7±2	-62.5±1.2[%]
$(Me^{4+})(OH^-)^4$ for $Me(OH)_4^s$	-44.7	(-53 ±2)	-55.2±1.2

Formation constants (logarithms of constants for reaction $Me^{4+} + nL^{z-} = MeL_n^{4-z}$):

	Th	Np	Pu
$MeOH^{3+}$	10.8 ±0.2*	12.51±0.05*	13.5±0.1*
$Me(OH)_2^{2+}$	21.1 ±0.2*	(25.2 ±0.7)	(25.7±0.6)
$Me(OH)_3^+$	(30.3)**	(36.4 ±1.1)	(36.7±0.9)
$Me(OH)_4^0$	40.1 ±0.3*	(46.1 ±1.4)	46.5±1.2
$Me(OH)_5^-$	(44)	(53 ±2)	(55 ±2)
$MeHPO_4^{2+}$	13 ±1**		13 ±1**
$Me(HPO_4)_2^0$	24 ±1**		24 ±1**
$Me(HPO_4)_3^{2-}$	33 ±1**		33 ±1**
$MeSO_4^{2+}$	5.45**	(5.7)	6 ±1**
MeF^{3+}	8.03**	(8.5)	8 ±1**
$MeCl^{3+}$	1.09**	(1.2)	0.9±0.7
$MeC_6H_5O_7^+$	13.0 ***		15.0 ***
Me-EDTA complex	25.3 ***		26.1 ***
Me-$C_7H_7O_2N$ complex	9.60***		12.73***

Values in parentheses are estimated. $H_3C_6H_5O_7$ is citric acid; EDTA is ethylenediaminetetraacetic acid; $C_7H_7O_2N$ is benzohydroxamic acid.

[%] Allard uses -57 for this number in his 1983 paper. See text for discussion.

Sources:

* Baes and Mesmer (1976)
** Phillips (1982)
*** Sillén and Martell (1971)
Others from Allard et al. (1980).

Table 3. Thermochemical data used in constructing Figures 1 and 2: Gibbs free energies of formation of plutonium and neptunium compounds and ions at 25°C and 1 atm pressure, in kilocalories per mole.

Pu^{3+}	-138.4	Pu^{4+}	-115.1*	PuO_2^+	-203.1*
$PuOH^{2+}$	-185.8	PuO_2^s	-238.7*	PuO_2^{2+}	-181.0
$PuCO_3^+$	(-272.8)	$Pu(OH)_4^s$	-340.8*	$PuO_2(OH)_2^o$	-280.2
$Pu(CO_3)_2^-$	(-404.4)	$Pu(OH)_4^o$	-329.0*	$PuO_2(OH)_3^-$	-323.8
PuF^{2+}	(-209.4)	$Pu(OH)_5^-$	(-378.1)	$PuO_2CO_3OH^-$	-378*
Np^{3+}	-123.7	$Np(OH)_4^o$	(-338.8)	$NpO_2HCO_3^o$	-377.4*
$NpCO_3^+$	(-263.0)	$Np(OH)_5^-$	-380.5*	$NpO_2CO_3^-$	-353.0
Np^{4+}	-120.2*	NpO_2^+	-218.7*	$NpO_2(CO_3)_2^{3-}$	-486.2
NpO_2^s	-239*	NpO_2OH^o	-263.1*	$NpO_2(CO_3)_3^{5-}$	-619.5
$Np(OH)_4^s$	(-352.4)	$NpO_2(OH)_2^-$	-307.8*		

Values marked with an asterisk are from Duda et al. (1982); others are calculated from stability constants in Allard (1983). Values in parentheses are particularly uncertain.

FIGURE 1

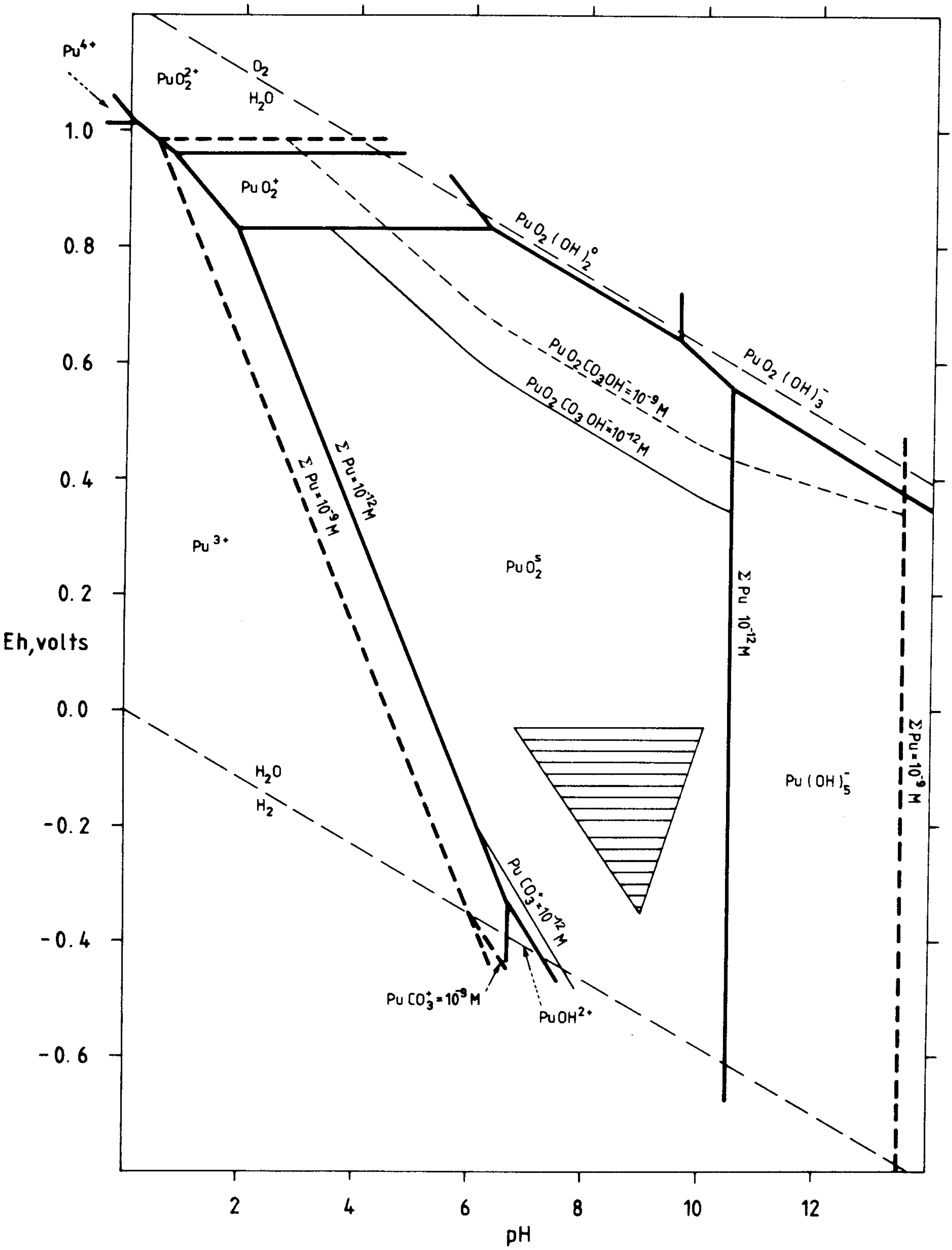
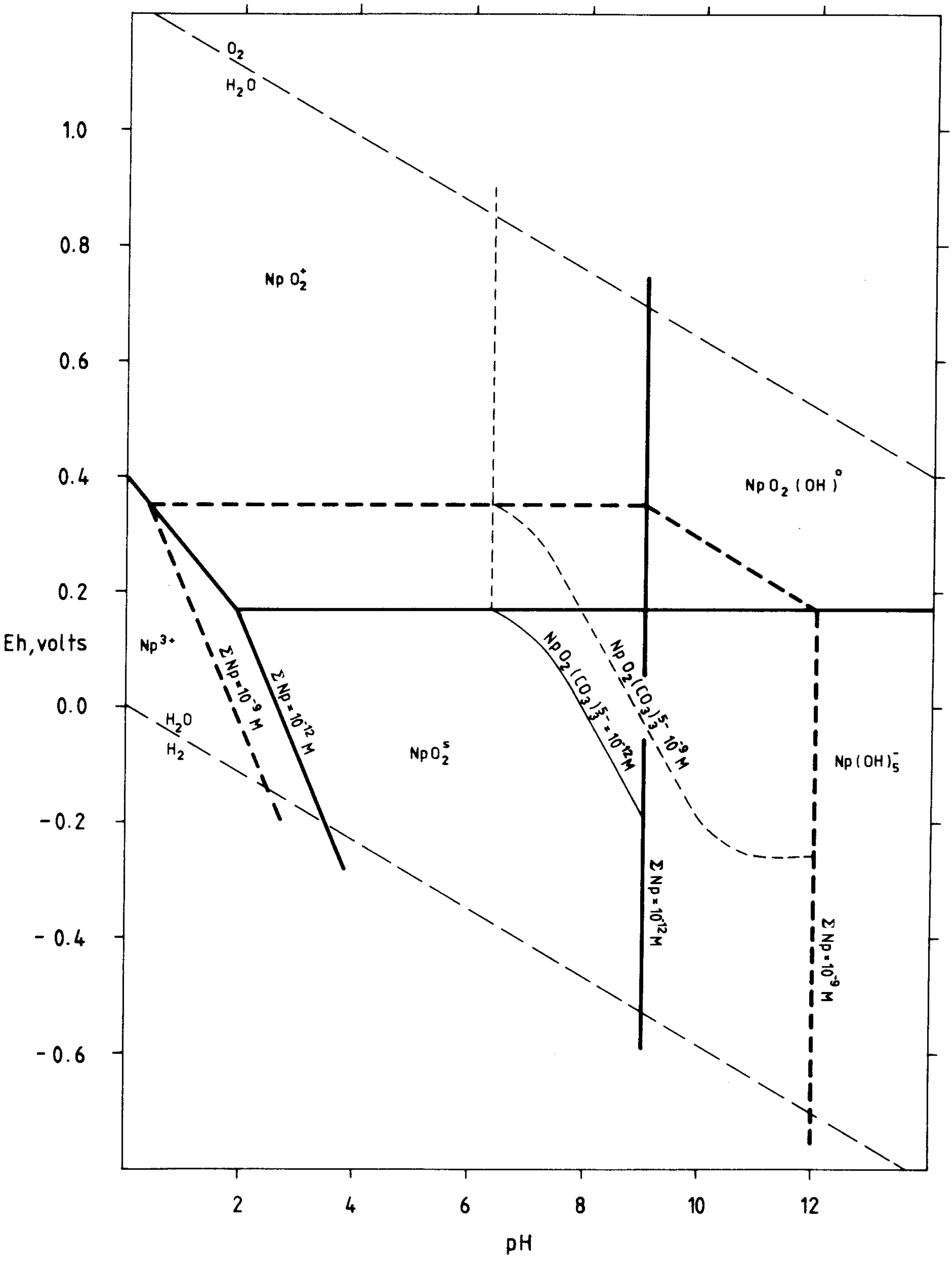

Pu^{4+}
PuO_2^{2+}
O_2
H_2O
PuO_2^+
$PuO_2(OH)_2^{o}$
$PuO_2CO_3OH^- = 10^{-9} M$
$PuO_2CO_3OH^- = 10^{-12} M$
$PuO_2(OH)_3^-$
$\Sigma Pu = 10^{-12} M$
$\Sigma Pu = 10^{-9} M$
Pu^{3+}
PuO_2^s
$\Sigma Pu\ 10^{-12} M$
$\Sigma Pu = 10^{-9} M$
H_2O
H_2
$Pu(OH)_5^-$
$PuCO_3^+ = 10^{-12} M$
$PuCO_3^+ = 10^{-9} M$
$PuOH^{2+}$
1.0
0.8
0.6
0.4
0.2
Eh,volts
0.0
-0.2
-0.4
-0.6
2
4
6
8
10
12
pH

FIGURE 2


O_2
H_2O
NpO_2^+
$NpO_2(OH)^o$
Np^{3+}
$\Sigma Np = 10^{-9}$ M
$\Sigma Np = 10^{-12}$ M
NpO_2^s
$NpO_2(CO_3)_3^{5-} = 10^{-12}$M
$NpO_2(CO_3)_3^{5-}$ 10^{-9} M
$Np(OH)_5^-$
H_2O
H_2
$\Sigma Np = 10^{-12}$M
$\Sigma Np = 10^{-9}$ M
1.0
0.8
0.6
0.4
0.2
Eh, volts
0.0
-0.2
-0.4
-0.6
2
4
6
8
10
12
pH

RADIUM MOBILIZATION AND TRANSPORT AT A LARGE THORIUM ORE DEPOSIT IN BRAZIL

E. Penna Franca[1], M.J. Campos[1], N. Lobão[1], H. Trindade[1], I. Sachett[1] and M. Eisenbud[2]

[1] Institut de Biofisica - UFRJ, Cidade Universitária, 21941 Rio de Janeiro, RJ, Brazil.
[2] New York Medical Center, Institute of Environmental Medicine, New York, USA.

ABSTRACT

A near-surface large deposit of thorium ore is located at Morro do Ferro (MF), a hill in the Poços de Caldas Plateau, Minas Gerais, Brazil. An estimated 30.000 metric tons of Th and 100 tons of U are contained in the deposit in a highly weathered matrix exposed to erosion and leaching. ^{228}Ra and ^{226}Ra were analyzed in surface water samples collected at various points of the drainage basin and in groundwater from seven wells drilled through and around the ore body. The ratio ^{228}Ra/^{226}Ra reaches up to 450 in groundwater inside the ore body but it is much smaller in surface waters. The results of groundwater analyses demonstrated that radium is markedly leached by rain water percolating through the ore body. In its transit underground, until seeping at the foot of the hill, radium is removed from groundwater by sorption on soil particles and this natural process greatly reduces the radium discharged to the environment. In dry weather, the concentration of dissolved ^{228}Ra in surface waters in the general MF basin range from 0.05 to 3.3 pCi l^{-1}. In the main stream draining the MF the average concentration is 1.70 $\pm$ 0.30 pCi l^{-1}, and in a control stream in an opposite hill it is 0.33 $\pm$ 0.11 pCi l^{-1}. Considering the difference between the two ^{228}Ra concentrations as a contribution from the MF source, the estimated mobilization rate due to radium solubilization is of the order of $10^{-7}a^{-1}$. The influence of rain storms on radium mobilization by erosion, and the relative importance of radium transport in particulate form, is discussed.

INTRODUCTION

Main Features of the Morro do Ferro Region

A highly weathered deposit of thorium and rare earths minerals, located near the summit of Morro do Ferro (Iron Hill) in the center of the Poços de Caldas Plateau, Minas Gerais, Brazil, is being studied as a radioactive waste analogue. Th^{4+} may serve as an analogue for Pu^{4+} and La^{3+} as an analogue for Cm^{3+} and Am^{3+}. Morro do Ferro is also being used as a natural laboratory to investigate radium mobilization and transport.

The Poços de Caldas Plateau has been characterized as a center of intrusive and extrusive alkaline igneous activity which occurred between 80 to 60 million years ago. It is in the form of a roughly circular caldera, about 35 km in diameter, surrounded by a rim of hard rocks. The geology of the plateau has been described by Frayha (1962), Wedow (1967), Almeida (1977), Ellert (1959) and Bushee (1971) and it has been recently summarized by Eisenbud *et al*. (1984).

In the Morro do Ferro (MF), Frayha (1962) and Wedow (1967) reported that the high grade ore, which is predominantely located near the surface of the hill, contains up to 1% thorium, as much as 4% rare earths oxides, and much less uranium. Present estimates for the deposit are 30.000 metric tons of thorium, 50.000 tons of rare earths and 100 tons of uranium (Eisenbud, 1984).

The underlying rock of Morro do Ferro shows extensive alteration due to weathering and hydrothermal activity, and tinguaite (fine-grained nepheline syenite), partly massive and partially breciated, has been identified. The only rock outcrops are magnetite which occurs as a set of dikes on the south face of the hill, as well as a network of underground veins and veinlets. Many of the small veinlets have been altered to limonite (Wedow, 1967). Frayha and Wedow pointed out that the thorium and rare earths are widespread in the surface material and are more concentrated near some dike contacts. The ore itself, a porous claylike material, is stained by iron oxides (limonite or hematite). According to Frayha, the more ferruginous the ore the higher is the thorium content. Carlos and Penna Franca (1983), using sequential selective extractions, demonstrated that in some ore samples 25 to 45% of the thorium and rare earths are associated with the iron and manganese oxide fraction.

Recent studies (Fujimori, 1983, Eisenbud *et al*., 1984) identified as the primary residual thoriferous minerals, thorianite, thorite, microlite, monazite, cheralite and a rare earth and thorium silicate. These minerals were found in micron size crystals. The most abundant secondary thorium mineral is thorobastnaesite, but the predominant geochemical form of thorium and rare earths in the Morro do Ferro is amorphous and associated with iron and aluminum oxides and also with the most abundant clay minerals.

Figure 1 is an aerial photograph of the Morro do Ferro region in which the important features are indicated. Grassland occupies the ridges and slopes of the hill whilst forest covers the valley floors. Most of the exposed surface of the ore body is on the south face of Morro do Ferro but a small fraction of it extends over the top toward the north slope. The total surface area of the deposit is 0.06 km^2 (Lei, 1984).

The main drainage basin of Morro do Ferro is self-contained to a distance of several kilometers, and a stream (South Stream) that receives most of the ore body drainage originates at the southwestern edge of the hill. The southern portion of the basin is bounded by hills, here referred to as the Opposite Ridge.

The South Stream flows all year round in the valley bed; its source of water is groundwater seepage from both sides of the valley during the dry season (baseflow) and a combination of seepage and runoff in times of rainfall. A flume was constructed in the location shown in Figure 1 and instruments were installed to permit continuous flow measurement. The area of the watershed that drains through the flume is only 0.5 km^2 and there are no impoundments.

The average annual rainfall in the region is 1700 mm, about 80% of it occurring during the Summer four-month rainy season, mostly as short-duration heavy rainstorms. In these occasions, surface runoff is rapid and it is often accompanied by intense scouring. The South Stream water, which in baseflow regime is quite limpid, becomes very turbid and the flow at the flume can increase in a matter of minutes from a year round dry weather value of 0.7 $m^3\ min^{-1}$ (stage height of 3 cm) to a flow as high as 66 $m^3\ min^{-1}$ (stage height 50 cm). Where the rain has ceased, the flow returns to its baseline value in a few hours.

Downstream from the flume only one surface stream runs year round entering the South Stream from the Opposite Ridge. This tributary serves as a control sampling site. Three hundred meters downstream from the flume the South Stream forms an extensive swamp (Figure 1). A second stream (North Stream) rises from the western edge of the north face but receives less drainage from the ore body than the South Stream. Lei (1984) estimated that the discharge at the North Stream is about 25% of the one at the South Stream.

In 1982, in order to obtain spoil samples and to allow periodic groundwater collection, seven wells were drilled to the depth of the water table in an around the ore body and two in the Opposite Ridge. The identification and location of the wells are given in the Figure 1. A study of the groundwater hydrology was then undertaken (IPT 1982) which demonstrated that the water table is a subdued replica of the Morro do Ferro surface topography. It is recharged from precipitation and discharged into a network of seepages at or near the stream level. High permeability in the deeply weathered ore body permits uniform groundwater flow. Near the magnetite dikes, however, the flow may be controlled by fractures. The composition of the well spoils, predominantly argillaceous silt, suggests that high permeability is prevalent through much of the Morro do Ferro and its drainage basin.

Scope of the Research

The main objectives of the research on radium migration at Morro do Ferro are:

- To investigate the mechanisms of radium leaching, retention and transport in the Morro do Ferro and its environs.
- To estimate radium mobilization rates from the ore body by solubilization and by erosion.

The research project is carried on at the Morro do Ferro region not only to exploit the unique peculiarities of the thorium deposit but also because it is important to understand the radium behavior in the Poços de Caldas Plateau, where the first Brazilian uranium mine and mill are located.

This paper reports results obtained up to now which are limited to baseflow regime, i.e. under conditions of no rain. The general investigative approach of this research is similar to the methods adopted by Eisenbud et al. (1982, 1984) and Lei (1984) in their study on thorium and rare earth mobilization from the Morro do Ferro.

MATERIALS AND METHODS

Field Monitoring Instruments

In order to provide the necessary meteorological and hydrologic data for the Morro do Ferro project, the following installations and instrumentation were set up in the region.

A meteorological station was emplaced at the top of the hill to permit continuous measurement of temperature, and wind direction and speed (Meteorology Research Inc., Altadena Ca. Model 1082). A rain gauge coupled to a continuous strip chart recorder was installed (Leupold and Stevens Ins, Beaverton Or. Model Type QA). A rectangular concrete flume was built in the South Stream, downstream from the drainage area of the ore-body (Figure 1). A continuous water level recorder (Manning Environmental Corp. Santa Cruz, Ca, Model F-3000A) was installed and calibrated, relating stage height in the flume with flowrate.

Of the nine wells recently drilled into the ore body and its environs (Figure 1) seven have provided data on groundwater height and permitted collection of samples. The remaining two wells (7 and 8) are dry.

Water Sample Collection

Groundwater samples (20 1) were collected periodically during 1981/82 in the seven "wet" wells. Samples were also taken from a horizontal gallery excavated though the ore body in the mid 1950´s. After heavy rainfall, water percolating through the ore body drips down from the roof and can be collected.

Surface water samples (20 or 40 litres) were collected periodically during the years of 1981/83 at the South Stream flume, at the North Stream, and at the Opposite Ridge (control stream). Samples were also taken at irregular intervals at the head of South Stream and at the nearest farm of the Morro do Ferro which is located about 1200 meters downstream and at the confluence, the point where the South Stream reaches the Anta River, the main river in the Poços de Caldas Plateau, about 7 km away from Morro do Ferro.

All the water samples were collected during dry days (baseflow regime) when the streams were limpid and the flow at the flume was equivalent to the year round basic stage height of 3-4 cm.

Analyses of ^{226}Ra and ^{228}Ra

In a field laboratory installed in the city of Poços de Caldas, the water samples were filtered under pressure through a 0.45 µm Millipore membrane filter. The filters were then dried and weighed and the filtrates were acidified with HNO_3 to pH 1, evaporated to about 200 ml, and then transferred to sealed plastic bottles for shipment to Rio de Janeiro.

At the Institute of Biophysics, the filtrate samples were further evaporated, transferred to platinum crucibles and dried. The filters with the particulate fraction were placed in platinum crucibles, wet ashed with HNO_3 and dried. Both types of residues were treated with HF, evaporated to dryness and then fused with a flux of lithium tetraborate and metaborate (Bennett and Oliver, 1976). The melt was cooled and dissolved in 1 N HCl. One aliquot of this solution was taken for ^{226}Ra analysis by the classical radon emanation method (Lucas, 1964), (Public Health Service, 1967).

For ^{228}Ra determination, a procedure reported by Kamath et al. (1964) was employed for samples analyzed prior to April 1983.

The method is based on purification of radium by repeated coprecipitation with $BaSO_4$, followed by redissolution in alkaline EDTA. After a final $BaSO_4$ precipitation in the presence of Pb^{2+}, Bi^{3+} and La^{3+} carriers, ingrown ^{228}Ac in the supernatant is coprecipitated with LaF_3, which is filtered and beta counted in a gas-flow low background Geiger counter. Since this method was time consuming and its reproducibility was not very satisfactory a second procedure was tested and adopted. It adopts the same initial radium purification steps as in the former method but the final determination is done by coincidence measurement of the characteristic ^{228}Ac β-γ emissions, as reported by McCurdy and Mellor (1979). Duplicate analyses carried out in a series of samples using both methods demonstrated a satisfactory statistical agreement between the two sets of data, so all the results could be pooled together.

RESULTS AND DISCUSSION

Radium, Thorium and Uranium in the Poços de Caldas Plateau

Some background data on the radium, thorium and uranium distributions in the Poços de Caldas Plateau and in the Morro do Ferro area are presented in order to facilitate the appraisal of the thorium deposit impact on the local environment.

Radium isotopes are normally present in any type of soil at varying levels of radioactive equilibrium with their parents. Uranium and thorium are widely distributed throughout the earth´s crust where they are generally present at the same activity concentration. Worldwide average concentrations of ^{238}U and ^{232}Th in the accessible lithosphere have been estimated to be about 2.8 $\mu g\ g^{-1}$ (0.9 pCi g^{-1}) and 7 $\mu g\ g^{-1}$ (0.8 pCi g^{-1}) respectively (United Nations, 1966, 1977). In large areas of Brazil thorium is more abundant than uranium in surface soils and rocks.

Tables I and II present available results of radium concentrations in various environmental regions of the Poços de Caldas Plateau and the Morro do Ferro basin. The thorium and uranium concentrations are higher than normal in soils and river sediments throughout the Plateau, reaching very high levels within the many radioactive anomalies existing in the region. In the Morro do Ferro basin, the mean ^{232}Th content in surface soil is 140 $\mu g\ g^{-1}$, 20 times higher than the worldwide average. Background uranium concentrations in soils are similar to values found throughout the Plateau, i.e. in the range of 5 - 50 $\mu g\ g^{-1}$ (1.7 - 17 pCi g^{-1}) (Carlos, 1984). Radium isotope concentrations in the area are generally in equilibrium with their parents.

In Morro do Ferro, analyses of well spoils resulting from drilling through the ore body showed that the richest thorium ore is near the surface extending to a depth of 15 m, although pockets of high concentrations exist at greater depths. The thorium content in well spoils near or outside the mineralized body is similar to the concentrations found in the control wells (1 and 3) drilled on the Opposite Ridge, or in the surface soil from the basin. The uranium content reaches maxima of 114 µg g^{-1} in the ore body and 86 µg g^{-1} in spoils of control wells in the Opposite Ridge (Carlos, 1984).

In the South Stream, the thorium content of the stream sediments shows an increasing gradient from stream head to the flume, before diminishing. However, the mean level at the flume is only three times that of sediments in other sampling locations, and soils in the general basin (Lei, 1984, Carlos, 1984).

Radium-226 in surface waters of the Poços de Caldas Plateau are elevated compared to normal areas, the most frequent values falling in the range of 0.5 - 2 pCi l^{-1} (Amaral, 1984, Paschoa 1979) (Table 1). A few recent unpublished data show that ^{228}Ra concentrations are in the same range.

Radium in Groundwater

Table III gives the soluble radium isotope concentrations in groundwater samples collected in seven wells and in the gallery. Suspended solids in groundwater were not analyzed because it was impossible to sample the water without disturbing the sediment in the well bottom.

Radium-226 average concentrations in all sampling locations are similar, the highest values inside the ore body being only 3.5 times greater than in the control wells. These values are smaller than the levels found in several rivers in the Plateau, reflecting the low uranium content of the Morro do Ferro deposit. By contrast, the ^{228}Ra concentrations in samples from wells outside and near the ore body are only slightly higher than in groundwater from the Opposite Ridge, but they increase sharply in waters from well 5 and the gallery, both of which are inside the ore body.

These results demonstrate that ^{228}Ra is markedly leached by rainwater percolating through the ore body. However, the much smaller concentrations in the other wells in Morro do Ferro seem to indicate that in its transit underground, radium is removed from groundwater by sorption on soil particles. This natural process greatly reduces the radium discharge rate to the environment. A recent hydrologic study (IPT 1982) supports that assumption. It demonstrated that the water table at MF is charged only by rainwater infiltration and that the net groundwater flow runs from the ore body toward wells 6 and 2 and then seeps into the South Stream. Thus, dilution alone cannot account for the observed sharp decrease of ^{228}Ra content in groundwater outside the ore body.

Radium in Surface Waters

As mentioned earlier, all the surface water samples were collected during baseflow regime when the stream waters were quite limpid. The particulate load was very small but variable present at levels of a few milligrams per liter in all samples. In large part the suspended soils were due to channel scouring and bank wash, although they might be influenced by any disturbances, such as falling tree leaves and branches, cattle stirring, etc., at the time of sample collection.

Tables IV and V present the mean concentrations of ^{226}Ra and ^{228}Ra respectively, in both the soluble fraction and suspended solids in surface waters from all collecting sites. Comparing results in the two tables it is noticeable that the soluble ^{228}Ra concentrations in the MF basin are roughly 10 times greater than those of ^{226}Ra; the ratios in suspended solids are more variable. The influence of the ore body on the soluble radium concentrations at the South Stream flume and at North Stream is significant, but is less evident for ^{226}Ra than for ^{228}Ra. However, the concentrations of both radium isotopes in the local streams are lower or similar to the levels found in many rivers in the Plateau (Table II), confirming the great capacity of the Morro do Ferro to retain the radium it produces.

The influence of the ore body on both radium isotope concentrations in suspended solids, reported in Tables IV and V, is not so evident. This is possibly due to the very small load and its many causes of variation. However, when the radium contents are expressed as specific activity in suspended solids, as in Table VI, the differences at the various sampling sites become evident for ^{228}Ra and the impact on the Th deposit shows up on the results from the South Stream flume, the Farm, and the North Stream. The ^{228}Ra specific activities of particulates at the flume and North Stream ore of similar levels to the average ^{228}Ra concentration in the ore body and its superficial soil (Table II). For ^{226}Ra though, the results are similar in all locations and apparently representative of the general background in large areas of the Plateau.

Lei (1984), during his investigation on thorium mobilization from Morro do Ferro, measured ^{232}Th concentrations in suspended solids in surface water collected at the same locations as described in this present paper. Although the samples were taken at different times, if one assumes the results recorded by Lei as being representative of each location, the ^{228}Ra specific activities in equilibrium with the reported ^{232}Th concentrations could be calculated and compared with results in Table VI. The actual ^{228}Ra specific activities found in this study are 5 to 20 times higher than the equilibrium values. The highest ratios are observed at locations influenced by the ore body. These findings demonstrate a high radium sorption on the fine suspended solids.

During the baseflow regime radium transport in suspended solids is less than that in the soluble form, possibly due to the very small solid loads in water. During rain storms, however, the particulates in the drainage streams increase sharply to 2 g l^{-1}. Under these circumstances suspended solids could become an important radium transport medium judging by the specific activities measured under the baseflow regime. However, there is the possibility that radium leaching from the ore body, sediment bed and suspended solids as a function of the very large water volume, might increase as well. The relative importance of these mechanisms will be investigated, but the lack of typical rainy seasons in the last two years has thus far prevented the collection of data.

^{228}Ra Mobilization Rates

Radium can be mobilized from the ore body by hydrologic means according to the following pathways:

1. Solubilization of radium at the surface of the deposit or by groundwater percolating through the ore body and seeping out at the foot of the hill. Transport by the drainage streams.

2. Physical erosion of the ore body surface by rainfall and transport by runoff and by drainage streams.

As it has been demonstrated by Eisenbud (1984) and Lei (1984), each pathway may have a different relative importance during the baseflow and stormflow regime. In this paper only results obtained during baseflow regime are reported.

The basic approach to estimating the mobilization rates is to measure the annual radium activity transported by each route, to divide this annual flux by the total radium activity in the ore body, and to obtain the annual fractional removal rate.

Lei (1984) measured the annual waterflow at the South Stream flume in a year when the rainfall precipitation was quite close to the 30 year annual average of 1700 mm and estimated the baseflow to be 4.75×10^{8} l a^{-1}.

Using the data in Tables IV and V, attempts were made to estimate the net concentration of each radium isotope at the flume representative of the ore deposit contribution. Considering the small importance of the Morro do Ferro deposit as a source of ^{226}Ra, the high background of the local basin and the very small differences in the concentrations in water at the different sites, no attempt were made to estimate ^{226}Ra mobilization rates. Moreover, the average concentrations of ^{228}Ra in suspended solids, at the flume and at the Opposite Ridge, were not statistically different, thus not allowing the identification of the ore body contribution. Therefore, only the soluble ^{228}Ra "net" contribution could be estimated by subtracting from the mean concentration at the flume the "background" at the Opposite Ridge, assuming, as a first approximation, that it is representative of the contribution of the general Morro do Ferro basin. The total ^{228}Ra in the ore body was calculated assuming equilibrium with the estimated 30.000 ton of ^{232}Th in the deposit.

The figures actually used are in Table VII and the mobilization rate by ^{228}Ra solubilization, the predominant pathway during baseflow regime, was calculated as 2.0×10^{-7} a^{-1}. To account for the discharge to the North Stream this value should be increased by 25%, resulting in a final value for the total mobilization rate of $2.5 \times 10^{-7} a^{-1}$. Since ^{228}Ra has a relatively small half-life (5.7 yr) in comparison with that of ^{232}Th, the ultimate persistence of ^{228}Ra in the thorium deposit is determined by its parent mobilization rates, which were estimated by Eisenbud *et al.* (1984) and Lei (1984). They concluded that the mobilization of thorium during baseflow regime is a small fraction of the total removal. Physical transport in surface run-off during rain storms dominates groundwater solubilization by three orders of magnitude, and is the primary mechanism for thorium removal from the ore body. The mean life of ^{232}Th in the deposit is 10^6 years if controlled by rainfall erosion and 10^9 years if determined by groundwater solubilization.

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Table I. Radium distribution in the Poços de Caldas Plateau (Soils, Sediments, Waters).

	N	^{226}Ra Minium (pCi g^{-1})	^{226}Ra Maximum (pCi g^{-1})	^{228}Ra Minimum (pCi g^{-1})	^{228}Ra Maximum (pCi g^{-1})	Reference and Method
Farm Soil	13	1.6	14.2	< 1.0	11.3	1 and 2
River Sediment	18	3.5	38.0	5.1	13.7	3
			(pCi l^{-1})			
Drinking Water	5	< 0.1	0.5	ND		3
River Water	59	< 0.1	8.2	ND		3 and 4

ND No data available

1 Carlos 1984; ^{232}Th and ^{238}U analysis by X-ray fluorescence, radium assumed to be in equilibrium.

2 Vasconcelos 1984; gamma ray spectrometry.

3 Amaral 1984; radiochemical procedure.

4 Paschoa 1979; radon emanation method.

Table II. Thorium, uranium and radium distribution in the Morro do Ferro basin (Ore, soils and sediments).

	N	^{232}Th (µg g^{-1})	^{228}Ra (pCi g^{-1})	N	^{238}U (µg g^{-1})	^{226}Ra (pCi g^{-1})
Ore Body	101			93		
Maximum		22,840	2,512		114	38
Mean		5,150	566		41	14
Surface soil (0-50 cm)	8	5,660	623		-	-
MF Basin Surface Soil						
Upstream the flume	8	180	20	7	43	15
Total	12	140	15	27	23	8
South Stream Sediment Bed	23			10		
Maximum		736	81		71	24
Minimum		35	4		< 18	< 6

After Lei 1984; ^{232}Th and ^{238}U analyzed by X-ray fluorescence.
Radium isotopes assumed to be equilibrium with their parents.

Table III. Soluble radium in groundwater.

Location	Description	N	^{228}Ra (pCi l^{-1})		^{226}Ra (pCi l^{-1})		Average ^{228}Ra / ^{226}Ra
			$\bar{X} \pm \sigma_{\bar{x}}$	Range	$\bar{X} \pm \sigma_{\bar{x}}$	Range	
Wells 1 - 3	Control wells in Opposite Ridge	12	4.4± 1.3	0.5- 16.2	0.19±0.04	0.06-0.44	23
Wells 2 - 4	Wells on MF, outside the ore body	12	5.0± 0.9	0.8- 9.7	0.48±0.07	0.07-0.82	10
Wells 6 - 9	Wells near the border of ore body	12	11.4± 3.3	1.1- 40.5	0.27±0.11	0.04-1.47	42
Well 5	Well inside the ore body	7	315.0±79.1	143.1-721	0.70±0.16	0.50-1.47	450
Gallery	Horizontal gallery inside the ore body	5	80.0±20.4	26.2-140.4	0.71±0.23	0.33-1.60	113

Table IV. Radium-226 in surface waters.

Location	N	Soluble Fraction (pCi l^{-1})		N	Suspended Solids (pCi l^{-1})		Total
		$\bar{X} \pm \sigma_{\bar{x}}$	Range		$\bar{X} \pm \sigma_{\bar{x}}$	Range	(pCi l^{-1})
Stream Head	3	0.09±0.01	0.08-0.09	3	0.12±0.08	0.04-0.28	0.21±0.08
Flume	13	0.19±0.03	0.06-0.48	13	0.03±0.01	0.01-0.13	0.22±0.03
Farm	3	0.04±0.01	0.03-0.05	3	0.03±0.01	0.01-0.04	0.07±0.01
Opposite Ridge	8	0.04±0.01	0.02-0.09	5	0.10±0.07	0.02-0.04	0.14±0.07
North Stream	10	0.10±0.01	0.05-0.18	7	0.04±0.01	0.03-0.07	0.15±0.02
Confluence	2	0.09±0.03	0.04-0.15	3	0.07±0.02	0.04-0.12	0.16±0.04

Table V. Radium-228 in surface waters.

Location	N	Soluble Fraction (pCi l^{-1})		N	Suspended Solids (pCi l^{-1})		Total
		$\bar{X} \pm \sigma_{\bar{x}}$	Range		$\bar{X} \pm \sigma_{\bar{x}}$	Range	(pCi l^{-1})
Stream Head	3	0.90±0.20	0.49-1.13	3	0.43±0.36	0.04-1.14	1.33±0.41
Flume	12	1.70±0.30	0.19-3.32	13	0.55±0.12	0.16-1.67	2.24±0.30
Farm	3	1.00±0.70	0.20-2.33	3	0.78±0.28	0.24-1.19	1.78±7.27
Opposite Ridge	8	0.33±0.11	0.05-0.89	6	0.39±0.08	0.14-0.68	0.72±0.14
North Stream	9	0.91±0.28	0.14-3.00	7	0.73±0.20	<0.14-1.56	1.7 ±0.36
Confluence	2	0.38±0.07	0.30-0.46	2	0.34±0.10	0.24-0.43	0.72±0.12

Table VI. Radium specific activities in suspended solids.

Location	N	^{228}Ra (pCi g^{-1})		N	^{226}Ra (pCi g^{-1})	
		$\bar{X} \pm \sigma_{\bar{X}}$	Range		$\bar{X} \pm \sigma_{\bar{X}}$	Range
Stream Head	3	57± 11	40- 78	3	12.27± 2.90	7-18
Flume	13	283± 87	41-1023	13	15.01± 4.95	4-70
Farm	3	166±115	40- 396	3	6.16± 2.24	2-10
Opposite Ridge	6	98± 29	22- 203	6	18.00±10.3	3-69
North Stream	7	277± 94	49- 650	7	19.02± 1.37	14-23
Confluence	2	83± 36	48- 120	2	19.52± 0.32	8-31

Table VII. Radium-228 mobilization rate by solubilization under baseflow regime.

^{228}Ra in the ore body	3.29×10^{15} pCi
Annual South Stream baseflow at the flume	4.75×10^{8} l a^{-1}
Net mean soluble ^{228}Ra concentration at the flume	1.37 pCi l^{-1}
Soluble ^{228}Ra annual flux	6.51×10^{8} pCi a^{-1}
^{228}Ra mobilization rate by solubilization	2.0×10^{-7} a^{-1}

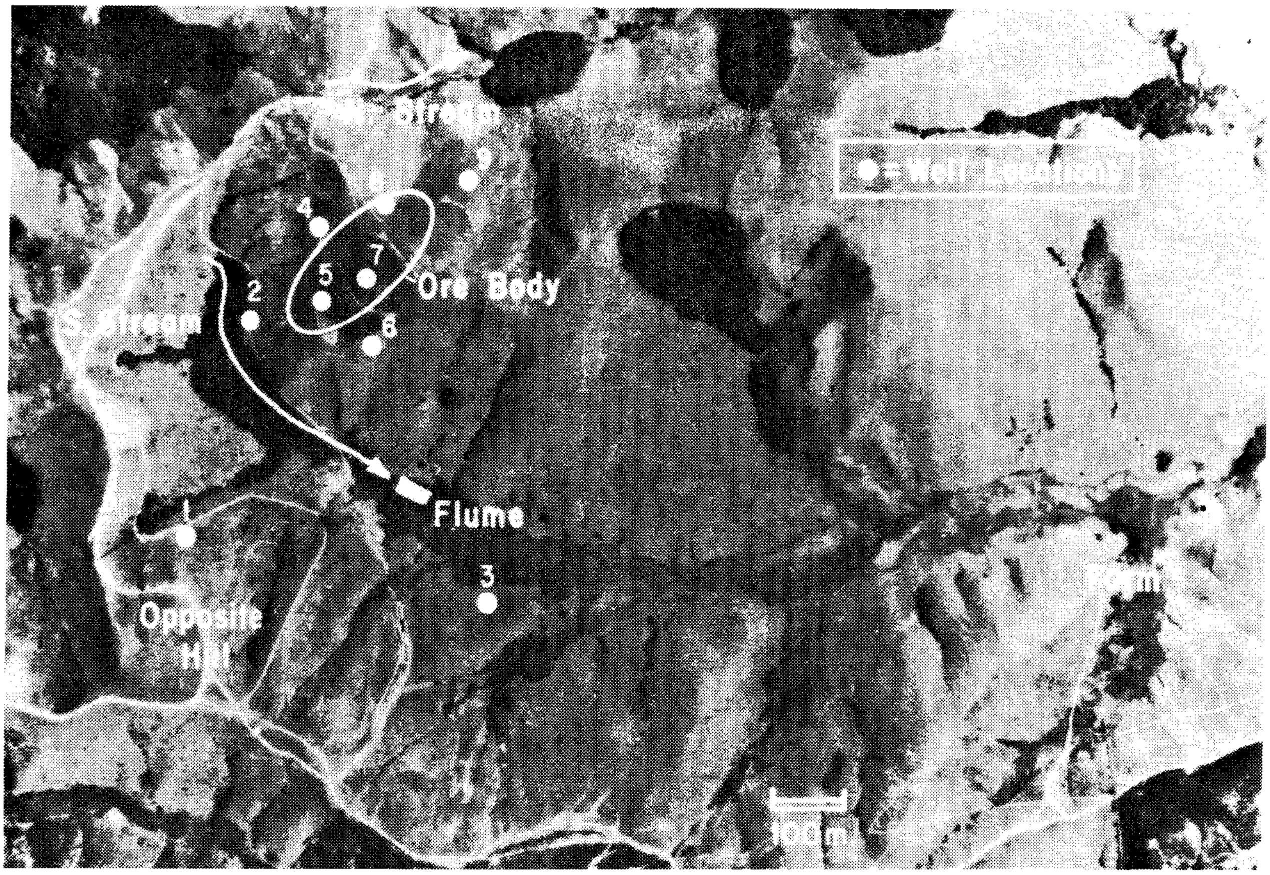

Figure 1. Aerial view of the Morro do Ferro and immediate environs showing the main features discussed in the text.

DISTRIBUTION AND MOBILIZATION OF CERIUM, LANTHANUM AND NEODYMIUM IN THE MORRO DO FERRO BASIN, BRAZIL

W. Lei[1*], P. Linsalata[1], E. Penna Franca[2] and M. Eisenbud[1].

[1] New York University Medical Center, Institute of Environmental Medicine, New York, USA.

[2] Federal University of Rio de Janeiro, Rio de Janeiro, Brazil.

ABSTRACT

The distribution of the light rare earth elements (REE) Ce, La and Nd in the Morro do Ferro ore body and drainage basin is presented. The ore body, which contains an estimated 30,000 metric tons of Th and more than 100,000 metric tons REE, is located near the summit of the hill. The REE are chemically similar to the trivalent actinides and therefore can be studied as analogues for certain of these elements.

Cerium is concentrated in the surface (i.e., 0-50 cm) layer of both the ore body and the drainage basin. There appears to be an association between Ce and Th and also between Nd and La in samples collected from the surface and at depths extending to 60 meters. Enrichment of Ce is especially evident in soils over the ore body while La and Nd appear to be depleted in this zone.

The mobilization rate of lanthanum by ground water solubilization is tentatively estimated to be 1.8×10^{-9} y^{-1}, which is very close to the rate previously estimated for Th. The mobilization rate of La due to stormflow erosion is on the order of 10^{-6} y^{-1} and is similar to that reported earlier for Th.

INTRODUCTION

Americium and curium are trivalent actinides which are present in notable quantities in high level nuclear waste (HLW). Since these elements have existed for only about 40 years, it is not possible to study their behavior in the environment over the periods of time required to assure the safety of HLW stored in a deep geologic repository. In the case of the trivalent actinides, it is both convenient and important to draw inferences regar-

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* Present Address: Carolina Power and Light Co., New Hill, North Carolina, U.S.A.

ding their mobility via the use of natural chemical analogues, such as memebers of the rare earth element (REE) family.

It is the objective of this paper to describe the distribution of Ce, La and Nd in the Morro do Ferro environs and to estimate La mobilization by physical and chemical processes. Finally, the utility of using naturally-occurring REE as chemical analogues for studying the behavior of the trivalent actinides in the environment is discussed.

The Morro do Ferro Basin

The general features of the Morro do Ferro (MF) basin and its environs have been described elsewhere (Frayha, 1962; Penna Franca et al., 1965; Wedow, 1967; Eisenbud et al., 1984; Lei, 1984). The following summarizes the salient characteristics.

The MF is a hill nearly at the center of the Poços de Caldas plateau in the State of Minas Gerais, Brazil, about 320 km WNW of Rio de Janeiro. The 35 km diameter, roughly circular plateau is underlain by alkalic intrusive and extrusive rocks and is noted for its uraniferous, thoriferous, and bauxitic regions. The MF, which rises about 140 m above its base, is near the middle of the principal thorium-rich area. Straddling the summit of the hill is an ore body enriched in thorium (up to 2%) and REE (up to 5%). The deposit is approximately 150 m at its widest point and 320 m in maximum length (Fig. 1; also, Frayha, 1962; Wedow, 1967) and extends from the surface to a depth of about 100 m. The south face of the MF forms the northern boundary of a shallow drainage basin through which flows a stream (the "South Stream") that rises from the foot of the hill. This creek flows in an easterly direction toward the only surface outlet in the basin. About 0.75 km downstream from the head of the stream is a swamp that serves as a catchment for sediment and bankwash from upstream sources.

Upstream of the point marked "Flume" in Figure 1, the basin is about 0.5 km^2 in area and is free of impoundments. The South Stream baseflow discharge is sustained by ground water seepage which averages 1,300 m^3/day in a typical year. During the rainy season of October through March, stormflow can rapidly increase the discharge manyfold before returning to the base level, after several hours of dry weather. The ground water regime has been studied using nine wells drilled in and around the ore body (Figure 1).

METHODS

Lanthanum Mobilization Rate

Preliminary estimates of the mobilization of La from the ore body have been given in an earlier paper (Eisenbud et al., 1984). The method assumes a first order model where the fractional removal rates result from erosion of La bearing particulates from the ore body surface during rainstorms and by dissolution in ground water.

The quantity of La removed from the ore body by erosion and dissolution was obtained by sampling and integrating the flow of the South Stream at a flume constructed downstream of runoff and seepage from the ore body (Figure 1). Flow measurements were made in the calibrated flume using a recording flowmeter. Sampling and measurements were conducte for a 12-month period in 1981-1982. Lanthanum removal by stormflow erosion was estimated by measurement of South Stream suspended solids (> 0.45 μm) in three storms during which the flow varied from 3 to 50 m^3/min. The relationship between flow and La flux in suspended solids was obtained and the quantity transported annually was estimated by integrating the annual stormflow in the South Stream. The La quantity removed by dissolution was quantitated by measuring the concentration (< 0.45 μm) in South Stream baseflow and integrating the annual baseflow in the channel.

Solid samples were obtained from well cuttings, solids, and sediments to a distance of 2 km downstreamm of the MF. The wells were drilled to depths of 20-60 m and representative samples of the cuttings taken every 1-4 m depending on the well depth.

Analytical

Twenty-liter stream water samples were pressure filtered through 0.45 μm membrane filters (Millipore). REE analysis in filtrates and filtered solids was accomplished using inductively coupled plasma spectrometry (ICPS). In this method, thorium and the REE were separated from the sample matrix by calcium oxalate coprecipitation following lithium borate fusion (Crock and Lichte, 1982). The REE were concentrated by cation exchange (BioRad^R AG-50W-X8) and then eluted with 8 M HNO_3 and analyzed by ICPS. Analytical yields were determined using a ^{144}Ce tracer.

An X-ray fluorescence (XRF) method was used to quantitate Th, La, Ce, and Nd, as well as Sm, Gd, Dy, Yb, Pr and Eu, in soil and sediment samples (Laurer et al., 1982). The typical sample size was 7.0 g and the typical counting time was 1,000 sec. Sensitivity for the light REE by XRF was typically 10 μg/g. The system was standardized, and investigated for accuracy and precision as a part of a previous study (Furfaro, 1982). Discussed in that reference are the self-adsorption and enhancement correction routines that were developed specifically for the laterized soil and sediment samples from the MF region.

RESULTS

Distribution of Nd, La and Ce in the Basin

Results of Nd, La and Ce measurements in soils, sediments and well spoils are presented in Tables 1 to 9. Thorium data are included for comparison. Mean values for all data have been reported with their associated standard errors (SE = $\sigma/n^{1/2}$). The distribution of these elements is described for three regions: ore body, swamp and the remaining basin to a distance of about 2 km from the South Stream head. The analysis is further separated into samples taken at all depths (Tables 4 through 6) and those samples collected in the surface soil to a depth of no more than 50 cm (Tables 1 through 3).

Table 4 shows that concentrations of the REE to depth in the ore body are higher than in the non-ore body basin by factors of 5 to 8. For comparison, the thorium concentration in the ore body was 37 times higher on average than in the non-ore body region. The swamp concentrations of REE and Th were similar to those found elsewhere in the non-ore body portion of the basin. Cerium concentration at the ore body surface was higher than at depth. The reverse was found for La and Nd.

Tables 2 and 5 give the mean ratios of La, Ce and Nd to Th. Only small differences were observed in the Ce/Th ratio between all regions and in the surface and at depth whereas the mean Nd/Th and La/Th ratios in surface samples were less than half the ratios observed at all depths. Especially marked decreases in the mean Nd/Th and La/Th ratios were seen in ore body soil. In contrast, the mean Ce/Th ratio increased in ore body surface material. The fact that the mean Th concentration is apparently not different at the surface and to depth (cf. Tables 2 and 4), suggests that Ce is being concentrated at the surface and that both Nd and La are being depleted with respect to Th.

As percentages of the total concentrations of the 9 REE measured in well spoils taken from the ore body (i.e., wells 5-9), La + Ce + Nd account for 89-94%. As shown in Figure 2, the relative enrichment of La, Ce and Nd in ore body well spoils is especially pronounced when compared to chondrites or North American shales and, in certain samples, e.g., well 5, resembles bastnaesite which has been identified at the MF (Wedow, 1967).

The relative abundance of Nd, La and Ce (Table 6) indicates that for samples collected at all depths, the proportions of Nd:La:Ce was close to 15:35:50 in all regions. The relative REE proportions in surface soil were closer to 10:30:60 (Table 3) indicating Ce enrichment or Nd and La depletion. The largest Ce enrichment was observed in ore body soil (6:12:82).

The chondrite normalized concentrations of La, Ce and Nd for well 5 spoils are plotted against depth in Figure 3. The relative enrichment of Ce in the surface 5 m is very evident. Below this depth to a maximum sampling depth of 27 m, the normalized La concentrations generally exceed Ce. Several of the other well profiles also resemble this pattern. It is likely that weathering has caused a fractionation among the REE at the MF, tending to deplete Nd and La and reconcentrate Ce (as CeIV) in the near surface regions.

The distribution of Nd, La, Ce and Th in samples of suspended solids collected during three storms at the South Stream is shown in Tables 7, 8 and 9. The results are of particular interest since stormflow suspended solids represent a "bridge" between upstream sediment sources and downstream deposition areas such as the swamp. Thus, the concentrations and relative distributions in the suspended solids can give some idea of the sediment origin, i.e., ore body or non-ore body sediment sources.

Comparison of Tables 4 and 7 suggests that the mean Th and REE concentrations in the 12 suspended solids samples were more similar to the mean concentrations observed in the non-ore body basin and swamp regions than in the ore body. This indicates that the solids transported from the ore body surface are diluted with lower Th and REE concentration particulates. In addition, the presence of prospect trenches (~1 x 1.5 x 100 m) that have girdled the south face of the MF since 1955, further mask the high Th and REE concentration soil being washed down to the South Stream channel.

The mean proportions of Nd:La:Ce in suspended solids is about 10:26:64. This, again, shows the relative Ce enrichment and/or La and Nd depletion making this parameter in suspended solids more characteristic of upstream non-ore body, surface zone material than media sampled at depth.

The simple correlation coefficient for thorium concentration versus the concentrations of La, Ce and Nd are presented in Table 10. The analysis shows that in all three regions Th correlates best with Ce ($0.69 < r < 0.75$). Fair correlations were seen between Th and La or Nd ($0.50 < r < 0.56$) in the ore body but poor correlations ($0.04 < r < 0.32$) observed in the non-ore body region. In the swamp, thorium concentration correlated well with all three REE. The good correlation between Th and Ce in all regions suggests that Ce may exist predominantly as Ce(IV).

The fact that there is a fair to good correlation of La and Nd with Th in both the ore body and swamp suggests that the distribution of these elements in the swamp muck has been influenced more by soil material originating from the ore body than from the non-ore body portion of the basin. This is not inconsistent with the earlier observation that the Nd/Th, La/Th and Ce/Th ratios in recent stormflow suspended solids reflect more the non-ore body surface ratios because the material sampled in the swamp (e.g., to depths of $\leq$ 3.5 m) is clearly much older than the current origin of the 12 stormflow suspended solids (Lei, 1984).

Lanthanum Mobilization by Rainfall Erosion

The mean La concentration in suspended solids for 12 samples collected during three storms at the South Stream flume was 560 ± 40 µg/g, and varied from 114 µg/L to 1,043 µg/L. The rate of La transport ranged from 824 mg/min to 38,960 mg/min and is highly correlated with flow rate as shown in the following equation (r=0.88).

$$\phi_{La} = 223\ Q^{1.28} \qquad \text{(Eq. 1)}$$

where: ϕ_{La} = Transport rate for La in the filterable fraction (mg/min) and

Q = Discharge (m^3/min).

Using Eq. 1, the total La transported in stormflow suspended solids during a total of 74 storm days (1981-82 rainy season) is estimated to be 63 kg. The La quantity in the ore body was calculated using the average La concentration of 4,340 µg/g observed in 101 samples (Table 4) collected within the deposit, an estimated ore body volume of 0.0062 km^3, and a density of 2.5. This gives an estimate of 67,300 MT of La in the deposit. Thus, 0.063 $MT \cdot yr^{-1}/67{,}300\ MT = 9.3 \times 10^{-7}\ yr^{-1}$ is the annual mobilization rate by stormflow erosion from the entire region upstream of the flume. Based on the relative proportions of surface area and surface concentrations of La upstream of the flume but outside of the area subtended by the ore body, the actual ore body contribution to the La mobilization rate is about 38%. Applying a 1.25 correction factor (Lei, 1984) for La lost from a smaller stream that drains the north face of the MF, the estimated mobilization rate from the ore body is:

$$(9.3 \times 10^{-7}\ yr^{-1})\ (1.25)\ (0.38) = 4.4 \times 10^{-7}\ yr^{-1}$$

This rate is similar to the $6.8 \times 10^{-7}\ yr^{-1}$ that was estimated for Th by the same removal pathway in an earlier study (Eisenbud et al., 1984).

La Mobilization by Ground Water Transport

The mean concentrations of La and Ce for 17 samples of South Stream baseflow (< 0.45 µm) were 0.31 ± 0.04 and 0.81 ± 0.09 µg/L, respectively. No ground water measurements are available but since South Stream baseflow is sustained by ground water seepage, these values should be representative of ground water concentrations. This is supported by the observation (Lei, 1984) that the mean concentration of "dissolved" Th in MF ground waters was only a factor of two greater than the mean value observed in South Stream filtrates during baseflow periods.

Because "dissolved" La concentrations have demonstrated little variability during baseflow, it is possible to estimate the quantity of La transported annually from regions upstream of the flume by ground water solubilization in the following manner:

$$(0.31\ \mu g/L)\ (1.300\ m^3/day)\ (365\ day/yr)\ (10^3\ L/m^3)\ (10^{-6}\ g/\mu g) = 147\ g \cdot yr^{-1}$$

Thus, mobilization of La by this pathway is:

$$\frac{1.47 \times 10^{-4}\ MT/yr}{67{,}300\ MT} = 2.2 \times 10^{-9}\ yr^{-1}$$

Based on proportionalities of the volumes in contact with ground water and La concentrations within the ore body and non-ore body volumes upstream of the flume, abut 68% of the La mobilized annually is attributable to the ore body. Applying this factor and the 1.25 factor for transport from the north slope, the mobilization rate of La from the ore body by ground water solubilization during baseflow is about $1.8 \times 10^{-9}\ yr^{-1}$. This rate is close to that observed for Th ($9.2 \times 10^{-10}\ y^{-1}$).

DISCUSSION

REE concentrations in soils and rocks are generally uniform at maximal concentrations of several hundreds of µg/g but usually < 150 µg/g (Schultz, 1965; Connor and Shacklette, 1975; Yliruokanen, 1975). Typically, REE are precipitated as carbonates and hydroxides in neutral to alkaline soils and are strongly adsorbed by clays and oxides in acidic soils. These mechanisms effectively limit the mobility of REE in the soil column and undoubtedly play an important role at the MF.

Elevated concentrations of REE and Th are observed in the MF basin downstream of the ore body. Since we have observed elevated concentrations of Th and the light REE in farm soils of the Poços de Caldas plateau sampled more than 10 km away from the MF (e.g., 2-9 times greater than U.S. soils; Eisenbud and Penna Franca, 1984), it is probable that soil enrichment within the MF basin has resulted from both physicochemical dispersion from the ore body and the natural enrichment present throughout the plateau. Because of our inability as yet to identify the original mineral(s) containing the REE and Th, it has not been possible to identify the weathering sequence that has led to the present distribution of these elements in the basin (Eisenbud et al., 1982; Wedow, 1967).

It is clear that some fractionation of the light REE has occurred in the basin. The depth distributions shown in Figure 3 suggest that Nd and La are distributed nearly identically while Ce is distributed differently especially in the near-surface material. This may be explained by the ability of Ce to coexist as Ce(III) and Ce(IV). Both La and Nd occur only in the (III) valence; thus, where Ce is expected to be reduced, these REE should have similar mineralogic distributions.

The presence of cerianite at the MF is proof that Ce(IV) exists at the surface environs in the basin (Frondel and Marvin, 1959). In the tetravalent form, Ce would tend to show chemical behavior analogous to Th(IV), i.e. exhibit similar hydrolytic tendencies, undergo similar lattice substitutions, etc. and in this way share the same distribution and limited mobility as thorium. The stability of the Ce/Th ratio in the surface layer and at depth in the MF basin suggests that Ce oxidation is probably occurring in the subsurface areas of the basin. In support of this suggestion, we note that the stability field of Ce(IV) (Brookins, 1983) encompasses the range of pH (5.3 - 8.4) and Eh (several hundred millivolts) measurements reported by Lei (1984) for several ground water samples at wells 5 and 6.

The immobility of La from the deposit is evident and is on the same order as for Th (Eisenbud et al., 1984). Even under sub-tropical weathering conditions, one can calculate residence times for La at MF which are quite long. This gives some assurance that long-lived isotopes of Cm and Am (e.g., ^{245}Cm) which would be expected to behave similarly, would decay in situ if emplaced under similar conditions as exist at MF. The majority of the La that is being transported from the ore body is by surface erosion, a condition that is very unlikely in nuclear HLW repositories proposed for 600 to 1,000 m depths (DOE, 1980).

Although REE fractionation has occurred in the MF basin, it is presently explained by Ce oxidation. To the extent that Nd and La are distributed similarly at least in the solid phase, it might be assumed that either could be used as an adequate chemical analogue for the trivalent actinides in transport models for HLW repositories. However, the removal pathway of concern in these models is usually via chemical dissolution and transport. It should be noted that the surface and subsurface water at the

MF consists of very dilute solutions that contain no extraordinary concentrations of organic or inorganic complexing agents (Miekeley et al., 1982; Lei, 1984). Solution concentrations and mobility of the REE and Th may be enhanced in the presence of higher concentrations of such ligands than exist at MF.

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Table 4. Distribution of Thorium and REE´s (All Depths)

Location	Mean Concentration (μg/g) ± SE				
	Th	Nd	La	Ce	n
Ore body	5,150 ± 490	2,320 ± 240	4,340 ± 410	9,360 ± 1,220	101
Basin, excluding ore body	140 ± 20	380 ± 30	890 ± 50	1,220 ± 90	104
Swamp	130 ± 15	260 ± 30	550 ± 50	890 ± 70	40

Table 5. Mean Ratio of Nd, La and Ce to Th (All Depths).

Location	Ratio ± SE			
	Nd/Th	La/Th	Ce/Th	n
Ore body	1.1 ± 0.2	2.3 ± 0.4	2.4 ± 0.2	101
Basin, excluding ore body	6.9 ± 1.4	13.0 ± 1.8	11.5 ± 0.6	104
Swamp	2.5 ± 0.3	5.0 ± 0.5	8.5 ± 0.7	40

Table 6. Nd, La and Ce Abundances Relative to Each Other (All Depths).

Location	Mean % of Total* ± SE			
	Nd	La	Ce	n
Ore body	16.3 ± 1.1	31.8 ± 1.4	51.9 ± 2.1	101
Basin, excluding ore body	15.4 ± 0.8	37.1 ± 1.2	47.5 ± 1.9	105
Swamp	14.7 ± 0.7	31.3 ± 1.1	54.0 ± 1.7	40

* Total = [La] + [Nd] + [Ce].

Table 7. Concentration of Th, Nd, La and Ce in Stormflow Suspended Solids (> 0.45 μm).

Mean Concentration (μg/g) ± SE				
Th	Nd	La	Ce	n
200 ± 15	235 ± 20	560 ± 40	1,390 ± 100	12

Table 8. Mean Ratio of Nd, La and Ce to Th in Stormflow Suspended Solids (> 0.45 μm).

Ratio ± SE			
Nd/Th	La/Th	Ce/Th	n
1.2 ± 0.1	2.9 ± 0.2	7.0 ± 0.4	12

Table 9. Nd, La and Ce Abundances Relative to Each Other in Stormflow Suspended Solids (> 0.45 μm).

Mean % of Total ± SE			
Nd	La	Ce	n
10.6 ± 0.4	25.7 ± 0.6	63.7 ± 0.8	12

Table 10. Association of Thorium with REE.

	Simple Correlation of Th Vs.			
Location	La	Ce	Nd	n
Ore body	0.53	0.69	0.50	101
Basin, excluding ore body	0.20	0.73	0.04	104
Swamp	0.73	0.75	0.62	40

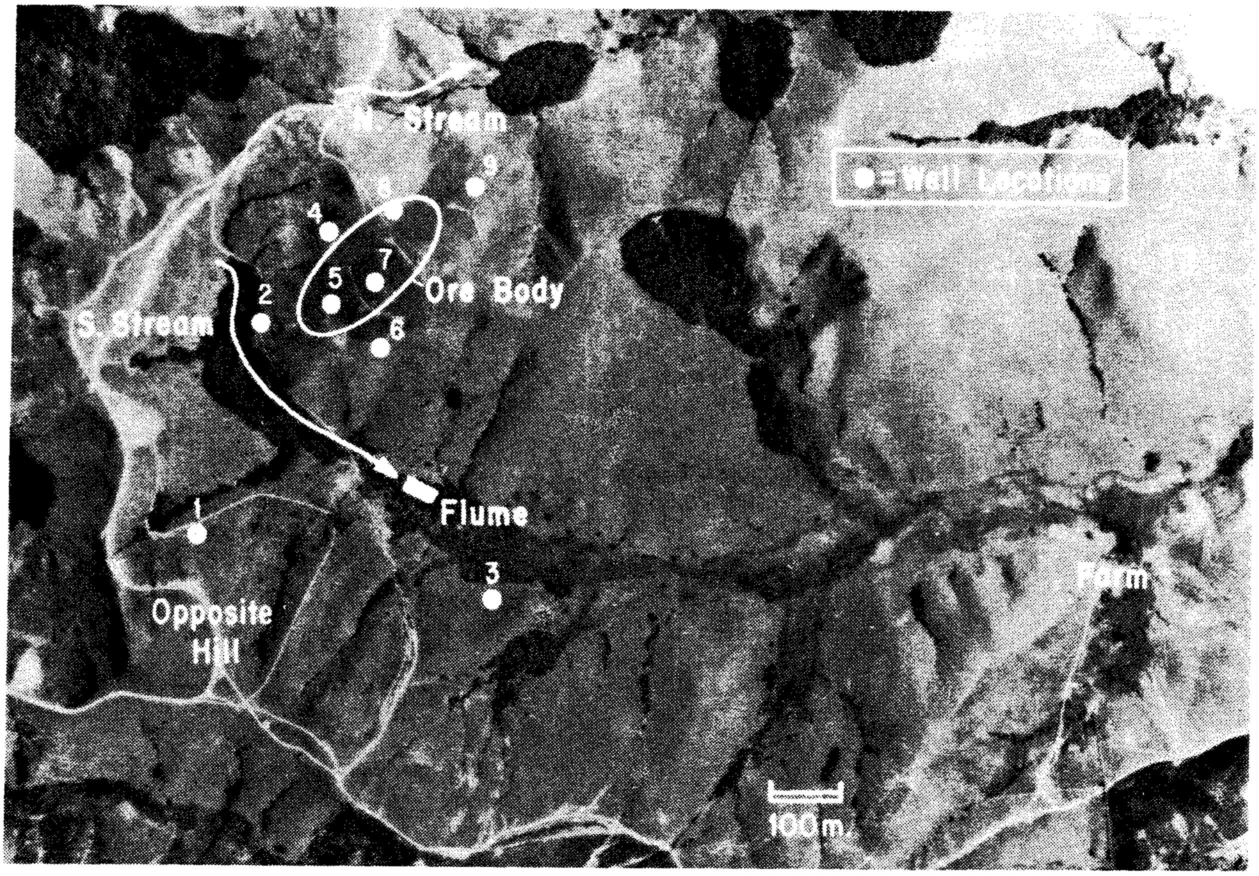

Figure 1. Aerial Photograph of the Morro do Ferro Basin.

Note: Outline of Ore Body is only approximate.

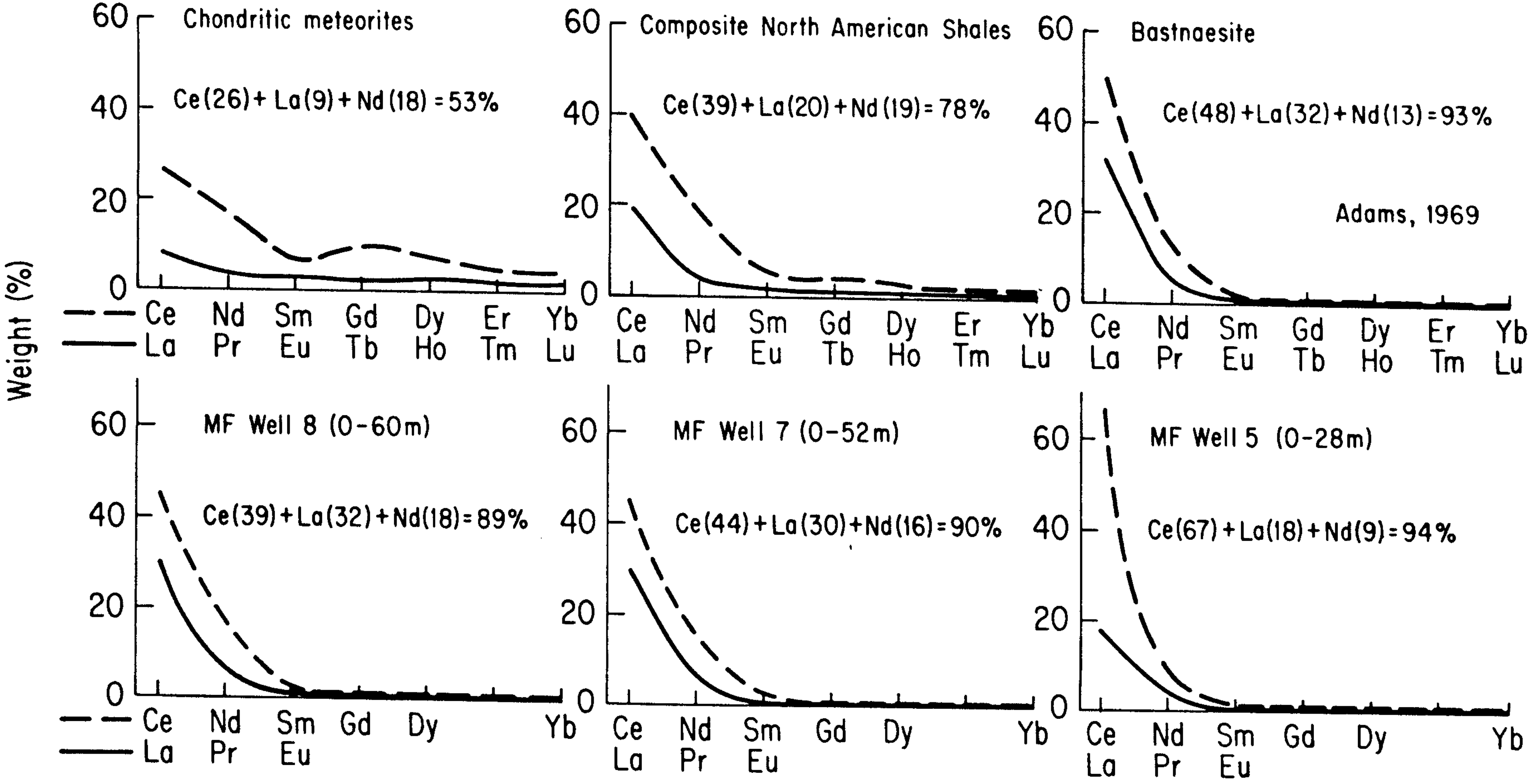

Figure 2. Rare earth element distributions in Morro do Ferro well spoils and other minerals.

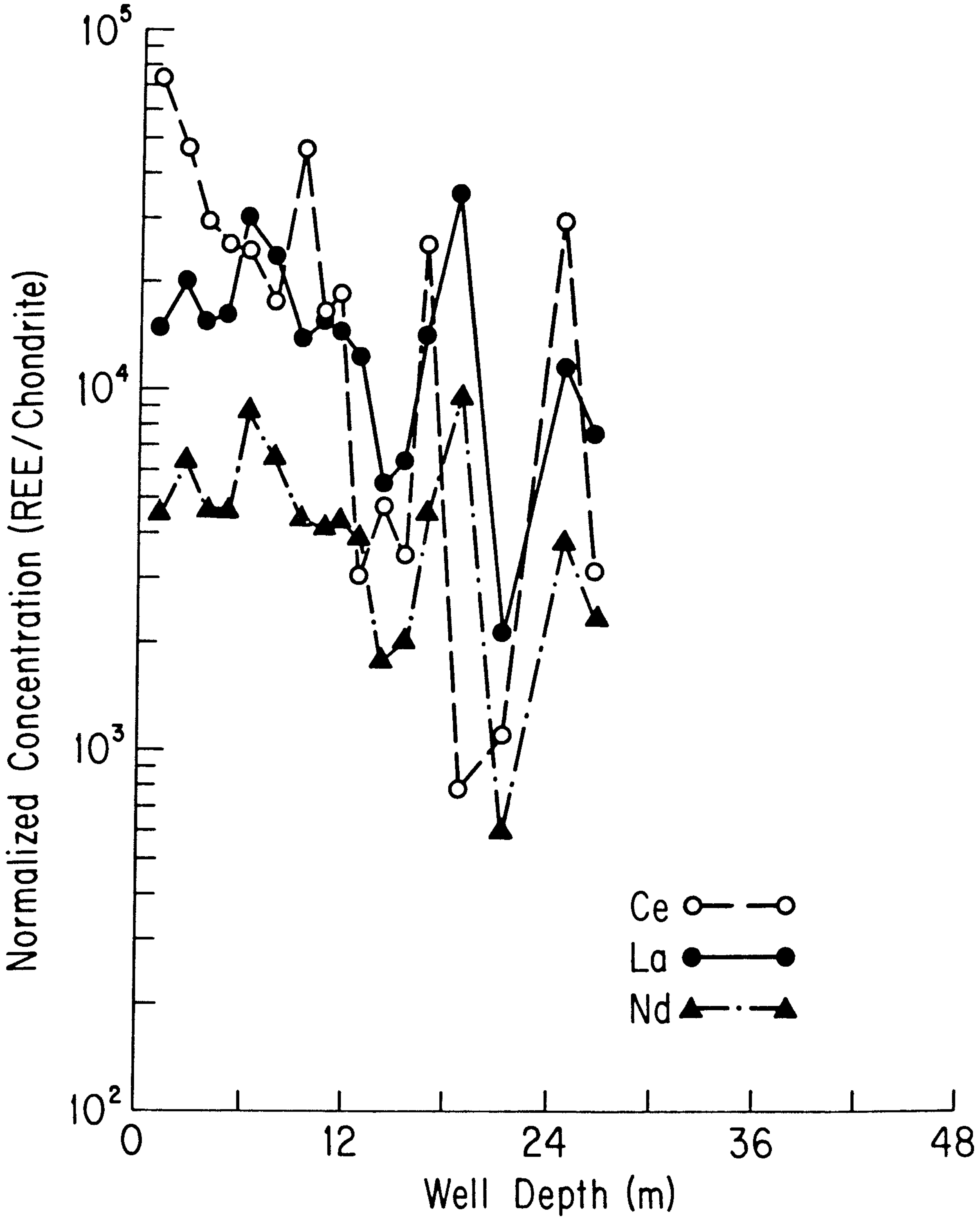

Figure 3. Chondrite-Normalized Depth Profiles of Ce, La and Nd in Morro do Ferro Well 5.

NATURAL ANALOGUE STUDIES: GEOLOGY AND MINERALOGY OF MORRO DO FERRO, BRAZIL

P.M.C. Barretto[1] and K. Fujimori[2].

[1] Brazilian Nuclear Energy Commission (CNEN), Rio de Janeiro, Brazil.

[2] University of Sao Paulo, Sao Paulo, Brazil.

ABSTRACT

Recent geological and mineralogical data provide a better understanding of the Th and REE rich orebody at Morro do Ferro as a possible natural analogue for high-level radioactive waste. The ore is contained in NW-SE elongated clay lenses resulting from in-situ concentration after the original host rock (54 Ma) was altered hydrothermally and later weathered. The thorium minerals consist of Zr, Ce, La and Nd rich resistates. The dominant form in which thorium is present is as amorphous complexes adsorbed on the surface of clay minerals and on Al- and Fe-hydroxides which, in this case, have provided an effective retardation factor for thorium immobilization within and away from the enriched zones. The large range of thorium concentration within short distances, the interfingering lenses and the exotic mineralogy underline the complexity of Morro do Ferro for radionuclide migration studies.

INTRODUCTION

The recommended method for confinement of high level radioactive wastes is burial in deep underground cavities where they will remain isolated from the surface environment and human activity (IAEA, 1981). The concern is that in spite of possible engineering barriers, the repository may be intruded by groundwater, and migration of radionuclides might occur in places where the long half-life radionuclides would become a harzard. Important in this context is a group of transuranic actinide elements which include Pu, Am, Cm and Nd, plus Ra, which accumulate in the waste residues.

To test the different hypotheses which may result in a potential risk to public health, mathematical models are used. These models, however, have certain limitations, some of them being the use of parameters (e.g. container corrosion rates, waste leach rates, solubilities, complexing, etc.) which are not quantitatively known. Therefore the modellers have to assume ranges for these parameters which may yield results different by orders of magnitude. A mathematical model is only valid when it represents a close approximation with reality in the natural environment.

These limitations emphasise the importance of natural analogues for high-level radioactive waste forms in order to develop a better understanding of the behavior of these wastes in the geological environment over periods of geological time. Morro do Ferro in Minas Gerais, Brazil, could be a suitable analogue for certain geological processes as Th^{4+}, under certain conditions, can be analogous in its behavior to Pu^{4+}, and Nd^{3+} to Am^{3+} and Cm^{3+}.

The possibility that Morro do Ferro might be used as a natural analogue for plutonium and other actinide elements was first discussed in 1979 by Eisenbud (1979). Since then the mobility of thorium from Morro do Ferro has been the subject of a joint investigation by the Institute of Environmental Medicine of the New York University and the Institute of Biophysics, Federal University of Rio de Janeiro, in association with other research institutions in Brazil. This joint project entitled "Mobility of thorium from Morro do Ferro", still under implementation, has produced several technical reports covering mobilization rates, geochemical studies, hydrology and speciation (Eisenbud, 1982). The interpretation of the results, however, has been hampered by the lack of adequate surface and subsurface geological information. Geologic observations are difficult due to the intense and deep surface weathering of Morro do Ferro, further altered by hydrothermal and tectonic processes.

This paper discusses recent geological and mineralogical information and provides an overview of the Morro do Ferro thorium and REE orebody.

GEOLOGY

Previous Work

Located in southeastern Brazil about 270 km west from Sao Paulo (Figure 1) and 15 km south of Poços de Caldas, the Morro do Ferro (Iron Hill) received its name from the thick magnetic dykes which outcrop at its summit and southern slopes; these dykes were once considered as a potential source of iron ore. Morro do Ferro is located in the center of a deeply eroded alkaline caldera of 34 km diameter and 1300 m average altitude, known as the Poços de Caldas plateau. It also constitutes the highest topographic expression within the caldera reaching an altitude of 1541 m. The caldera geology, due to its exotic type of alkaline rocks and ores (the Zr-rich "caldasite"* and REE ores) has attracted interest and has been described by many geologists (Derby, 1887; Gorsky and Gorsky, 1974; Ulbrich, 1983). It has been studied in detail by the Brazilian Nuclear Energy Commission (CNEN, 1974) and NUCLEBRÁS (NUCLEBRÁS, 1978) in their search for uranium.

The extensive radioactivity in the plateau was noticed in 1953 during an aerial radiometric survey when several anomalies were found within the caldera; this included Morro do Ferro. Ground investigations confirmed a large and strong radiometric anomaly (0.8 km^2 with 150 mR/h and a central zone with more than 1% ThO_2) associated with lateritic soils and rare-earth elements (Figure 2).

During the 50´s and early 60´s Morro do Ferro attracted the attention of uranium prospectors (Tolbert, 1955; Frayha, 1962) due to its high surface radioactivity over such a large area. This high natural radioactivity also attracted the interest of radiobiologists who studied the plants (so radioactive that they can be autoradiographed), the exposure of indigenous borrowing rodents to thorium and its daughter products (Drew and Eisenbud, 1966), and the uptake of radium-228 by flora and fauna.

Several internal reports were submitted to the Brazilian National Research Council (CNPq) then in charge of exploration of nuclear raw materials and to the Departamento Nacional da Produção Mineral (DNPM)), equivalent to a National Geological Survey. Of this early work very little has been published. The most comprehensive report from this period is the work of Wedow (1967) who was part of a USGS team of geologists working for CNPq in a joint programme of uranium exploration in Brazil.

Considerable ground investigations were carried out on Morro do Ferro in the late 50´s and early 60´s. DNPM bored more than 100 auger and diamond drill holes to depths of 5 to 100 m. A 180 m long adit was driven by the DNPM along the trend of the orebody and parallel to one of the magnetite dykes. Another adit, closer to the foot hill, was abandoned due to continuous wall collapsing. Surface work included some 500 m of trenching complemented by pits.

The range of thorium concentrations found in 431 trench channel samples within the ore zone was 0.1 to 2.9% ThO_2 and a fairly good agreement was reported for the radiometric and chemical analysis (Wedow, 1967). Uranium concentrations varied from 40 to

* Caldasite is an intergrowth of ZrO_2 (baddeleyite) and $ZrSiO_4$ (zircon) with 40-65% zirconium, 0.25% uranium and 0.80% thorium. The name comes from the locality: Poços de Caldas (caldas = caldasite).

260 ppm and for REE the range was 1.5 to 21.1%. With respect to mineralogy the reports mention kaolin, hydromica, some gibbsite and limonite in certain samples and magnetite. Among the Th-bearing rare-earth minerals bastnaesite was identified in 1954 (Spengler et al., 1954), thorogummite and allanite in 1955 (Tavora, 1955) and cerianite in 1959 (Frondel and Marvin, 1959).

The results of the sampling, the gamma-ray logs plus the Th and REE chemical analysis, resulted in an estimation of 30,000 tonnes of thorium (1% ThO_2) and 50,000 tonnes of REE (4% total REE) by Frayha (1962) and about 15,000 tonnes ThO_2 by Wedow (1967) depending on the depth considered.

The idea that some undiscovered uranium concentrations might exist somewhere deeper in Morro do Ferro persisted throughout a decade. By the mid 60´s it was verified that 1) Morro do Ferro did not conceal any uranium mineralization of interest; 2) that no perspective existed for the use of thorium in the immediate future, and 3) the REE ores were very refractory to conventional extraction methods making their recovery costly. As a consequence, all exploration activities ceased leaving the site untouched until the radioecology investigations mentioned above.

Recent Investigations

The suggestion that Morro do Ferro might be a natural analogue to a radioactive waste repository (and that this possibility should be investigated) renewed the interest on the local geology and hydrological conditions. In 1981 nine holes were drilled in the site by CNEN, five of them through the ore zone with the primary objective of studying water percolation through the ore and the local hydrological pattern. The location of these holes is given in Figure 3 and indicated as SR-1 to SR-9; core recovery for these nine holes was poor due to the intense weathering. Most of the results reported below are based on the analysis of the clay core materials, interpretation of the gamma-ray logs, plus CNEN and NUCLEBRÁS internal reports.

LOCAL GEOLOGY

Based on slight textural and mineralogical variations, several alkaline rock members can be identified around Morro do Ferro; the dominant types being phonolites, foyaites and tinguaites. The dominant minerals in these rocks are potash feldspar and nepheline with smaller amounts of sodic pyroxene and some biotite. The agpaitic nephelinic members (excess of alkaline elments with respect to alumina) are characterized by rare-metal silicates (like eudialite) while miaskitic varieties (excess of alumina) exhibit sphene and fluorite. Potash feldspar is usually rich in orthoclase with highly ordered microcline in coexistence with less ordered feldspars suggesting late magmatic re-equilibration. Magmatic crystallization for the fine grained rock varieties is estimated at 750 - 800°C, and near-surface temperatures for the agpaitic members (Ulbrich, 1983).

K-Ar age dating of the Plateau rocks (Amaral et al., 1967; Bushee, 1971) indicates the following magmatic chronology: ankaratrites and associated pyroclastics 87 Ma, tinguaitic intrusions 80-74 Ma, nepheline syenites including lujaurites 63-60 Ma, and phonolite dykes 54 Ma.

The country rock of Morro do Ferro itself seems to have been tinguaites. This identification is difficult as there is no fresh bedrock outcrop either on the hill, near the surface, or even down to 458 m (maximum extent of the deepest hole drilled by NUCLEBRÁS in the area; SC-038 in Figure 3). Deep weathering is known as a common factor to the whole plateau; it was revealed by more than 150,000 m drillings during the twenty years of uranium exploration. For example, at the Osamu Utsumi uranium open pit located 5 km SE of Morro do Ferro, the mineralized B^- orebody is located 200 m below the surface in an altered and fractured rock. However, nothing like the intense and deep alteration found in Morro do Ferro was known before. Core recovery at the deep hole could only start at 132 m, and the less altered cores at a depth of 426 m are described (M.J.C. Coutinho, pers. commun. 1984) as brecciated, dark coloured hydrothermalized tinguaite, with molybdenite and fluorite fracture fillings and phylosilicates (chlorite?), pyrite and gypsum crystals. In the fine trachytic ground mass feldspars (60%) are present, mostly K-rich feldspars but some albite; the remaining 40% is made up of isotropic clay aggregates (30%) resulting from alteration of nepheline and the opaque minerals, fluorite, etc. (10%).

The alkaline rocks of Poços de Caldas are anomalously enriched in thorium and uranium. Some 46 fresh samples collected at various locations within the plateau were analysed. The results of the natural gamma-ray analysis show uranium and thorium concentrations ranging up to 57 and 288 ppm, respectively (Figure 4).

The local geology and surface radioactivity according to a survey carried out by CNEN is given in Figure 2. Attention is drawn to the term "potassic rock" which is a local designation for the hydrothermally altered and weathered foyaite or tinguaite. It consists of orthoclase, sericite, quartz, and other clay minerals with accessory pyrite. The K_2O concentration may reach 10-17% in the "potassic rock" found in the plateau. For that reason it is being considered as raw material for the manufacture of K-fertilizer.

The proportion of these three minerals vary according to the place and degree of alteration. Close to the surface this alteration product is friable whereupon the pyrite is oxidized and transformed into limonite. The X-ray diffraction pattern of this "potassic rock" of Morro do Ferro is given in Figure 5, where the abundant presence of sericite and kaolin is clearly shown. Chemical analysis of the potassic rock from a nearby prospect (Campo do Agostinho) are presented in Table 1.

Soil

The surface material of Morro do Ferro is white-grey (sometimes brownish with iron staining), clayish, highly compacted, lateritic soil, 1 to 3 meters thick and full of eluvial magnetite rubble of all sizes (Plate 1). Locally it can be darker (manganese oxides) or yellowish green (more REE). This soil constitutes a cover formed by aggregates of magnetite cemented by limonite and aluminium hydroxides protecting the weathered material below. Over the ore zone this soil can be very radioactive, therefore it is considered part of the orebody (see gamma-logs for holes number SR-7 and SR-5).

Host Rock

Below the lateritic soil the nine drill holes cut through a thick zone of weathering and alteration made of a silt/clay-like material varying in colour from white/yellowish, grey, to reddish brown. None of the holes fully penetrated this alteration zone. Sometimes it is very ferruginous and with abundant veinlets of magnetite limonite (Plate 2). These colour zones are normally related to magnetite veins or dykes and might consist of alteration components.

Autoradiographs made from polished sections of the kaolinic alteration material indicated a homogeneous distribution of the radioactivity in the ground mass. Pyrite, magnetite, zircon, rutile or anatase were optically identified by Fujimori (1983) but no conspicuous radioactive minerals could be seen. Identification of the radioactive minerals was only possible using scanning electron microscope and electron microprobe techniques. The minerals consist of REE silicates, silica-rich monazite, REE and Th-rich zircon, coffinite and possibly pyrochlore as discussed later.

In this case, apart from the radioactivity, it is impossible to distinguish the host rock from the ore. Table 2 gives the chemical composition of this alteration product in the ore zone. The low concentration of silica, potassium, sodium, magnesium, as well as phosphorus and Fe^{++}, indicates a high degree of leaching. On the other hand, there is a concentration of aluminum (gibbsite) and Fe^{+++} (magnetites are oxidized to hematite and limonite). Also abundant are the low mobility elements such as titanium, thorium and certain rare-earth elements confirming the dominant oxidation conditions and residual concentration. The LOI is also noteworthy as its high value is due to the loss of water from the aluminium and iron hydroxides. The host rock/ore then is indeed a ferruginous bauxite.

MAGNETITE VEINS

Magnetite veins associated with the anomalous radioactivity are the dominant features of the surface. Major veins strike N 50-60 W (Figure 3) and dip 60-80 NE ranging from 1 to 5 m in thickness. Numerous magnetite veinlets cut randomly accross the hill, some of them completely or partially altered to limonite as shown in Plate 3. Small manganese concentrations are present in certain veins. These veins (dykes?) and veinlets are present throughout Morro do Ferro, but they seem more abundant on the SE slopes. In the interpretative geologic sketch of Morro do Ferro given in Figure 6 the abundance of such magnetite veins can be observed in the lithological log. Only the major veins are indicated by their apparent thickness; due to their random nature it is impossible to estimate the true thickness. Their presence at depth, at least to 100 m, is confirmed by the recent drillings, plus the fact that the first core recovered in NUCLEBRÁS SC-038 hole revealed an 8 m thick magnetite vein at a depth of 132 m.

The abundance of such veins, their thickness and mode of emplacement, suggests that they are the backbone of a magnetite skeleton which has sustained and preserved Morro do Ferro as the highest topographic feature of the plateau. Without this skeleton and the cover of lateritic soil, the highly weathered clayish maerial of the hill would have been eroded away.

The time of the magnetite emplacement is not yet determined with respect to the chronological order of events. They could be contemporaneous with the zirconium-rich magmatic events which produced the abundant baddeleyite and veins throughout the plateau. The zirconium veins (explored from 1935 to 1963) contain uranium and thorium in such large concentrations that around the early 60´s they where considered as a possible source of uranium. Three magnetite samples from the outcropping veins at Morro do Ferro were analyzed for uranium and thorium after careful cleaning and washing to remove any surface contamination and oxidation. The results (Table 3) indicate they reflect the same elemental pattern for Morro do Ferro, i.e. low uranium and high thorium concentrations.

The question arises as to whether the magnetitic magma was already enriched with radioactive elements (as in the case of the caldasites), or, were thorium and uranium absorbed from an already existing thorium ore in Morro do Ferro? The thorium to uranium ratio favors the second hypothesis.

The role of these magnetite veins as a structural control for the Th and REE mineralization was postulated by Wedow (1967) due to the asymmetric surface distribution of the ore zones with respect to the veins. However, this type of control was not observed during subsurface drilling. The high X-ray fluorescence thorium concentrations as well as the high radiometric values on the natural gamma-ray logs for the nine recent holes have no apparent relation with the magnetites. This lack of control is evident, for example, in the NW-SE geological section of the orebody (Figure 6).

OREBODY

The search for an economic deposit of uranium, thorium or REE has been the reason for extensive surface and subsurface work at Morro do Ferro. These exploration activities were carried out by different companies and Government organizations with little or no collaboration. As the objective was ecoonomic and the ore is on the surface (at present no exploration problem) the scientific aspects of the geology of Morro do Ferro never received adequate attention. Furthermore, each group used a different topographic base which makes it difficult, if not impossible, to compare the little geological information available. As a consequence, the characterization of the orebody is far from complete. This is regarded as an important aspect to be considered in any continuation of analogue studies at Morro do Ferro.

An interpretative sketch of the orebody is given in Figure 6 which presents a longitudinal (NW-SE) and transversal (SW-SE) radiometric sections. These sections were constructed using all geological, chemical and radiometric information available to date. Not represented are the magnetic dykes as their subsurface positions are not known.

From the sections the following characteristics can be observed:

a. The orebody consists of NW-SE elongated lenses.

b. The high grade material ($> 2.0\%$ ThO_2) is not located near the top of the hill as originally thought but midway down the SE slope approximately between drill holes SR-7 and SR-5.

c. Most of the high grade material is very close to the surface (drill holes P, R and Y) and contained in the first 10 m depth.

d. Using a cut-off grade of 0.5% ThO_2 the overall dimensions of the orebody are: 410 m long, 215 m wide and 35 m thick. Using the radiometric and the X-ray fluorescence concentrations obtained for samples from the recent and old drill holes, plus the channel samples from the adit, the following thorium resources have been estimated:

$\geq$ 0.5% ThO_2	15.500 tonnes
1.0 - 1.5% ThO_2	10.400 "
1.5 - 2.0% ThO_2	5.920 "
$\geq$ 2.0% ThO_2	2.580 "
Total:	34.400 tonnes ThO_2 with an average grade of 0.9% ThO_2 or 18.900 tonnes with a grade of 1.3% ThO_2.

Attention is drawn to the fact that these figures are estimated resources and not measured reserves. This is because a) the number of drilled holes is small, b) their location inadequate, c) the distance between them too large and d) the core recovery (around 40%) is very poor for any reasonable reserve calculation. Furthermore, thorium concentrations obtained from gamma-ray logs should be confirmed by chemical analysis as radiometric disequilibrium is expected within the orebody by mobilization of Ra-226 and its adsorption on to clays and along ferruginous zones. All these factors should be considered when planning future work on Morro do Ferro.

e. The orebody shape and position (section SW-NE) suggest that it is the result of an in-situ residual concentration of previously mineralized rock.

There are other interesting points to be considered. None of the drill holes on the A-B section, or any of the other holes, completely crossed the mineralized zone. Good grade ore could exist, for example, below holes SR-7 and SR-5. It should be noted that the objective of the recent drillings (SR-1 to 9) was the hydrological studies, therefore, their location and depth were not planned to study the geological characteristics of the orebody. The fact that mineralization goes deeper is already known. Indeed, the two deeper holes (SC-038 and XIX) cut mineralized zones below 100 m; for example the 132 to 145 m interval in hole SC-038 is mineralized and the 106 to 109 m interval in hole XIX contain 0.4% ThO_2.

MINERALOGY

The identification of the mineralogy of the Morro do Ferro orebody, apart from their main constituents, has been a challenge for decades. Optical microscopy and conventional mineralogical procedures failed to identify any of the radioactive minerals as they are finely distributed within the "potassic" host rock and therefore problems of separation and concentration arise. In order to identify these minerals, the following procedure was used:

The first step was to identify the mineral fraction containing thorium. To do this the orebody samples were crushed and separated with bromoform into two density fractions. Alpha counting indicated thorium present in about identical concentrations, in both fractions. The light and heavy fractions were then separated using a Frantz magnetic separator and analyses again showed that radioactivity was present in the magnetic and non-magnetic fractions of the sample. These two experiments showed that thorium is homogeneously disseminated in the groundmass, in the silicates as well as oxides, and that it could not be separated from them. It was found later that a substantial part of the thorium is in the amorphous form and associated with the clay and iron oxides/hydroxides (surface adsorption).

The identified thorium and REE minerals separated from relatively "fresh" rock samples are of two kinds: primary and secondary.

Primary Minerals

These were formed at the time of the emplacement of the alkaline rock or by later hydrothermal processes.

Th-rich "REE silicate" (REE, Th, U, Ca)SiO_4 identified recently by Fujimori (1982) is present as very fine grains and largely distributed in the "fresh" cores with pyrite (Figure 7). This silicate seems to be the most important source of radioactivity and REE elements for the formation of the secondary minerals present in the orebody. The leaching of this silicate is accelerated by H_2SO_4 and HF produced in situ by the decomposition of pyrite and fluorite. Evidence of this process is the presence of gypsum ($CaSO_4 2H_2O$) filling fractures and open spaces occupied earlier by fluorite.

Cheralite (Th, REE, Ca, U) (PO_4, SiO_2) was found simultaneously by Freeborn (1980) and Fujimori (1983) in samples prepared from "fresh" cores. It is also found in the alteration zone above. Figure 8 shows a typical small size cheralite crystal disseminated in soil. It was identified by point analysis and scanning for thorium along the line R. Thorium and REE are also largely adsorbed in a non-crystalline form on the soil aggregates.

Monazite (REE, Th, U)PO_4 is relatively abundant. Figure 9 shows a grain of this mineral richer in Ce than La; normally it shows larger concentrations of La over Ce and Nd over Eu. Most of the monazite crystals are smaller than cheralite. The Si and P concentrations can also be sufficiently high to result in a distinct REE silicate phase.

Microlite (or pyrochlore) (Th, Ca, $REE)_2(Nb)_2O_6$(O, OH, F) was also identified although in small amounts. It is present in the sericitic matrix as indicated in Figure 10; the associated white grains are the niobates. The Al, Si and K contents of the sericite clearly appear in the X-ray spectrum.

Zircon (Zr, Th)SiO_4 is the only mineral found in Morro do Ferro with crystal faces. It should be noted that it belongs to the same mineralogic group of thorite $ThSiO_4$ (or huttonite) or thorogummite (Th, U)$(SiH_4)_8$, depending on the thorium concentration. This wide range of thorium concentration is an indication of the fast cooling of the hydrothermal fluids. The zircon crystal in Figure 11 has approximately 10% ThO_2 and almost no REE.

Allanite (Ca, Ce, $La)_2$(Al, $Fe)_3Si_3O_{12}$(O, OH) was reported by Oliveira (1956) but not confirmed by any other researcher nor observed by ourselves. Allanite is subject to alteration and leaching.

Contrary to the Th-rich REE silicates, cheralite, monazite, microlite (or pyrochlore) and zircon are refractory minerals and are therefore not susceptible to marked alteration and leaching. As a consequence they should not contribute, in substance, to the formation of secondary minerals within the orebody.

Secondary Minerals

The identification of secondary thorium or REE minerals in the soil or in the alteration zone in Morro do Ferro is not an easy task. In order to obtain an adequate sample for analysis they also must be concentrated. This was done by slight hand crushing and careful washing with distilled water. The suspended solids were filtrated through successive millipore filters of hole diameter 5, 2.5, 2.1 and 1.3 µm; the material retained in the filters was analysed by X-ray fluorescence spectrometry. La, Ce, Nd and Th were found in all filters except for the 1.3 µm. However, the absence of REE in the 1.3 µm filter does not indicate they were not present, but rather reflects the lower detection limit of the X-ray spectrometer. The very fine particles may be amorphous oxides or hydroxides of Th and REE adsorbed on clay minerals. This test confirmed that the Morro do Ferro mineralization is not only complex but also can involve very small particles, in fact smaller than one µm.

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Contrary to the Th-rich REE silicates, cheralite, monazite, microlite (or pyrochlore) and zircon are refractory minerals and are therefore not susceptible to marked alteration and leaching. As a consequence they should not contribute, in substance, to the formation of secondary minerals within the orebody.

Secondary Minerals

The identification of secondary thorium or REE minerals in the soil or in the alteration zone in Morro do Ferro is not an easy task. In order to obtain an adequate sample for analysis they also must be concentrated. This was done by slight hand crushing and careful washing with distilled water. The suspended solids were filtrated through successive millipore filters of hole diameter 5, 2.5, 2.1 and 1.3 µm; the material retained in the filters was analysed by X-ray fluorescence spectrometry. La, Ce, Nd and Th were found in all filters except for the 1.3 µm. However, the absence of REE in the 1.3 µm filter does not indicate they were not present, but rather reflects the lower detection limit of the X-ray spectrometer. The very fine particles may be amorphous oxides or hydroxides of Th and REE adsorbed on clay minerals. This test confirmed that the Morro do Ferro mineralization is not only complex but also can involve very small particles, in fact smaller than one µm.

richment process assisted by the deep weathering. This enrichment process is still active. The residual material constitutes the present orebody.

2. The dominant form in which thorium is present in the orebody is amorphous complexes adsorbed on the surface of the clay minerals and in the Al, Fe oxides and/or hydroxides. The primary minerals are thorianite, thorite, microlite, monazite, REE silicates and cheralite. The most abundant secondary mineral is thorbastnaesite.

3. Th and REE elements were found in various size fractions; those present after using the 1.3 μm millipore filters indicate the small size of the crystal and the complexity of the mineralization.

4. The Th/U ratio is very large even in the poorly mineralized rocks. This is seen as evidence of uranium removal during alteration and deep weathering processes. This ratio in the fresh alkaline rocks of the plateau varies from 0.2 - 49. In the orebody it is one to two orders of magnitude higher.

5. The effective thorium adsorption on clays from where it is difficult to be remobilized is an important point for consideration in the development of an engineering concept of waste repositories. This geochemical behavior suggests the possibility of an efficient engineering barrier for Th (and thus for Pu^{4+}) migration.

6. Although several lithological units have been mapped, only two main types of magma are tentatively identified; the miaskitic and agpaitic types. Nepheline syenites are intrusive into genetically related vulcanoclastic rocks (now mainly eroded) and the tinguaites seem to have crystallized in closed magmatic chambers at shallow depth. Morro do Ferro could be one of these chambers.

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Table 1. Average values for the "potassic" rock of Morro do Agostinho, an uranium prospect near Morro do Ferro.

Oxide	Concentration %	Oxide	Concentration %
SiO_2	50.5	SrO	0.19
Al_2O_3	21.39	As_2O_3	0.009
CaO	4.93	MoO_3	0.39
K_2O	8.96	ZrO_2	0.98
TiO_2	0.85	U_3O_8	0.11
		ThO_2	0.005

Table 2. Whole-rock composition of the high-grade Th-REE ore.

Element	Concentration %	Element	Concentration %	Element	Concentration %
SiO_2	18.9	P_2O_5	0.65	Pr_6O_{11}	0.56
Al_2O_3	26.6	TiO_2	2.00	Eu_2O_3	0.06
Fe_2O_3	22.4	CO_2	0.20	Nd_2O_3	1.40
FeO	0.6	S	0.03	Gd_2O_3	0.12
MgO	0.21	F	0.62	Dy_2O_3	0.16
CaO	0.11	ThO_2	1.30	Sm_2O_3	0.27
K_2O	2.14	La_2O_3	2.35	Yb_2O_3	0.008
Na_2O	0.06	CeO_2	3.60	L.O.I	15.4
MnO	0.76	Y_2O_3	0.22		

Source (23)

Table 3. Uranium and thorium concentrations in magnetites from Morro do Ferro.

Sample	U (ppm)	Th (ppm)
Large dyke (mid slope)	9.0 ± 0.8	357 ± 25
Near entrance of DNPM adit	19.0 ± 1.0	2170 ± 120
Dyke near hole SR-8	7.0 ± 0.5	1170 ± 80

Plate 1. Morro do Ferro lateritic soil with magnetite rubble (upper left) and the white-grey lateritic soil from trench 1 (see Figure 3). The hill is covered by scarce grass used as pasture.

Plate 2. Host rock in the DNPM adit where one can observe the intense alteration and kaolinization of the rock (lower right) and fractures penetrated by magnetite and limonite.

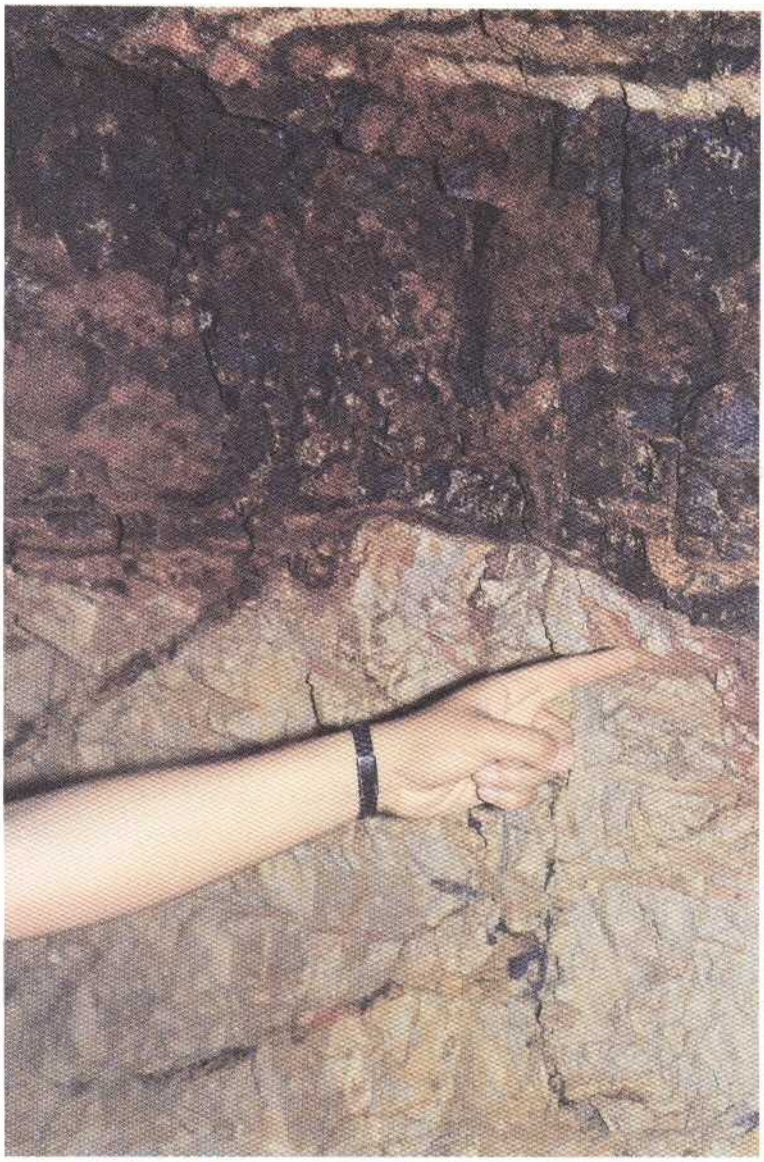

Plate 3. Magnetite dyke in the DNPM adit. The magnetite emplacement caused little contact effects on the host rock. Oxidation free zones can be found (lower right) due to the low permeability of the clays which constitute the groundmass of the host rock.

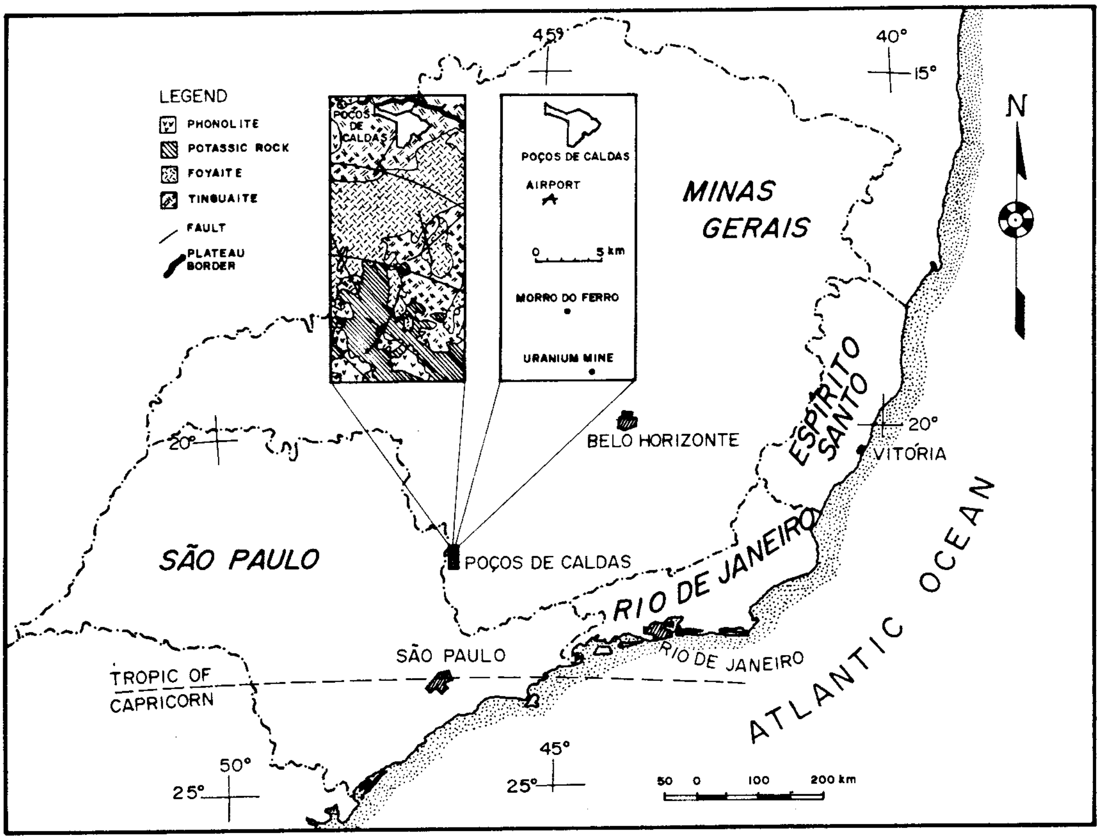

Figure 1. Location of Poços de Caldas in SE Brazil. The insert shows its approximate relation with other geological sites within the alkaline plateau.

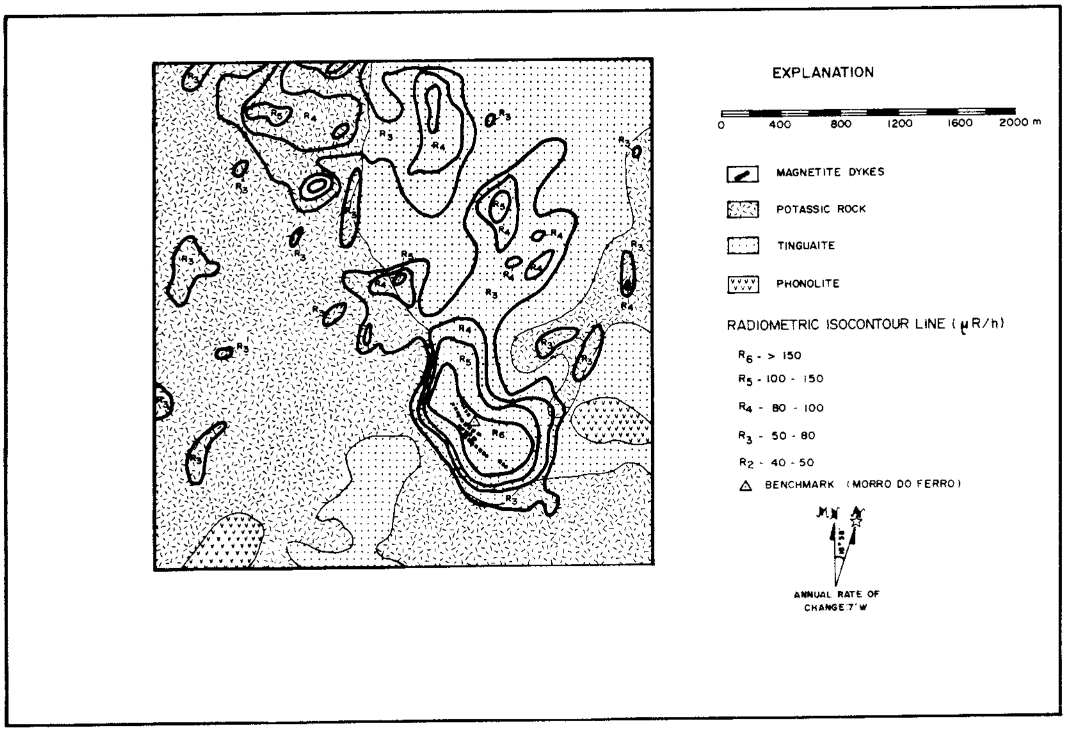

Figure 2. Radiometric isocontour map of Morro do Ferro and the near-vicinity anomalies superimposed on the local geology.

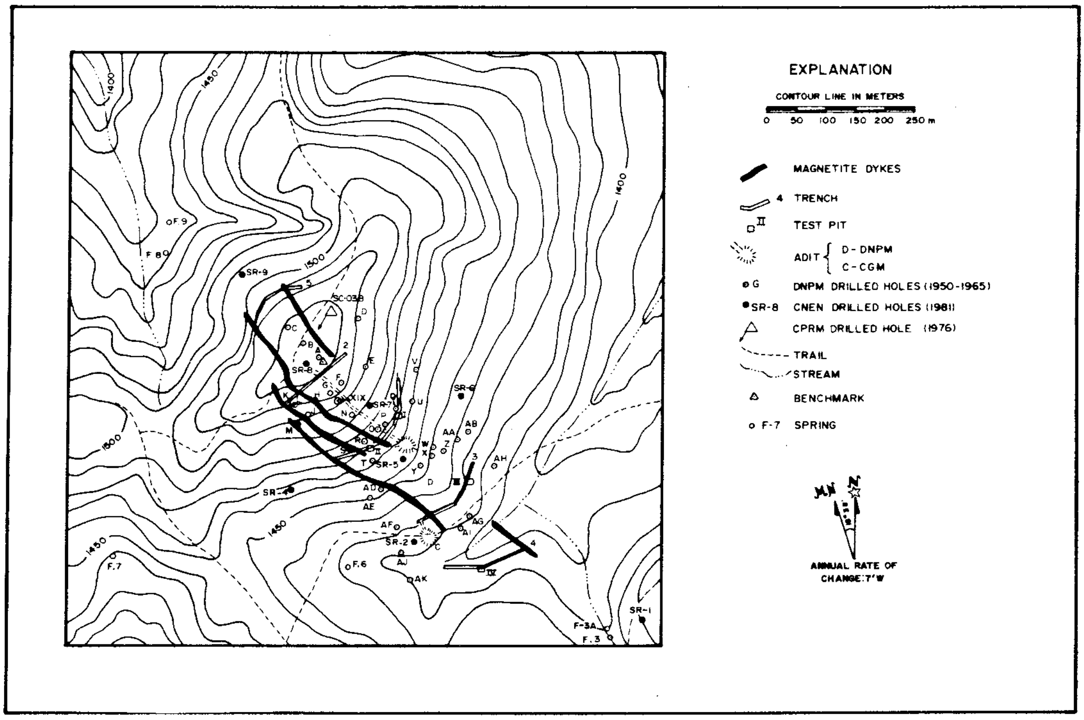

Figure 3. Topographic map of Morro do Ferro showing the approximate position of the magnetite dykes, trenchs, pits and adits from previous works and the nine recently drilled holes.

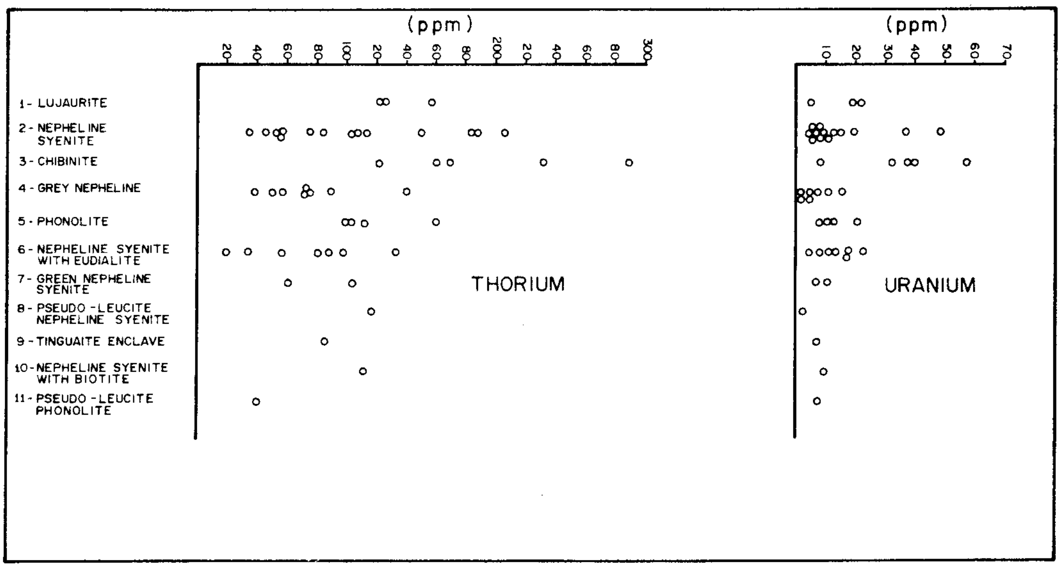

Figure 4. Range for the uranium and thorium concentrations in the alkaline rocks of Poços de Caldas.

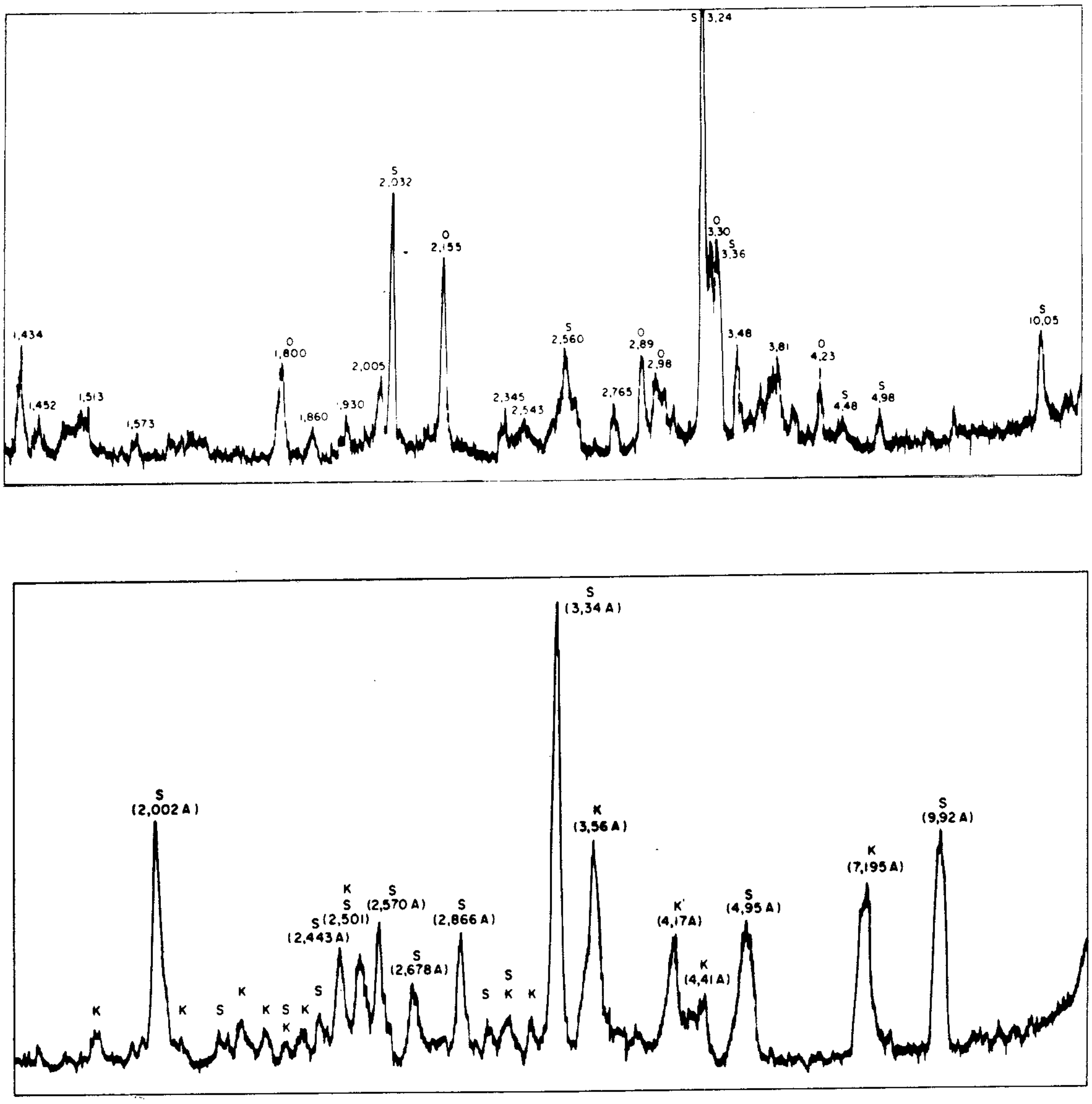

Figure 5. X-ray diffraction pattern of the normal potassic rock where the presence of orthoclase is clearly indicated (above). Below, identical X-ray diffraction pattern for the "potassic" rock of Morro do Ferro (ore material) where the orthoclase has been transformed into kaolin.

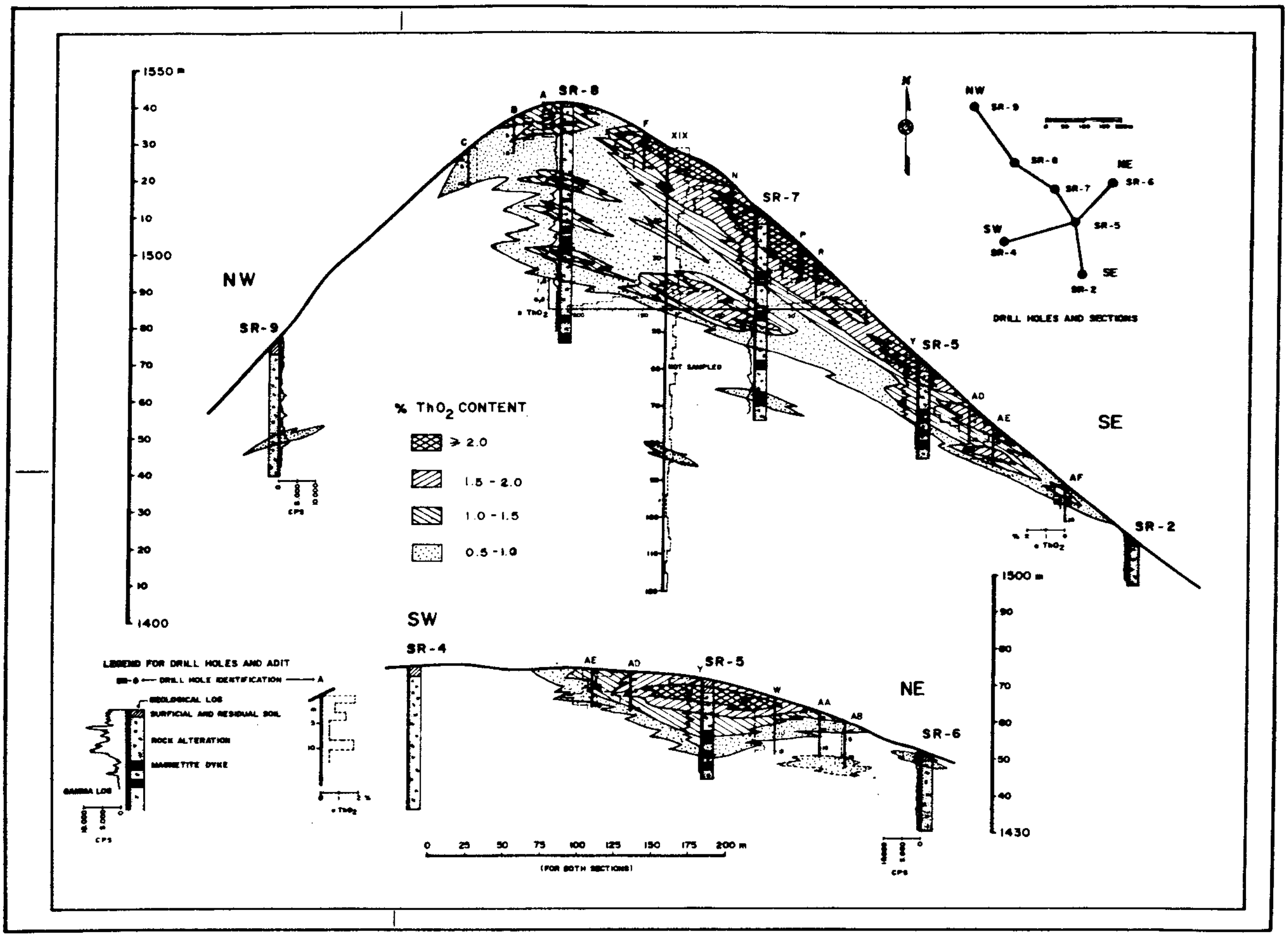

Figure 6. Longitudinal and transversal cross sections of the Th-REE rich orebody. This interpretation, based on existing data, should still be considered preliminary until adequate geological information is obtained.

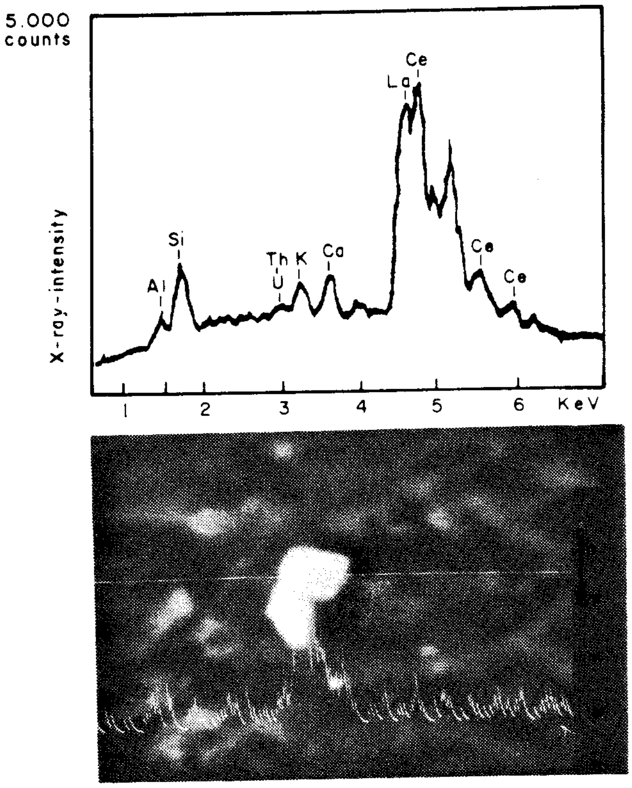

Figure 7. X-ray diffraction pattern of a rare earth silicate.

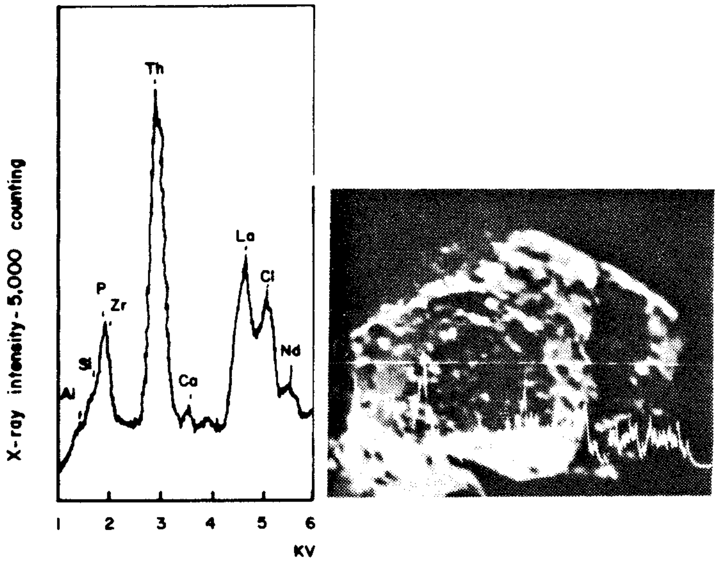

Figure 8. Distribution of thorium along the line R on a sericitized orthoclase crystal with surface presents cavities. On this surface a Th rich cheralite grain was identified as indicated by the X-ray pattern to the left.

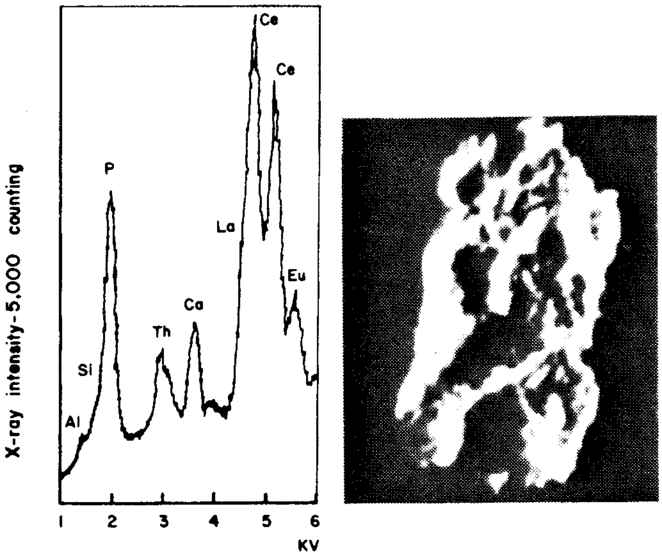

Figure 9. X-ray diffraction pattern and microphotograph (2 000 x) of a monazite crystal.

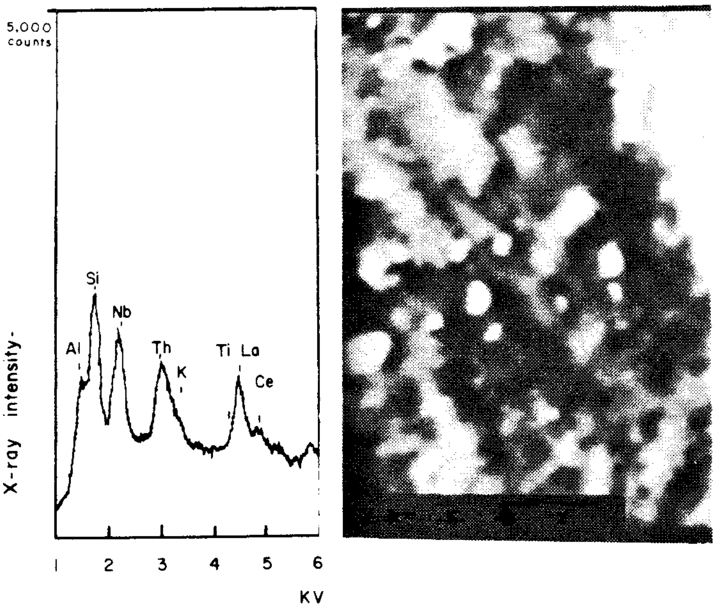

Figure 10. X-ray diffraction pattern of a small microlite crystal and the microphotograph of the sericitic host rock matrix (3 000 x).

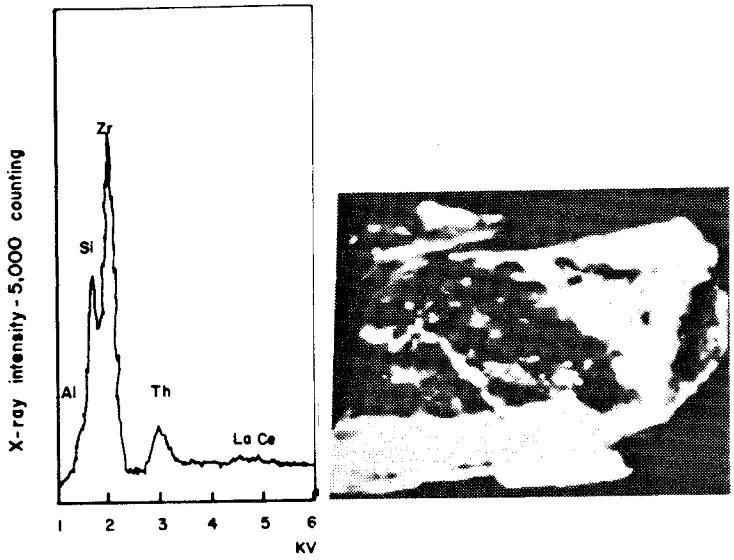

Figure 11. Microphotograph (2 000 x) of a zircon crystal. The X-ray diffraction pattern is noteable by the low abundance of La and Ce.

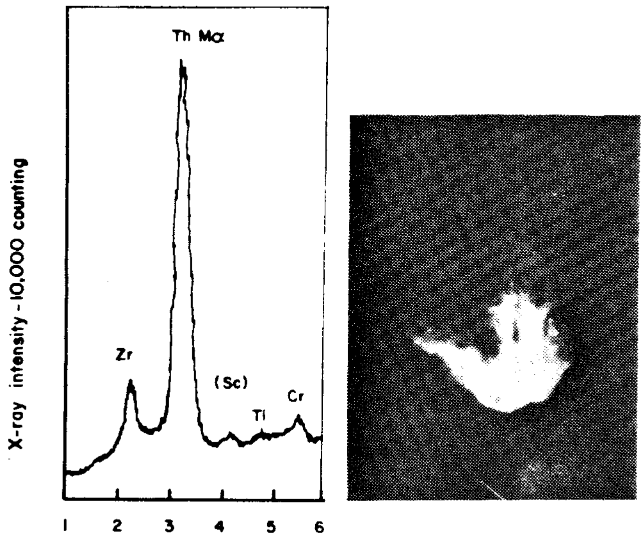

Figure 12. X-ray diffraction pattern of a thorianite microcrystal (1 000 x).

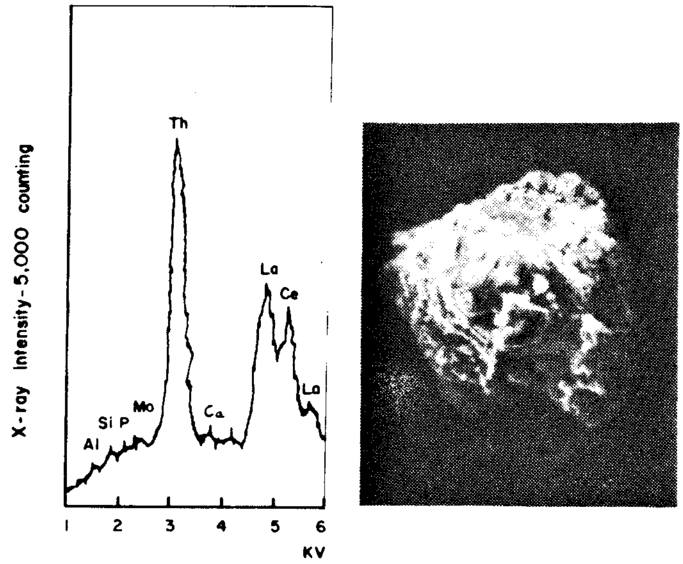

Figure 13. X-ray diffraction pattern and microphotograph (100 x) of a thorbastnaesite.

SESSION D

URANIUM DEPOSITS AS NATURAL ANALOGUES

Chairman: Harold Wollenberg

RADIONUCLIDE MIGRATION AROUND URANIUM ORE BODIES IN THE ALLIGATOR RIVERS REGION OF THE NORTHERN TERRITORY OF AUSTRALIA - ANALOGUE OF RADIOACTIVE WASTE REPOSITORIES

P.L. Airey

Australian Atomic Energy Commission, Lucas Heights Research Laboratories, Sutherland NSW 2232, Australia.

ABSTRACT

A number of uranium ore bodies in the Northern Territory of Australia have been evaluated as geochemical analogues of high-level radioactive waste repositories. The aim of the study is to contribute to the understanding of the scientific basis for the long-term prediction of the transport of radionuclides. Particular attention is being paid to investigations of - (i) mechanisms of mobilization and subsequent retardation of uranium series nuclides following the weathering of metamorphic host rocks, (ii) the role of iron minerals in the retardation of uranium and thorium, (iii) the role of groundwater colloids in the transport of radionuclides, (iv) experimental methods for studying the time-dependence of adsorption coefficients, and (v) conceptual methods for studying the effect of transport of uranium series nuclides through crystalline host rocks over geological time. The possibility of incorporating certain transuranic and fission product elements into the analogue is discussed.

INTRODUCTION

The United States Nuclear Regulatory Commission (NRC) has the responsibility for determining whether the disposal of high level radioactive wastes (HLW) at selected geologic sites can be achieved without undue risk to public health and safety, and has proposed a rule (10CFR60, US.NRC, 1981) which specifies criteria for the disposal of such wastes. Further, geological repositories in the United States will have to comply with standards set by the Environmental Protection Agency (EPA). The draft EPA Standard No 19 applies to integrated releases of radioisotopes over 10 000 years. There is a pressing need to establish the scientific principles whereby laboratory and field observations made over a timescale of days, months or a few years, may be used to predict transport over thousands to tens of thousands of years. One approach to the problem of long-term extrapolation is the study of naturally occurring geochemical analogues of waste repositories.

In 1981, the Australian Atomic Energy Commission (AAEC) contracted with the NRC to undertake systematic investigations around uranium ore bodies in the Alligator Rivers Region of the Northern Territory of Australia (Figure 1). The deposits have been chosen for study for the following reasons:

(i) There are a number of accessible deposits which may be compared to establish general features of radionuclide redistribution within and down-gradient of the ore bodies.

(ii) At least four of the deposits interesect the ground surface. Weathering leads to mobilization and provides a rational basis for the definition of zero time, which is essential for the mathematical modelling of transport.

(iii) Groundwater intersects all deposits and not only induces redistribution of radionuclides within the ore zone, but also leads to down-gradient transport. Aspects of migration in the oxidized and reduced zones may be compared.

(iv) The transuranics ^{237}Np and ^{239}Pu and the fission products ^{129}I and ^{99}Tc may, in principle, be incorporated into the analogue.

Broadly speaking, the programme is implemented in three stages:

Stage 1. The validity of Alligator Rivers ore deposits as analogues of radioactive waste repositories is investigated. A detailed understanding is sought of the redistribution of radionuclides within and their migration down-gradient of the deposit.

Stage 2. Correlations are established between the results of sorption/leaching studies and those properties of the ore which reflect the cumulative effect of transport over geological time.

Stage 3. A basis is sought for applying the correlations which were developed for the geochemical analogue to a wide range of geological settings.

This investigation is an extension of previous studies of uranium series disequilibria in the region (Shirvington, 1980; Dickson and Snelling, 1980). Accounts of the project have been presented to the NRC (Airey et al., 1983a; 1984a).

The structure of this report is as follows. Section 2 comprises an outline of the global model of the migration of radionuclides in the upper sequences of the ore bodies; in Section 3 the distribution of uranium, thorium and radium in identifiable phases of the weathered ore is discussed; Section 4 is concerned principally with aspects of the hydrogeochemistry of groundwater intersecting the deposits; and in Section 5, comments on the possible extension of the analogue are presented.

THE INVESTIGATION AREA

The uranium deposits of the East Alligator River (Figure 1) are the most significant mineral resources of the Pine Creek geosyncline (Ranger Inquiry, 1977). The geosyncline comprises up to 14 km of Lower Proterozoic sediments with interlayered tuff units, resting on granite late Archean complexes (Needham, 1980). The sediments were regionally deformed and metamorphosed at 1800 My. Cover rocks of Middle Proterozoic and younger ages rest unconformably on all of 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 chloritisation 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 (Needham and Roarty, 1980). It is also believed that association with the granite Archean basement is also important (Needham, 1980).

Relevant aspects of the geology of individual deposits have been outlined elsewhere (Airey et al., 1984a). Schematic representation of the cross sections of Nabarlek and Koongarra and the location of the sampling wells are shown in Figures 2 and 3. The groundwater flow patterns at Koongarra were interpreted by Snelling (Snelling, 1979).

GLOBAL MODEL OF URANIUM SERIES MIGRATION IN THE UPPER SEQUENCES OF THE ORE BODIES

General Description

The principal features of the open system model have been described (Airey, 1984a). the upper sequences of the ore bodies were classified into four zones (Table 1). These zones correlate broadly with the mineralogical description of the area. Additional evidence for the classification comes from the systematic variation of $^{230}Th/^{234}U$ activity ratios, ARs (Figure 4A). Data from Ranger One, Jabiluka One and Nabarlek show similar trends. Zone I exhibits large $^{230}Th/^{234}U$ ARs due to systematic leaching of uranium. Zone II generally shows a ^{230}Th deficit which is attributed to deposition. The transition zone III gives some evidence of a loss of uranium associated with mobilization of the element during the weathering process.

A schematic representation of the model is shown in Figure 4B. The dynamics of the system is determined not only by the groundwater flow characteristics, but also by the rate of advance of the weathering front, W, which is assumed to balance approximately the rate of surface erosion, E, and the time-averaged position of the water table over a very long period. If E and W were not roughly in balance, the thickness of the weathered zone, which has been developing since the Tertiary, would either be very small (E>W) or very large (W>E).

The principal purposes of the model is to calculate the averaged residence time, t, of uranium within a particular zone and the net rate of leaching (or accumulation). Knowing t and the location h_i of the sample above the zone boundaries (Figure 4B), the rate of advance of the weathering front W (= rate of surface erosion E) may be calculated from the average value of the quotients h_i/t. The mathematical formulation of the model has been previously described (Airey, 1984a).

The model may be used to calculate leaching/deposition rates and the rate of advance of the weathering front which is equated approximately to the surface erosion rate. The values for each drill core studied are listed in Table 2, together with the ranges of parameters from various ore bodies.

Applications of the Model

The mobilisation of uranium and radium by groundwater

The rates of leaching and deposition of uranium are listed in Table 2. In general, leaching occurs in zone I and deposition in zone II. The net loss of uranium by groundwater solution can be calculated from the rate of flow and the increase in the uranium concentration up- and down-gradient of the deposit. In the case of Ranger One, it was shown that if all the leached uranium remained in solution, the groundwater concentrations would be at least 20 times grater than those observed.

Estimates of the rate of radium leaching and deposition are also listed in Table 2. There is no correlation between the radium and uranium values, due clearly to differences between the chemical and the adsorption properties of the two elements. It is shown below that, within the weathered zone, uranium and thorium concentrate in the iron phases, whereas radium accumulates in the clay/quartz minerals.

Role of surface erosion in the redistribution of uranium

Estimates of the erosion rates at Ranger One and Jabiluka One vary between 0.02 and 0.25 mm/y with mean values of about 0.05 and 0.1 mm/y respectively; at Nabarlek, the average surface erosion rate was calculated to be about 0.05 mm/y. Independent estimates of the erosion rates before the mining yielded a value of about 0.07 mm/y (Duggan, 1983). There remains the problem of accomodating these values with the assumed stability of the landscape since the Tertiary period. However, erosion is a local phenomenon and estimates at specific sites over relatively restricted time periods (< 500 000 y) cannot necessarily be generalized over geological time. The values have been used

(i) to demonstrate that surface erosion and not groundwater leaching is the principal method by which uranium is transported from the ore body, and

(ii) to estimate the depth of shallow burial to meet defined criteria.

Koongarra

Koongarra differs from the deposits discussed above in two important respects:

(i) There appears to be a net accretion of material from the neighbouring escarpment rather than from erosion.

(ii) A well-defined region of secondary mineralization was formed by the deposition of uranium leached from the major deposit by the groundwater which infiltrates principally in the region of the boundary fault. The schematic representation of the groundwater flow patterns developed by Snelling (1979) is shown in Figure 3b.

A detailed study has been made of the uranium and thorium disequilibria in the groundwater and in the secondary ore. The data have been interpreted in terms of a formulation developed by Osmond and Cowart for roll front deposits (Osmond and Cowart, 1981) assuming that ^{234}U migrates more slowly than ^{238}U. This is not the normal case; however, it is consistent with the observation that in all but one well the $^{234}U/^{238}U$ ARs are less than unity.

This result means that modern values reflected activity ratios over geological time. The mathematical model is being modified to describe this roll front and to calculate the average rate of advance of the zone of mineralization.

Multiphase model

Experimental techniques have been developed to study the distribution of uranium, thorium and radium isotopes through a number of separable mineral phases, including

- amorphous iron,
- crystalline iron, and
- clay/quartz

Extensive isotopic fractionation observed between the phases is caused by a combination of

- recoil across phase boundaries,
- isotopic redistribution on accessible phase surfaces via groundwater dissolution,
- exchange between amorphous and crystalline iron phases over geological time.

Analytical expressions for $^{234}U/^{238}U$, and $^{230}Th/^{234}U$ ARs have been found for all phases in terms of parameters describing decay, recoil and exchange between iron phases. Mathematical details have been outlined in (Airey et al., 1983b) the significance of the modelling is discussed below.

Mobilization of transuranic elements and fission products

The rate of mobilization of uranium and the incorporated transuranics and fission products can be calculated from the rate of advance of the weathering front and the appropriate isotopic assay. Source terms can therefore be estimated and a basis established for studying the efficiency of groundwater transport over geological time.

MICROSCALE REDISTRIBUTION OF URANIUM SERIES NUCLIDES

Selective Phase Extraction Techniques

Selective phase extraction techniques are used to study the distribution of isotopes between identifiable phases within the ore assemblage. The samples chosen for initial study were taken from the upper sequences of the Ranger S1/146 core. These samples were chosen because they showed no evidence of secondary mineralization. Preliminary experiments indicated that only small levels of radionuclides were associated with ion exchange sites or with amorphous aluminium. Three phases were of significance

- amorphous iron (and manganese),
- crystalline iron, and
- clay/quartz resistate phases.

These were separated sequentially with the following reagents: Tamm's acid oxalate solution (Schwertmann, 1964); a citrate, dithionite-bicarbonate solution; and a fusion of sodium peroxide (Mehra and Jackson, 1960; Fellet et al., 1965). Since both aqueous reagents contain strong complexing agents, the possibility of a chemically-induced exchange of radionuclides between the phases cannot be entirely excluded. It is planned to check the techniques using magnetic and paramagnetic mineral separation procedures.

Isotopic Fractionation Between Mineral Phases

Schematic representations of the distribution of uranium, thorium and radium between the iron and clay/quartz phases are shown in Figures 5-7. The following features of the data should be noted:

(i) The uranium and thorium are concentrated principally on the iron phases even though iron comprises only between 1 and 4% of the weathered ore.

(ii) By contrast, the activity of radium in the clay/quartz phase exceeds that of its parent thorium.

(iii) The ^{230}Th/^{234}U activity ratios in the crystalline iron (goethite) are large but substantially constant. The average values for the four samples are 2.3 ± 0.4. By contrast, the ARs in the amorphous iron vary by more than a factor of ten. There is a large excess of ^{230}Th in zone I associated with leaching and a substantial deficit in zone II associated with the deposition of uranium.

The ^{230}Th/^{234}U ARs in the amorphous iron are consistent with the zonal classification outlined above if, as with a number of heavy metals (Zielinski et al. in press), the uranium in the amorphous phase is accessible to that in the groundwater. Since the levels of uranium and thorium are relatively constant in the goethite, it is assumed that they are determined principally by their efficiency of uptake during crystallisation of the amorphous iron combined with radiogenic decay and interphase recoil.

Evidence for interphase transfer of radionuclides, either by direct recoil or by groundwater solution and re-adsorption, is obtained from the radium-226 results. Radium-226 is in deficit in the iron phases but in excess in clay/quartz. At this stage it is not possible to determine the relative importance of the two effects. Recoil is certainly expected to be significant because the process is non-discriminatory and α daughters would be most likely to lodge in the phase with the greatest mass. Clay/quartz comprises more than 95% of most weathered ore samples. The importance of α-recoil is confirmed by the observation that $^{234}U/^{238}U$ ARs are greater in the clay/quartz than in the associated iron phases.

Care must be taken when relating these findings to the prediction of the long-term migration of radionuclides from repositories. Many significant isotopes such as ^{99}Tc, ^{129}I, ^{239}Pu are purely allogenic. However, over the timeschales of interest (10 000 years), ^{226}Ra and a significant proportion ^{237}Np in spent fuel elements which derives from ^{241}Am, are formed by α-decay. Recoil may therefore be significant when assessing retardation over long periods. In addition, uptake by the goethite phase is a mechanism for reducing average migration velocities as the radionuclides (M) within the crystalline iron phase are believed to be inaccessible to groundwater.

M(solution)   M-Fe(amorphous)   M-Fe(crystalline
largely inaccessible
to groundwater)

Because of the relevance to long-term transport phenomena, attempts are being made to model mathematically the dynamics of the redistribution of radionuclides between the three phases.

RADIONUCLIDE DISTRIBUTION COEFFICIENTS - NON-CLASSICAL EFFECTS

Selective Adsorption

It has been concluded that the uranium in the amorphous iron is accessible to that in the groundwater over short timescales. This is confirmed by running a number of batch adsorption and leaching experiments to relate laboratory observations to parameters describing the distribution of uranium through the weathered ore sample. The tracer ^{236}U is added to monitor the adsorption of readily accessible uranium and the $^{234}U/^{236}U/^{238}U$ ARs measured as a function of pH, Eh, concentration and time. Two results are of direct relevance to this discussion:

(i) The ratio of the distribution coefficients for ^{236}U and ^{238}U is close to the fraction of uranium associated with the amorphous iron.

(ii) The sequential extraction technique showed that approximately 93% of the uranium was associated with the amorphous iron.

Recoil Effects

Alpha-recoil leads to the displacement of daughter nuclei by distances of about 20 nm (Fleischer and Raabe, 1978). Direct recoil of adsorbed ^{234}Th ($\xrightarrow{\beta}$ ^{234}Pa $\xrightarrow{\beta}$ ^{234}U) into solution is one of the reasons for the large ^{234}U/^{238}U ARs frequently found in groundwater (Kigoschi, 1971). Clearly, the complementary process of recoil into the substrate lattice is also possible. This would result in an increased fraction of adsorbate inaccessible to the groundwater, and to an increased distribution coefficient.

To test this effect experimentally, solutions of ^{228}Th (from which the daughter ^{224}Ra was removed) and ^{226}Ra were added to suspensions of the sodium form of kaolinite, illite and montmorillonite. A pH of 4.25 was chosen to ensure the complete (>99%) adsorption of thorium; the percentate of ^{226}Ra adsorbed in the dilute suspension ranged between 60 and 80.

Radium-224 was formed by decay on the clay surface. The ratios of the distribution coefficients for ^{224}Ra and ^{226}Ra varied from about 1.5 for bentonite to about 4 for illite. As expected, equilibrium conditions were not established. The proportion of ^{224}Ra on the solid phase increased with the extent of leaching. Illite exhibited extreme behaviour; after 99.9% of the radium had been removed, the ^{224}Ra was found to be enriched by a factor of 134 (Per. commun. D. Roman, 1984).

Time-dependence of Thorium/Radium Distribution

The aim of this experiment was to obtain evidence for the effect of time on the distribution coefficients of radium and thorium. The principle involves the systematic study of the parent/daughter pairs ^{230}Th/^{226}Ra, ^{232}Th/^{228}Ra, and ^{228}Th/^{224}Ra. There were a number of experimental difficulties. In filtered solutions the thorium activities were very low; ^{230}Th activity was typically less than one per cent of the dissolved ^{234}U.

Preliminary data from Nabarlek are listed in Table 3. Two points should be noted. First, there is substantially more ^{228}Th than ^{230}Th despite the very large amount of ^{238}U in the deposit. No data are available from the immediate vicinity of the observation bores sampled. However, it should be noted that OB20 and OB25 are immediately down-gradient of the deposit. In addition, even in low level samples, the uranium activity exceeds that of ^{232}Th.

Clearly, the intermediate ^{228}Ra formed by α-recoil is playing an important role; it would appear that the radium tends to associate with the clay/quartz minerals. Thorium-230 on the other hand tends to adsorb on the amorphous iron. Because of its long half-life, this isotope would in part be incorporated into the crystalline iron phase which is inaccessible to groundwater. In addition there would be time for diffusion throughout the microporous structure of the lattice.

The $^{226}Ra/^{224}Ra$ ARs, although greater than for the $^{230}Th/^{228}Th$, are much smaller than those anticipated from the overall uranium and thorium levels. Both are formed by α-recoil and therefore would tend to initially have the same general distribution. Accordingly, both would accumulate preferentially on the clay minerals. The relatively lower accessibility of ^{226}Ra to groundwater is probably associated with the diffusion effects associated with its greater mean residence time.

GROUNDWATER TRANSPORT

Two-component Model of Uranium Migration

Groundwater is the principal agent of the sub-surface migration of radionuclides leached from the ore bodies. In this study, isotope hydrology (particularly ^{14}C) techniques have been used to assess the cumulative effects of groundwater migration over thousands of years.

The uranium concentrations generally decrease with distance down-gradient of the mine. Systematic trends are also found with the $^{234}U/^{238}U$ ARs (Airey et al., 1984a). The variation with the uranium concentration of the activity ratios from Nabarlek groundwater is shown in Figure 8. The locations of wells are shown in Figure 2.

As with Ranger groundwater, the data were interpreted in terms of a two-component model: component 1, characterized by relatively high uranium concentration and $^{234}U/^{238}U$ ARs close to unity, is the groundwater intersecting the deposit; component 2, with a low uranium concentration and high $^{234}U/^{238}U$ ARs represents uranium leached from host rock down-gradient of the deposit. If the fraction of component 2 is assumed to be proportional to the distance down-gradient of the deposit, it can be shown that

$$^{234}U(x)/^{238}U(x) = \xi + (^{238}U_2 - {}^{238}U_2\ \xi)/^{238}U(x) \qquad (1)$$

where $^{234}U(x)$ and $^{238}U(x)$ are the concentrations of the uranium isotopes at distance (x) from the deposit, $^{234}U_2$ and $^{238}U_2$ are the concentrations in component 2 of the groundwater, and $\xi \sim {}^{234}U(o)/^{238}U(o)$. The experimental validity of equation (1) has been verified (Airey et al. 1984a).

Uranium Retardation Down-gradient of the Ranger Deposit

The $^{234}U/^{238}U$ activity ratios in groundwater close to the Ranger One deposit have values close to unity. They increase with distance up to 4 km down-gradient, owing to mixing with a dispersed infiltrating groundwater characterized by a large ^{234}U excess. Further down-gradient there is no environmental isotope evidence for local recharge. The $^{234}U/^{238}U$ activity ratios return to secular equilibrium because of a combination of radiogenic decay and the possibility of exchange with the host rock. Assuming that radioactive decay is the major process, the maximum relative retardation of the groundwater relative to the host rock is 1/250. Groundwater velocities were calculated from ^{14}C.

Qualitatively similar behaviour has recently been found in groundwater sampled from the Carizzo aquifer in Texas:

"At distances from 0 to about 20 km, where the Carizzo is oxidizing and uranium dissolution is occurring, $^{234}U/^{238}U$ activity ratio (AR) values of 1.0 ± 0.3 are found. Between 20 and 33 km, uranium concentrations drop dramatically and AR values as high as 9 occur. Below about 33 km, low dissolved uranium persists, accompanied by a regular decrease in the AR towards a secular equilibrium value of 1." (Pearson et al., 1981)

A schematic representation of this behaviour is shown as an insert to Figure 9.

The Role of Groundwater Colloids

The mobility of radionuclides in groundwater depends on the distribution coefficient which is a function of the chemical state of the element and the physico-chemical nature of the accessible mineral surfaces. The mobility would be reduced by the formation of significant amounts of colloids.

In a preliminary investigation of the role of colloids, particulate matter was collected on 0.45 μm pre-filters and the $^{230}Th/^{234}U$ and $^{234}U/^{238}U$ ARs compared with those in solution. Between only 0.8 and 11% of the uranium was associated with particulates; the corresponding ratio for thorium was between >0.22 and >5.7. Particulates from well OB21 (Nabarlek, Figure 4) contained 10% quartz, and the minerals kaolinite, muscovite (medium level), smectite (medium level) and chlorite/vermiculite (low level). The iron oxide lepidocricite was also found. In contrast to thorium, the uranium particulate appeared to be in isotopic equilibrium with the solution.

Considerable improvements were made to the experimental methods (Short, in preparation). About 500 L was pumped through a 1 μm pre-filter and an Amicon H.10P100 anisotropic hollow fibre ultrafiltration cartridge over a 4 h period. The cartridge (0.88 m^2, 5.3 nm cut-off) was mounted in an Amicon DC10 ultrafiltration rig operating in the single phase diafiltration mode. This enabled the collection of a concentrate of the whole colloid (5-1000 nm) in 1-2% of the total filtered volume, in the absence of air.

The principal findings were as follows:

(i) The ratio of ^{238}U on the colloid to that in solution varied between 0.01 and 2%. In contrast to the preliminary experiment, there was no evidence of isotopic equilibrium between the colloid and the solution.

(ii) The percentage of ^{230}Th carried by the colloid varied from 0.30 to 39; again, there was no evidence for isotopic equilibrium.

The differences are readily explained in terms of the experimental conditions. In the preliminary work, particulates (>0.45 µm) were collected under conditions in which air was present. The apparent isotopic equilibrium between the solution and the colloid may have been due to the co-precipitation with the lepidocricite formed during the collection process. It is important to note that in both cases, between one and two orders of magnitude more thorium was associated with the colloid than uranium.

Attempts are being made to "date" the colloids in order to assess the relative rate of colloid to groundwater transport.

MIGRATION OF RADIONUCLIDES THROUGH CRYSTALLING ROCKS

Much of the work until now has been directed to a study of the migration of uranium series nuclides through the weathered sequences of the ore bodies. Attempts are now being made to extend the concept to crystalline rock systems. Specifically, the aim is to test the validity of the matrix-diffusion mechanism of migration over geological time (Neretnieks, 1980; Gleuckauf, 1981). This mechanism involves the convective transport of solute through major fractures; retardation is induced by adsorption on accessible mineral surfaces and by diffusion into the bulk material through microcracks and fissures.

Proton induced X-ray emission (PIXE) and proton induced γ-ray emission (PIGME) techniques are used to determine the complete suite of significant anions and cations. In a preliminary run, seven samples of rough-sawn schists from Ranger One, Ranger Three and Jabiluka One were assayed for 22 metals (including uranium and thorium) and 4 non-metals (excluding oxygen which was calculated from the theoretical oxide concentrations). Each sample was assayed at seven spots along a transect using a 1 mm proton beam from a 3 MV Van der Graaff accelerator.

Standard petrological slides of sections transverse to fractures are being prepared by the Department of Soil Science, University of Sydney. It is planned to extend the work to include a two-dimensional mapping of the elemental distribution, using a higher resolution proton beam, and to correlate the data with the mineralogy. If an estimate can be made of the total time of access of groundwater to the fracture (perhaps by studying the uranium series disequilibrium in the deposited surface minerals) there will be an experimental basis for assessing the validity of the matrix diffusion theory over geological time.

CONCLUSIONS

(a) Uranium ore deposits in the Alligator Rivers region of the Northern Territory of Australia are acceptable geochemical analogues of high level radioactive waste repositories which have been leached by groundwater.

(b) The redistribution of uranium in the upper sequences of the ore body subsequent to weathering has been described by an open system mathematical model. The model has been extended to rationalise observed $^{234}U/^{238}U$; $^{230}Th/^{234}U$ and $^{226}Ra/^{230}Th$ fractionation between the amorphous iron, the crystalline iron and the clay/quartz components of the weathered ore.

(c) Groundwater colloids are involved in the transport of uranium and particularly thorium. In neither case is there isotopic equilibrium between the colloid and the solution. Hydrogeochemical evidence of uranium retardation factors up to 250 has been presented.

(d) From systematic studies of a number of thorium/radium parent-daughter pairs, it is concluded that radionuclide distribution coefficients increase with increasing residence time. Alpha-recoil effects over geological time are important for determining the distribution of daughter products within the mineral assemblage comprising the ore sample.

(e) At least three non-classical factors would lead to greater radionuclide retardation factors over geological time than those predicted from laboratory distribution coefficients:

- The very significant levels of radionuclides associated with the crystalline iron phase are effectively inaccessible to the groundwater.

- A significant proportion of nuclides formed by α-decay over geological time is lodged in sites which are inaccessible to groundwater.
- The "colloid" fraction of "mobile" radionuclides would be expected to migrate more slowly than that in solution.

(f) Work is under way to assess the validity, over geological time, of the matrix-diffusion mechanism of the migration of radionuclides through crystalline rocks.

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Table 1. Four-zone model of the upper sequences of the ore bodies.

Zone	Hydrology	Mineralogy	Comments
I	Unsaturated in the dry season; oscillating table	Oxidized ferricrete or ferruginous zone grading into a mottled zone	Uranium leaching
II	Permanently saturated	Generally corresponds to the pallid zone	Some U deposition
III	Saturated	Transition zone between weathered and unweathered rock; oxidized material; evidence of layering inherited from Cahill formation; in lower region weathering away from pre-existing cracks and fissures observed	Region of some U leaching
IV	Saturated	Unweathered rock from Cahill formation	

Table 2. Drill core samples - model parameters.

Ore Body	Zone	Depth Range (m)	Uranium Leaching (L) or Deposition (D) Rate (% per 1000 y) (1)		Radium Leaching (L) or Deposition (D) Rate (% per 1000 y) (1) (2)		Erosion Rate (E), Advance Weathering Front (W) (m per 1000 y)	
			Mean	Range	Mean	Range	Mean	Range
Ranger One	I	0- 8±1	0.7 (L)	0.03 (D)-1.5 (L)	18 (D)	67 (D)- 19 (L)	0.06	0.02-0.18$^{(4)}$
	II	8-17±1	0.3 (D)$^{(2)}$		1$^{(2)}$			
	III	17-30±5	0.2 (D)	0.3 (D)-0.6 (L)	0.16 (D)	5 (D)- 30 (L)		
Jabiluka One	I	0- 8±1	0.3 (L)	0.3 (D)-1.5 (L)	3 (L)	3 (D)- 8 (L)	0.1	0.03-0.25
	II	8-17±1	0.4 (D)	0.3 (D)-2.0 (L)	384 (D)	2546 (D)- 6 (L)		
	III	17-30±5	0	0.3 (D)-0.3 (L)	308 (D)	12 (D)-1061 (D)		
Nabarlek	I	0-1.7	1.8 (L)	1.2 (L)-2.5 (L)			0.05	0.01-0.08
	II	1.7-10	0.2 (D)	0 -0.3 (D)				

NOTES:

(1) These values do not represent the net loss (or gain) of uranium or radium to the deposit; rather they show the rate of localized redistribution through the vertical profile.
(2) The calculated value is an instantaneous rate averaged over 1000 y to allow comparison with geochemical timescales. Large values reflect localized effects and are clearly artefacts of the calculation procedure.
(3) One estimate only available.
(4) One value (0.96 m per 1000 y) from eight omitted.

Table 3. Thorium and radium isotope activity ratios in Nabarlek groundwater.

Sample	$^{230}Th/^{228}Th$	$^{226}Ra/^{224}Ra$
20473 Nabarlek*	0.2	0.7
OB25 "	0.15	1.8
OB20 "	0.1	1.7

* Location - Figure 4.

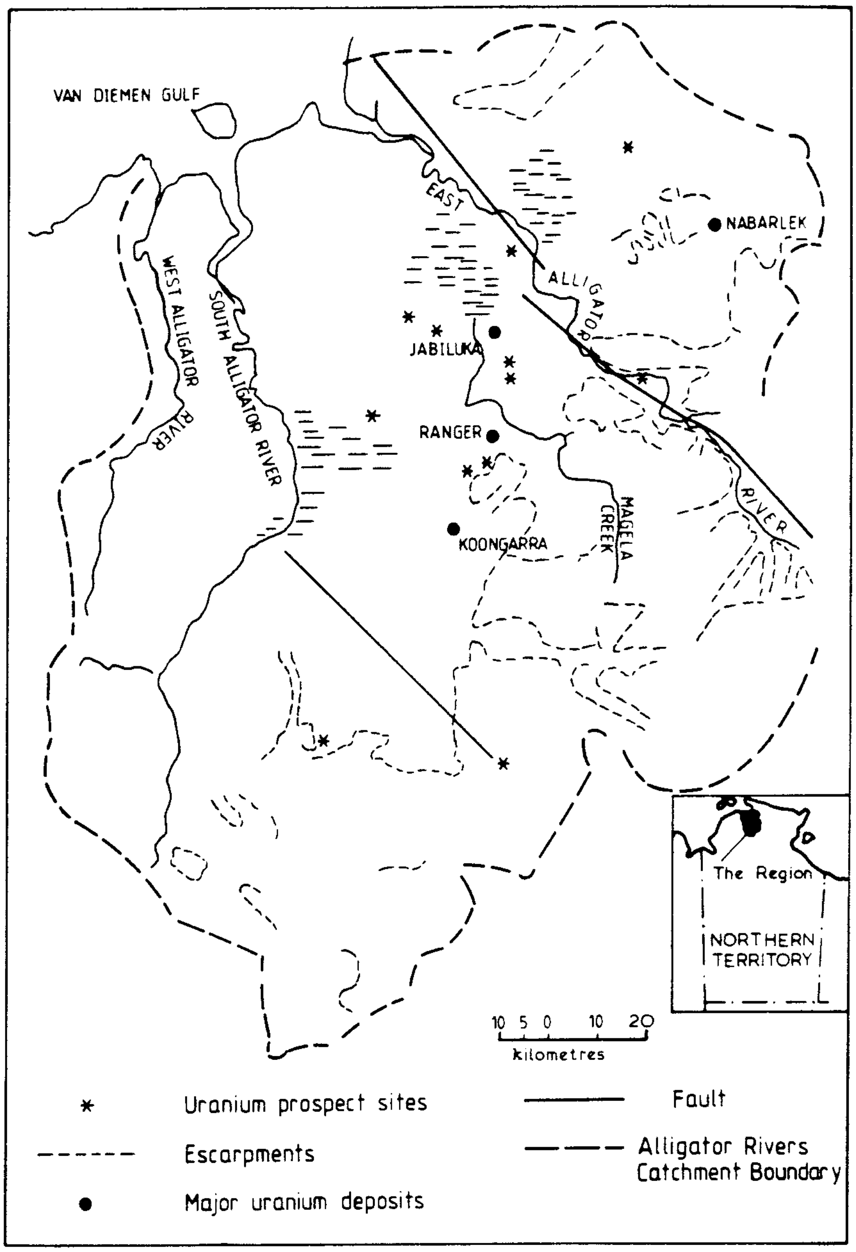

Figure 1. The location of the principal uranium ore bodies and prospects in the Alligator Rivers area of the Northern Territory of Australia. (Map 9, modified after Ranger Uranium Environmental Inquiry, 1977).

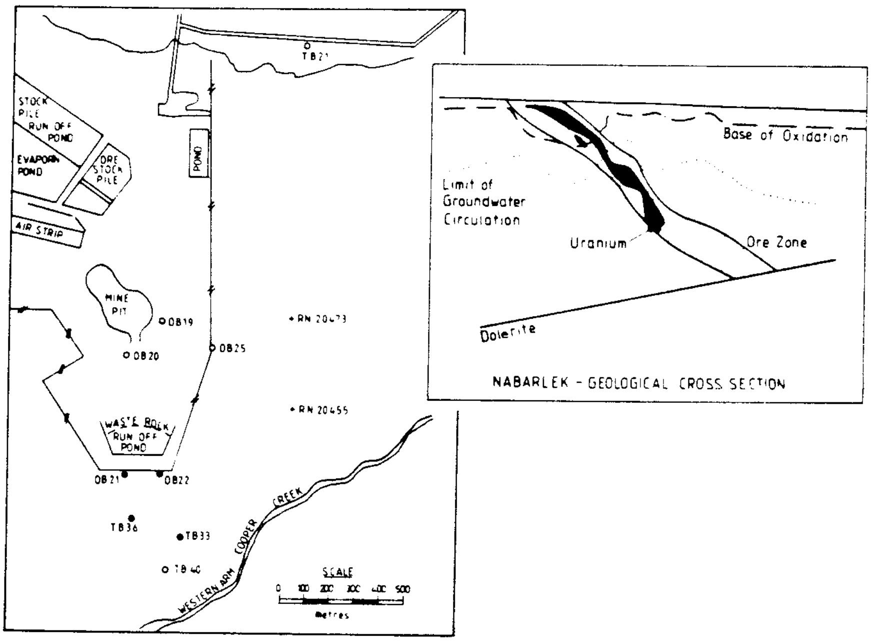

Figure 2. Location of the sampling wells at Nabarlek.
<u>Insert</u>: General geological cross section.

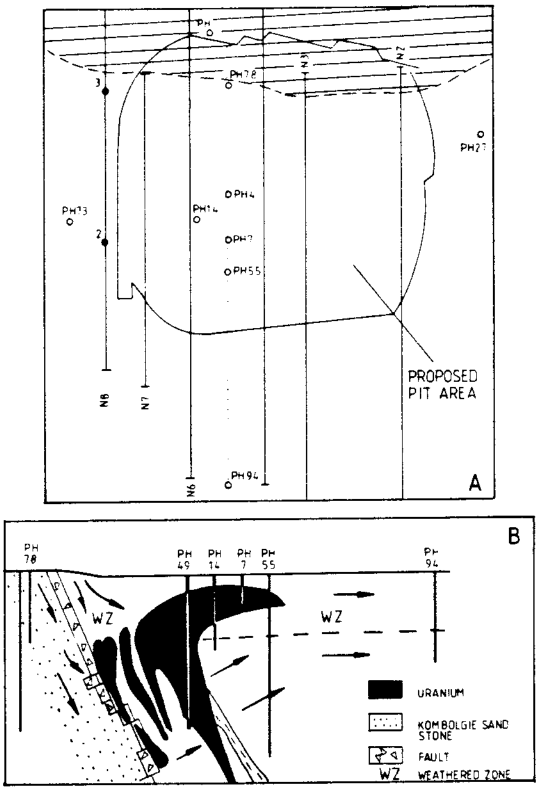

Figure 3. A. Location of the sampling wells at the Koongarra deposit.

B. A section between wells PH 78 and PH 94 showing the location of a major fault, the extent of the uranium deposits, the boundary of surface oxidation and the groundwater flow paths (adapted from Figure 1, Snelling, 1979).

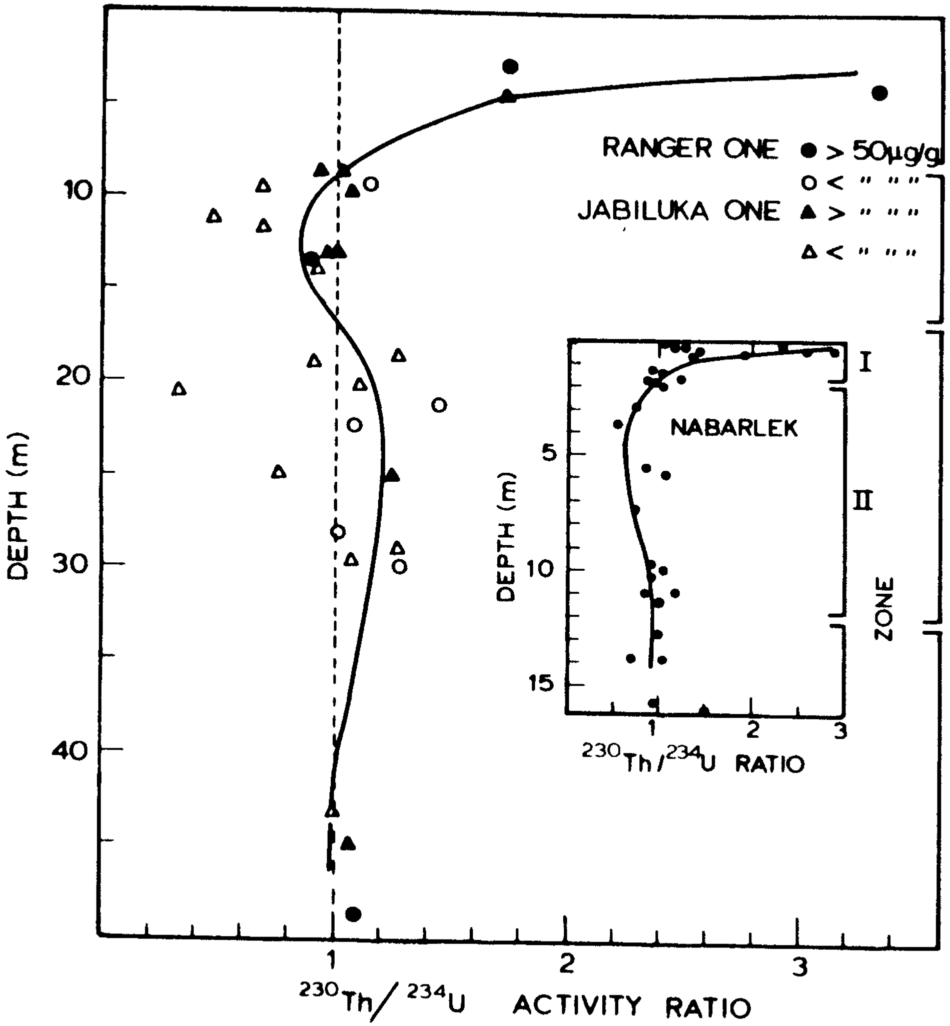

Figure 4A

Composite illustration of the variation with depth of the $^{230}Th/^{234}U$ activity ratios from the Ranger One, Jabiluka One and Nabarlek (insert) ore bodies. A zonal classification based both on the activity ratio variation and systematic changes in the mineralogy (Table 1) is shown.

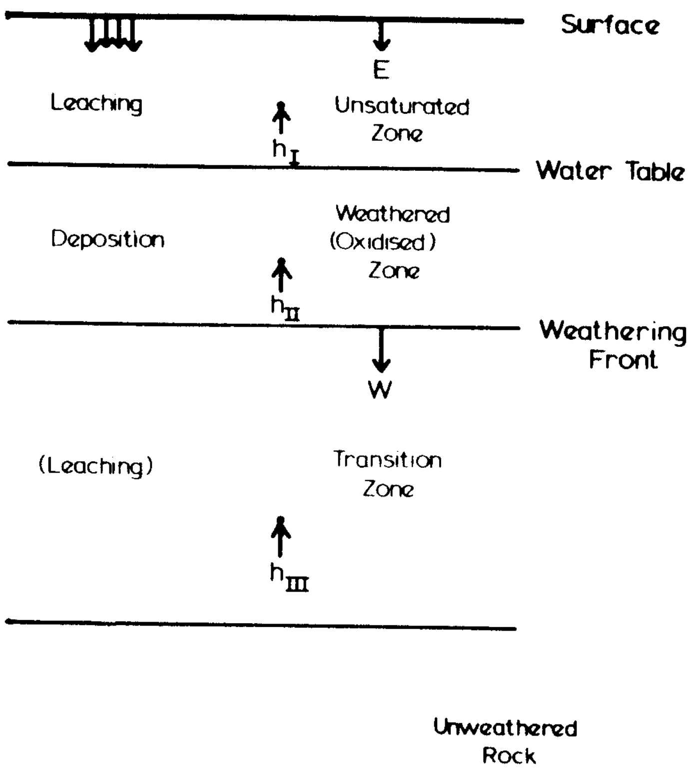

Figure 4B

Schematic representation of the four-zone model. E and W are the rates of surface erosion and advance of the weathering front; h is the position of the sample above the zonal interface.

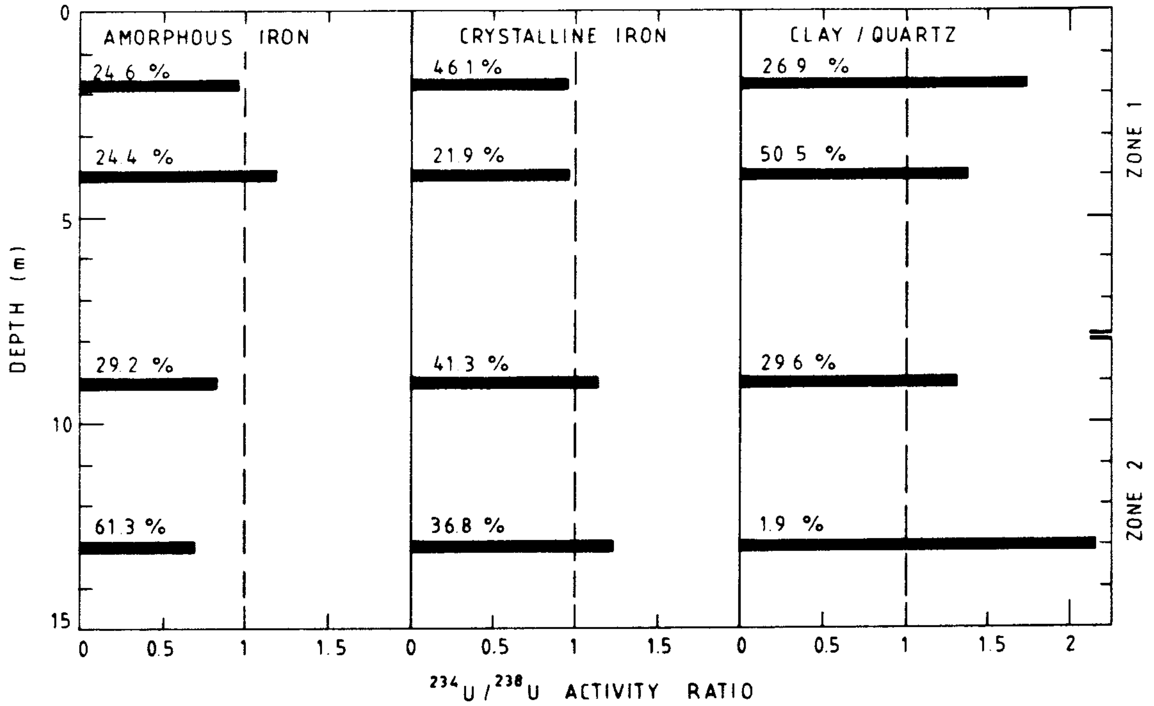

Figure 5. Variation of the $^{234}U/^{238}U$ ARs in selectively extracted phases from samples from the S1/146 core of the Ranger One ore body. The percentage of uranium on each phase is shown (Snelling, 1979; Figure 5).

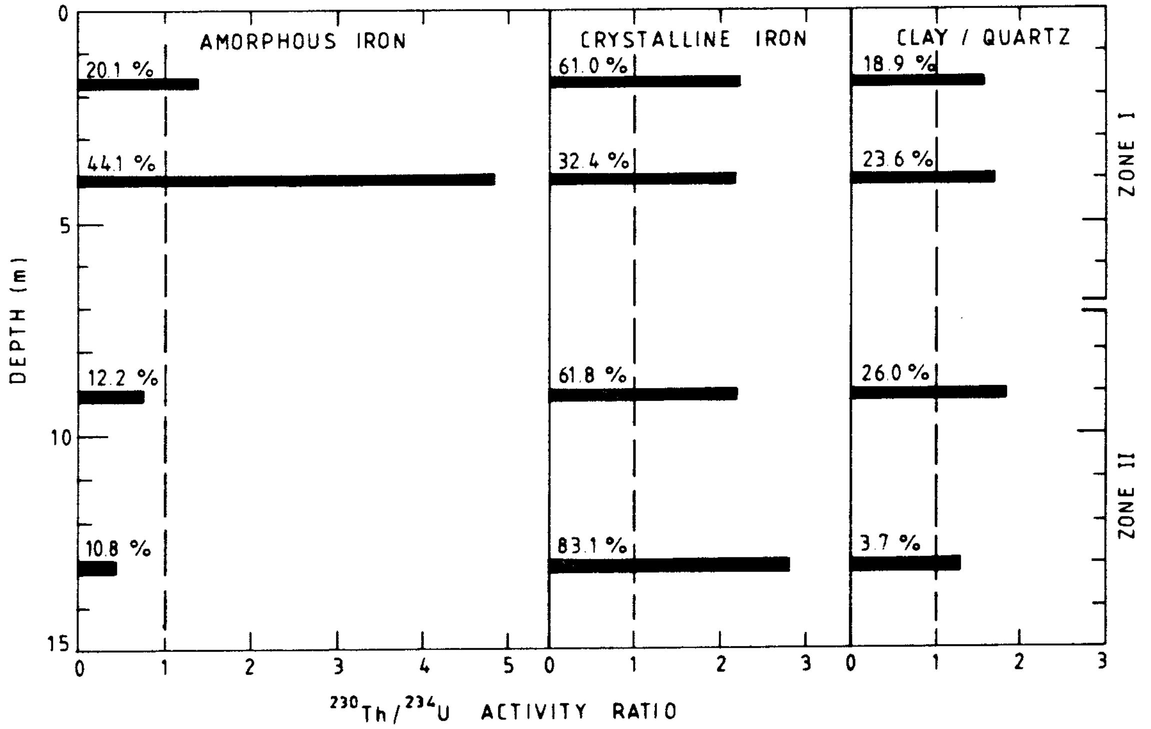

Figure 6. Variation of the $^{230}Th/^{234}U$ ARs in selectively extracted phases from samples from the S1/146 core of the Ranger One ore body. The percentage of uranium on each phase is shown (Airey et al., 1983a, Figure 6).

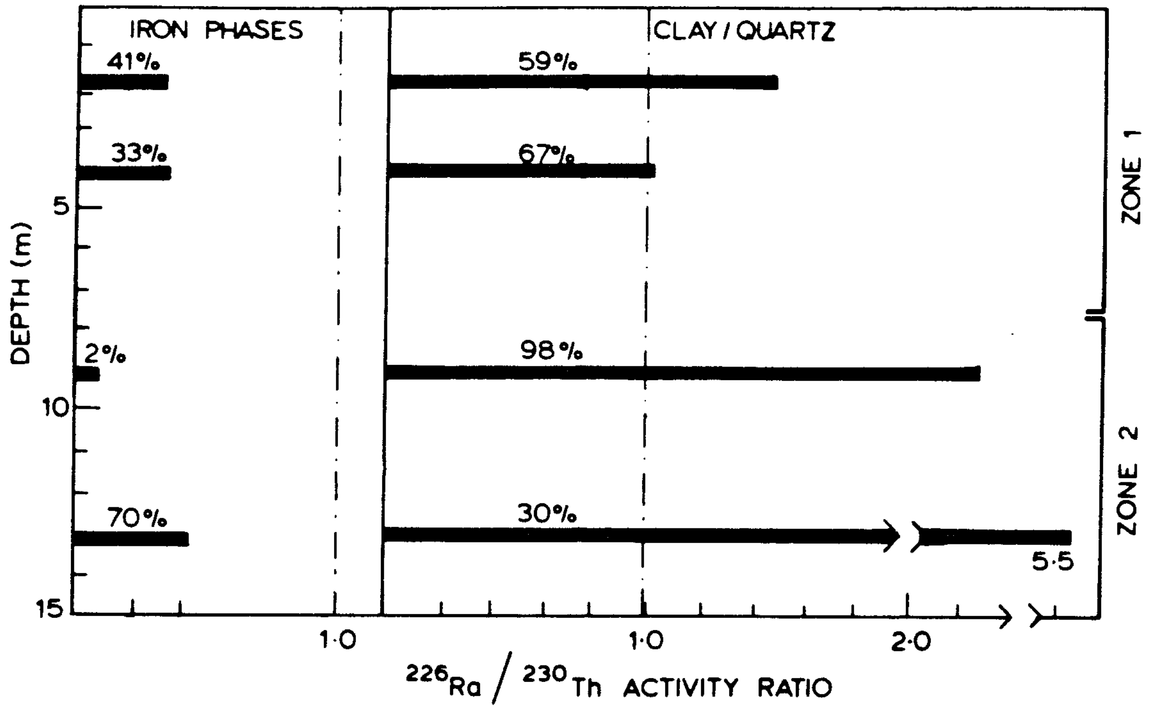

Figure 7. Variation of $^{226}Ra/^{230}Th$ ARs in the iron and clay/quartz phases of the S1/146 core of the Ranger One ore body. The percentage of radium in each phase is shown.

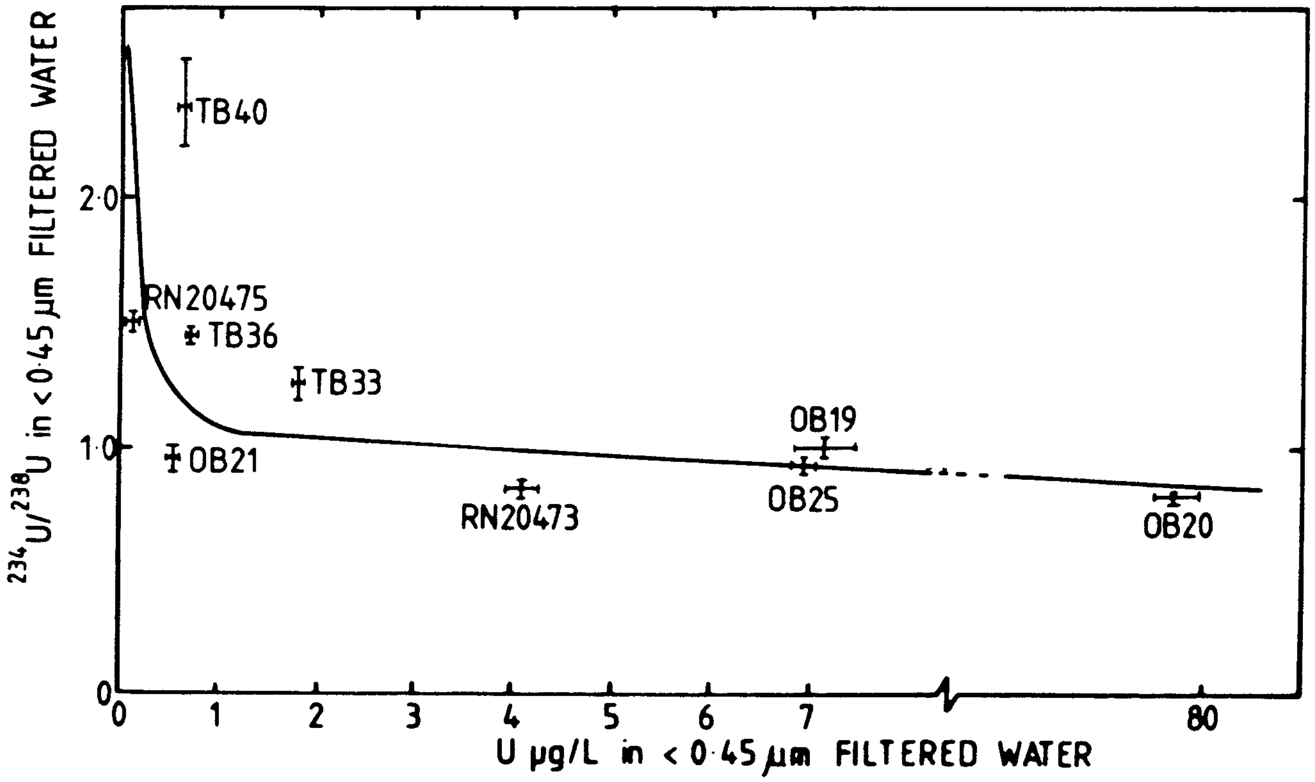

Figure 8. Variation of $^{234}U/^{238}U$ ratios with uranium concentration in Nabarlek groundwater (Figure 8; Airey et al. 1983a).

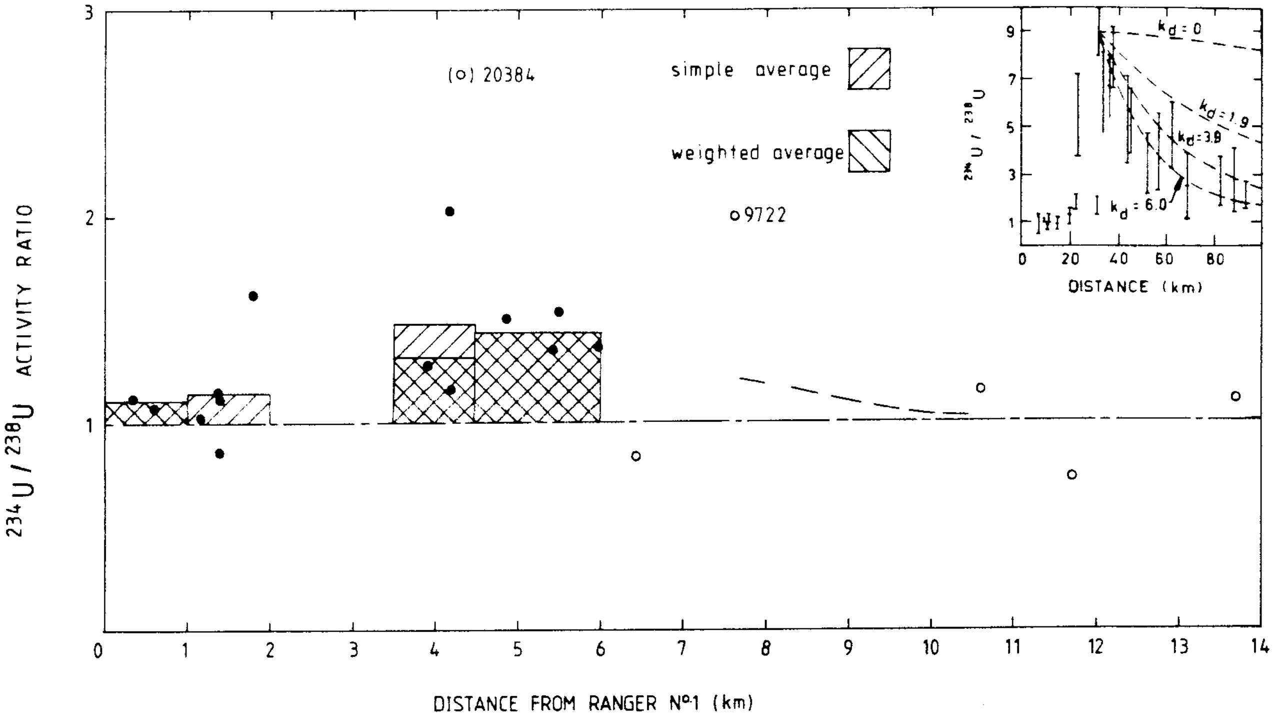

Figure 9. Variation with distance from the Ranger One ore body of the $^{234}U/^{238}U$ ARs. Where appropriate simple averages and weighted averages are shown. <u>Insert</u>: Schematic representation of the variation of $^{234}U/^{238}U$ ARs down-gradient from the outcrop of the Carizzo sandstone aquifer, Texas (Pearson et al. 1981).

SANDSTONE-HOSTED URANIUM DEPOSITS IN NORTHERN SASKATCHEWAN AS NATURAL ANALOGS TO NUCLEAR FUEL WASTE DISPOSAL VAULTS

Jan J. Cramer, Atomic Energy of Canada Limited, Whiteshell Nuclear Research Establishment, Pinawa, Manitoba ROE 1LO, Canada.

ABSTRACT

Proterozoic U deposits have been preserved in sandstone formations on several Precambrian Shields, and give testimony to the compositions and conditions required for the safe disposal of nuclear fuel wastes. The unconformity-type U deposits in the Athabasca Basin of northern Saskatchewan are discussed here in detail.

Conditions for ore formation in the Saskatchewan deposits were similar to those expected around a waste package in terms of pressure, temperature and salinity of the solutions. Secondary dispersion of U and other elements of interest, resulting from groundwater interactions, is very limited. Only radiogenic Pb appears to have been dispersed to any extent.

Two processes involved in the ore formation have a direct bearing on the stability of fuel waste and of buffer and backfill in the nearfield. These are quartz dissolution and redox control of groundwater by methane, with the latter process still active.

INTRODUCTION

In the Canadian Nuclear Fuel Waste Management Program, the concept being assessed for disposal of nuclear fuel wastes is burial at considerable depth in a granitic pluton in the Precambrian Shield of Ontario. Should the engineered containment barriers fail with time, transport by groundwater is the only credible mechanism for radionuclides to migrate from the vault to the biosphere. Groundwater is present throughout the Precambrian Shield in open fracture systems within both metasediments and igneous rocks (Frape et al., 1984).

An understanding of the processes of rock/water and waste/water interaction is essential for the long-term safety assessment of deep underground disposal of nuclear waste. Laboratory studies into these processes are restricted in terms of time, by slow reaction kinetics at low temperatures, and in terms of complexity of the geological system. Therefore, studies of natural examples of rock/water and ore/water interactions are necessary complements to the laboratory research. Carefully selected geological analogs provide information for the extrapolation of laboratory results, and this increases the level of confidence in the assessment of the disposal concept.

Natural analogs to disposal vaults should not be restricted to occurrences of natural reactors but should also include ordinary deposits of actinide ores. It is important to analyze specific aspects of such deposits, which have survived geological phenomena (e.g., tectonic disturbance, groundwater interaction, etc.) for hundreds of millions of years. These include spatial and age relationships, thermal history, composition of the ore, host rock and groundwaters, plus the dispersion and fixation of important trace elements. The sandstone-hosted U deposits in northern Saskatchewan provide an excellent opportunity to study many of these aspects in a relatively uncomplicated system compared with the vein-type U-deposits in metamorphic and igneous rocks.

UNCONFORMITY-TYPE U DEPOSITS IN NORTHERN SASKATCHEWAN

Northern Saskatchewan is an important U-producing area, with several mines active since the early 1950s. All the so-called "unconformity-type" U deposits are associated, either directly or indirectly, with the Athabasca Basin Sandstone Formation that unconformably overlies the older Precambrian basement (see Figure 1). The uppermost part of the basement consists of a paleo-weathering profile that formed prior to the deposition of the Athabasca sandstones. Most of the deposits are situated in, or are related to, the unconformity contact between the Sandstone Formation and the basement. There are several episodes of U mineralization, of which the two major ones have been dated at around one billion years ago (Bell, 1981; Baadsgaard et al., 1984; Höhndorf et al., 1983).

A typical U mineralization occurs in a fracture zone, has an elongated shape (veins, lens), and can be massive or occur as breccia filling. This fracture zone cuts across both sandstone and basement stratigraphy, and it often offsets the unconformity contact. The mineralization may be located in the sandstone above the unconformity, along the unconformity, or just below the unconformity in the basement rocks. The primary uranium minerals are pitchblende (U_3O_7-U_3O_8) and coffinite ($USiO_4$), which occur in massive concentrations or as impregnations in the host rock. Extensive alteration of the host rocks surrounding the mineralization is marked by the production of illite at the expense of kaolinite, and the removal of quartz by dissolution, in both the sandstones and the basement rocks. In addition to illite, chlorite has formed as an alteration mineral in the basement. This alteration occurred at the same time as the U mineralization.

In a generic working model for unconformity-type U deposits in the Athabasca Basin, mineralization is considered to have resulted from the interaction of diagenetic U-bearing solutions from the sandstone formation with reducing, basement-derived solutions along the unconformity. The fractures associated with these mineralizations are reactivated, basement, fault structures that acted as the major plumbing system for the mineralizing solutions and subsequently for all groundwaters. This is confirmed by regional studies of the Sandstone Formation stratigraphy and mineralogy, which shows little evidence for vertical crossflow of groundwaters across unit boundaries other than along these fault structures (Ramaekers, 1981).

ANALOGY

A comparison of the data on the sandstone-hosted unconformity-type U-deposits in northern Saskatchewan with the concept and scenario for waste disposal shows similarity on the following points (see Figure 2):

(1) There is a strong resemblance between the cross section of a U deposit and that of the waste vault concept. In both instances, the U concentration is surrounded by a clay-mineral-rich halo, and this whole assemblage is separated from the biosphere by several hundred metres of hard rock. During ore formation, the thickness of the overlying sandstone sequence was at least 1000 m.

(2) The thermal regime at the time of U-ore deposition peaked around 150 to 200°C (Pagel, 1977), which is similar to the predicted peak temperatures of the thermal transient in the nearfield of the waste vault. Whereas the temperatures of ore deposition lasted for several million years, as indicated by age dating of the U ores, the thermal transient in the waste vault is predicted to last a few ten thousand years (Acres et al., 1980).

(3) The ore-forming solutions and late diagenetic solutions had high salinities in the range of 25 to 35% equivalent weight NaCl or about 250 to 350 g/L total dissolved solids (TDS). Concentrations in saline groundwaters deep in the Canadian Shield are in the range of 100 to 250 g/L TDS (Fritz and Frape, 1982).

(4) Isotopic ratios in the U ores indicate that fractionation of uranium and lead, through groundwater interaction, occurred after initial ore formation. Several fractionation events can be distinguished for each deposit, but the youngest basin-wide event occurred around 300 million years ago. In a waste disposal scenario, a waste/water interaction and a

subsequent dispersion of waste elements are similar to a fractionation event, as recorded by the isotopic ratios in the U ores.

In addition, there are essential differences that permit the sandstone-hosted U deposits to be assessed as an open system in comparison with the disposal concept. These differences, with respect to the deposits, are the obvious lack of engineered containment barriers, the close association with fault structures, the higher porosity (about 10 to 100 times) of the sandstone, and the significant change in burial depth with time due to erosion of the overlying rock formation.

The dispersion of U in the clay-mineral-rich halo around individual, well-defined ore bodies is very limited, often to only about 5 m from the ore body. With the ore formation dated at more than 10^9 years ago, subsequent groundwater interaction with the ore has resulted in only a very limited remobilization of U. Remobilization is even less significant if the U dispersion halo in the host rocks is interpreted as being of primary origin, as is indicated by petrographic and geochemical data.

Furthermore, the present "closed system" behaviour of these U deposits is evident in mineral exploration, where highly sensitive geochemical techniques have failed to locate even shallow deposits (e.g., Parslow, 1983). The U deposits in the Athabasca Basin were discovered from physical (due to erosion) or geophysical (associated conductor zones) indicators, combined with primary lithological indicators, rather than from secondary dispersion indicators at the surface (i.e., groundwater and host rock chemistry).

The unconformity-type U 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 an underground disposal vault.

ORE/WATER INTERACTION

Ore Forming Solutions

Data on the pressure, temperature and composition of the paleogroundwaters associated with ore formation can be obtained from the analysis of fluid inclusions. Pressure estimates, based on the dissolution of halite daughter crystals upon heating of the fluid inclusion, give a crystallization pressure of 750 ± 150 MPa for the host mineral quartz from Rabbit Lake, one of the shallowest deposits in the Athabasca Basin (Pagel, 1977). However, Nash et al. (1981) points out that this estimate, equivalent to a sediment thickness of about 2 500 m, should be considered a minimum because of the uncertainty in the halite-solution method. Homogenization studies of fluid inclusions in euhedral quartz from several deposits (Pagel, 1977; Pagel et al., 1980; Little, 1974; this study) show a maximum temperature of formation in the range of 150 to 200°C, and salinities in the range of 25 to 30% equivalent weight NaCl. Both homogenization temperature and salinity of the trapped fluids increase with depth in the sandstone formation.

Quartz occurs as euhedral overgrowth on detrital quartz grains and as cement between the grains, showing growth in different stages, from early diagenetic through mineralization to late diagenetic. The fluid inclusions provide a record of fluid composition associated with each stage. Quartz growth contemporary with U mineralization is distinguished by the absence of hematite inclusions and by the association with dolomite and solid amorphous hydrocarbons. Pagel (1977) and Pagel et al. (1980) found that the conditions and compositions of the mineralizing solutions were very similar to those of the diagenetic solutions. However, in addition to a high salinity (Na-Ca-Cl type), fluid inclusions of mineralizing solutions in euhedral quartz and dolomite from highly altered sandstone contain noticeable amounts of carbon dioxide and hydrocarbon (mainly methane), both near the U ore and away from any mineralization.

Uranium precipitation probably occurred at the interface of two mixing flow systems containing an oxidizing U-bearing solution and a reduced solution, respectively. Evidence for oscillations in the redox potential in the ore zone is preserved in small-scale alterations of oxidized and reduced mineral assemblages. Also, hematite-rich horizons, in addition to solid hydrocarbon buttons, are invariably in close spatial association with the ore zone. The occurrence of hematite in the otherwise strongly reduced host rocks in this case suggests that the Fe redox couple may have contributed to the precipitation of U from solution and/or the fixation of U during subsequent remobilization attempts from groundwater interaction. However, the large extent of bleaching (i.e., removal of iron) in the sandstone host rocks (see Figure 3(A)) shows that the reducing potential of the solutions away from the ore zones could not be controlled by the iron redox couple, but must be due to another reductant. The same argument applies to reduction by H_2S, since the occurrence of sulphides in the sandstone is restricted to the ore zones. On the other hand, the presence of large amounts of methane in solution can be explained by hydrothermal reaction on graphite-rich pelites in the basement.

Figure 3(A) shows a typical cross section for an unconformity-type U deposit. The section illustrates the alteration of both basement and sandstone along a vertical fracture zone in which U mineralization occurs around the intersection with the unconformity contact. The difference in width of the alteration zone is related to the difference in permeability between the sandstones and the basement rocks. Solutions flowing along the permeable fracture zone in the basement have altered the rocks to clay-rich assemblages characterized by illite and chlorite. Where this alteration zone intersects graphitic pelites, graphite has been corroded or has totally disappeared (Hoeve et al., 1980; Sopuck et al., 1983). At temperatures around 200°C (as indicated by the fluid inclusion data), graphite could have reacted with water to produce CH_4 and CO_2 (French, 1966) in significant amounts on a time scale of 10^6 to 10^7 years (Frank et al., 1974). In fact, the study by French (1966) indicates that, at $T \leq 200°C$ and P = 100 MPa, graphite in contact with water will react to produce predominantly CH_4 and H_2 when oxygen is controlled by the magnetite-iron and wüstite-iron buffers, or predominantly CH_4 with some CO_2 when the quartz-fayalite-magnetite buffer is used. At temperatures below 100°C, the kinetics of nonbiological graphite/water reactions are very slow (Frank et al., 1974), but could still account for the observed accumulation of methane and other hydrocarbons in interstitial pore water and in semiclosed flow systems (Hoeve and Sibbald, 1978; Earle and Drever, 1983). The low U concentrations in modern groundwaters from known mineralized areas in the Athabasca Basin (Earle and Drever, 1983) are likely due to the strong effect of methane on the redox potential.

Present Day Solutions

The U concentrations in groundwaters from drillholes that intersect mineralization appear to be controlled by the solubilities of the U ore-minerals. Figure 4(A) gives the main assemblage of U minerals and their crystallization order with respect to quartz as observed in the Key Lake deposit (Dahlkamp, 1978). This general schematic also applies to most other unconformity-type deposits in the Athabasca Basin (Hoeve and Sibbald, 1978). Pitchblende I occurs as crystalline and colloform (amorphous) aggregates surrounded and veined by "sooty" pitchblende II, which is always amorphous. Poorly crystalline to amorphous coffinite occurs associated with, and as pseudomorphs of, pitchblende II, indicating a secondary origin after pitchblende II. Coffinite can be as adundant (by volume) as pitchblende I and II combined. Thus, the ore minerals contain U mainly in the valency states of 4 to 5, and hence U concentrations in groundwater should be mainly controlled by tetravalent and pentavalent species. However, the largely amorphous nature of the ore minerals must also be considered, since the solubilities of the amorphous and well crystallized phases can be significantly different (e.g., by 10^6 for UO_2, Langmuir 1978). Thus, the U concentrations in groundwater in contact with both amorphous and crystalline tetravalent plus pentavalent phases can be expected to be several orders of magnitude higher than the solubility of uraninite.

Figure 4(B) shows the U concentration in six groundwaters from the Dawn Lake deposit (Table I) plotted on a U-solubility diagram for a reducing groundwater with low carbonate content. For pH values of 8 and higher, the maximum solubility is determined by the tetravalent species, $U(OH)_4(s)$ and $U(OH)_5^-$, respectively. Below pH = 8, the maximum solubility is determined by the pentavalent UO_2^+ species and is several orders of magnitude higher than the solubility of crystalline UO_2. Five of the groundwaters have a pH close to 7 and one groundwater has a pH = 6. Only one groundwater plots above the maximum solubility curve and its higher U content may be correlated with a higher sulphate concentration (Table I); however, at the overall low sulphate concentrations of less than 10 mg/L, it is doubtful whether there is any significant sulphate complexing (Langmuir, 1978). The low sulphate levels also indicate that the redox potential of the groundwater must straddle that of the sulphide/sulphate couple, or was lower when in contact with the U minerals, and some sulphate was picked up subsequently.

In Figure 5, the Eh diagram at pH = 7 shows two values for the U solubility (from Figure 4(B)) and three redox couples for which evidence is found in the ore deposits. At 25^oC and pH = 7, oxidation of dissolved Fe^{2+} (at 10^{-5} m) will precipitate ferric hydroxide at Eh = 0 V, rather than hematite at Eh = -0.236 V, because of slow kinetics. However, if precipitation of ferric hydroxide were controlling the Fe^{2+} concentration in the groundwaters from the Dawn Lake deposit, their sulphate concentrations (from oxidation of sulphides) should be much higher than 10 mg/L. In these groundwaters, the low sulphate content and the presence of methane rather indicate that the Fe^{2+} concentrations are controlled by the dissolution of hematite, for which the Eh value approaches that of the CH_4/CO_2 couple. The low total-carbonate level (av. 30 mg/L, Table I) indicates further that, in the presence of CH_4, the redox potential of the groundwater must be very low. This is supported by the reported low U concentrations. Thus, an estimate for the Eh of the groundwaters at Dawn Lake must be in the range -0.20 to -0.25 V, and is likely lower than -0.25 V.

ROCK/WATER INTERACTION

The Manitou Falls Formation (Ramaekers, 1981) is the basal unit in the eastern part of the Athabasca Basin, and forms the host rock to the sandstone-hosted U deposits. The clay mineralogy of the unaltered rock (i.e., rock removed from any known mineralization) consists essentially of kaolinite and illite in roughly equal proportions, whereas smectite and mixed-layer clays are absent (Hoeve et al., 1981a). This clay matrix changes in composition as well as in abundance when going from unaltered sandstone to the host rock immediately surrounding an ore body (Figure 3). Initially the illite/kaolinite ratio increases with increasing degree of iron removal ("bleaching") until kaolinite disappears in the intensively altered, friable sandstone around the ore (Hoeve et al., 1981b). The volume percentage of clay matrix in the host rock near the ore increases (to 60-90%) to form a clay-rich halo containing illite in the sandstone above the unconformity, and illite plus chlorite in the basement rocks below the unconformity.

Figure 3(B) shows the distribution of U in the same section as shown in Figure 3(A). Uranium enrichments in sandstone are found in the bleached rocks on either side of the fracture zone, with locally lateral extensions along bedding planes. The correlation of U enrichment with the extent and intensity of rock alteration, plus the geochemical and mineralogical data, indicates that this enrichment of U in the sandstones is a primary feature related to the ore formation.

Figure 6 shows the distribution of U and Hf in a profile through the clay-rich halo around one ore body in the Dawn Lake deposit. Uranium values show a distinct enrichment (av. 5.5 times) in the first 5 m from mineralization compared with the outer half of the profile, with peakvalues around 1 2.2 and 4 m from the contact. The U concentrations in the outer half of the profile are more uniform, although they are not yet background levels. The diagram for Hf, an immobile element compared with U, shows less difference between concentrations in the inner and outer halves of the profile than for U. This suggests that, if enrichment of these two elements is of primary origin (i.e., associated with ore formation), the higher enrichment factor for mobile U may be the result of secondary dispersion. However, a closer inspection of the correlation between the three peak values for U and hafnium reveals that local enrichment is essentially of primary origin for both elements.

Two sets of elemental concentrations (in decreasing order of abundance) are plotted in Figure 7 for two intimately associated host rock samples from the clay-rich halo. Both samples are from an unfractured sandstone section where one half (sandstone on Figure 7) contains about 30 vol. % clay matrix and the other half (massive clay section on Figure 7) consists of at least 90 vol. % of clay minerals, with the remainder quartz and abundant zircon. The suite of elements consists of trace elements with widely varying solubility and chemical mobility. The diagram illustrates the constant enrichment factor (av. 3.1) that correlates the two sets of values. This constant enrichment of widely different trace elements can only be explained through removal of a "barren" phase, such as quartz, from the sandstone. The removal of a phase containing some of the elements shown in Figure 7 could not result in a similar distribution pattern for all these elements in both the sandstone and the clay section. Furthermore, to interpret the clay section as fracture infilling can not explain the fixation of the different elements from solution onto the clay minerals in the same proportions as found in the sandstone. Also, this interpretation can not explain the abundance of rounded zircon in the massive clay section; this zircon is most likely of detrital origin. On the other hand, quartz dissolution and reprecipitation (solidification) have been observed on both local and regional scales (Ramaekers, 1981), and are ascribed to both advanced diagenetic processes and ore-forming processes. At the pressures, temperatures and salinities (as inferred from fluid inclusions) associated with ore formation, significant quartz dissolution is not only possible at the mixing interface of, for instance, a saline diagenetic solution and a more dilute, basement-derived solution, but is also necessary in order to provide space for the precipitating ore minerals. Dissolved silica is then precipitated further down the thermal gradient, where it is found as quartz overgrowth and cementation in the sandstone overlying the ore body. In the field, this silicified rock is commonly referred to as the "quartz-cap" rock. Thus, the enrichment of U in the massive clay section (Figure 7) is probably the result of the concentration of the clay matrix in the original sandstone through the dissolution and removal of quartz during initial ore formation.

CONCLUSIONS

The sandstone-type U deposits associated with the sub-Athabasca unconformity provide a good natural analog for a nuclear fuel waste disposal vault. Evidence for many important processes has been preserved over many millions of years in these deposits. Some of the processes discussed in this paper show the following:

(1) Conditions and compositions similar to those expected in the buffer and backfill of a waste vault occurred in the sandstone during diagenesis and ore formation, resulting in mineral reactions that produced illite and dissolved quartz and iron.

(2) Redox conditions and low-carbonate concentrations are the important parameters for the fixation of U, both at high temperature about 1 billion years ago and at low temperature at present. Secondary dispersion of U appears to have been minimal, possibly because of redox reactions involving graphite consumption and methane production.

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Table 1. Chemical composition of groundwaters from the Dawn Lake U-deposit, Saskatchewan. DDH-samples are groundwaters from diamond-drill holes intersecting mineralization.

	DDH 14-129	DDH 249	DDH 283	DDH 371	DDH 372	DDH CW
Na (mg/L)	2.3	3.0	4.8	2.5	4.0	nd
K	1.42	1.26	1.56	1.46	1.67	nd
Ca	0.34	4.3	7.9	2.8	3.1	nd
Mg	0.25	2.3	4.8	1.5	2.2	nd
Fe	3.23	< 0.06	1.20	1.39	0.25	nd
Ni	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	nd
As	0.005	< 0.002	0.16	1.9	0.010	nd
Pb	0.08	< 0.06	< 0.06	< 0.06	< 0.06	nd
Co	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	nd
V	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	nd
F	0.05	0.12	0.23	0.12	0.12	nd
Cl	0.49	0.22	2.75	0.54	0.38	nd
P	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	nd
NO_3	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	nd
SO_4	0.60	1.34	1.59	6.41	2.28	nd
HCO_3	7	32	61	15	31	nd
CO_3	< 2	< 2	< 2	< 2	< 2	nd
U (μg/L)	0.42	0.38	1.77	17.03	0.15	0.18
pH (field)	5.93	7.10	7.46	6.74	7.01	7.05

nd = not determined.

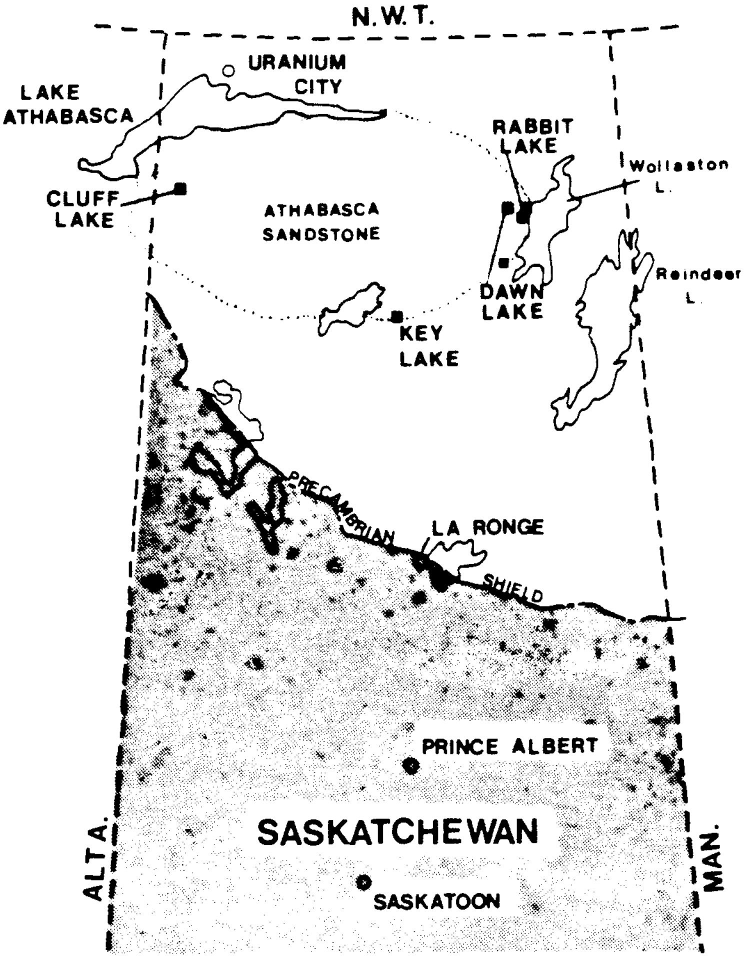


Figure 1. Location of some important unconformity-type U deposits in the Athabasca Sandstone Basin of northern Saskatchewan.

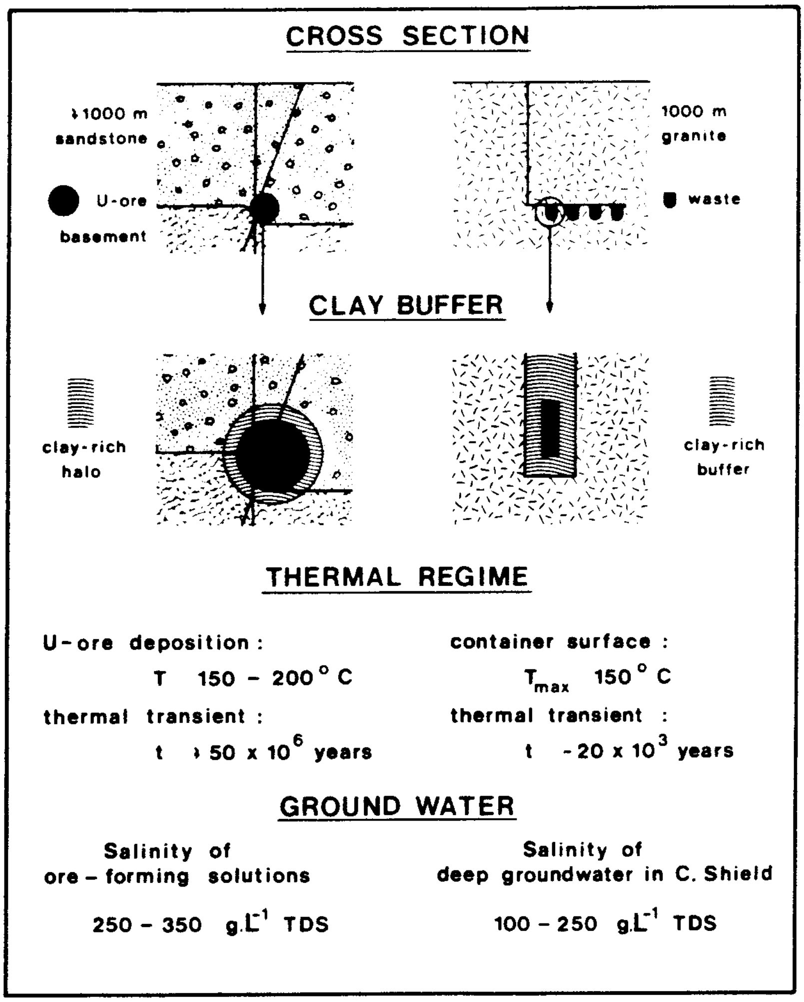


Figure 2. Comparison of some important parameters for the sandstone-hosted U deposits (left) and the waste vault concept (right).

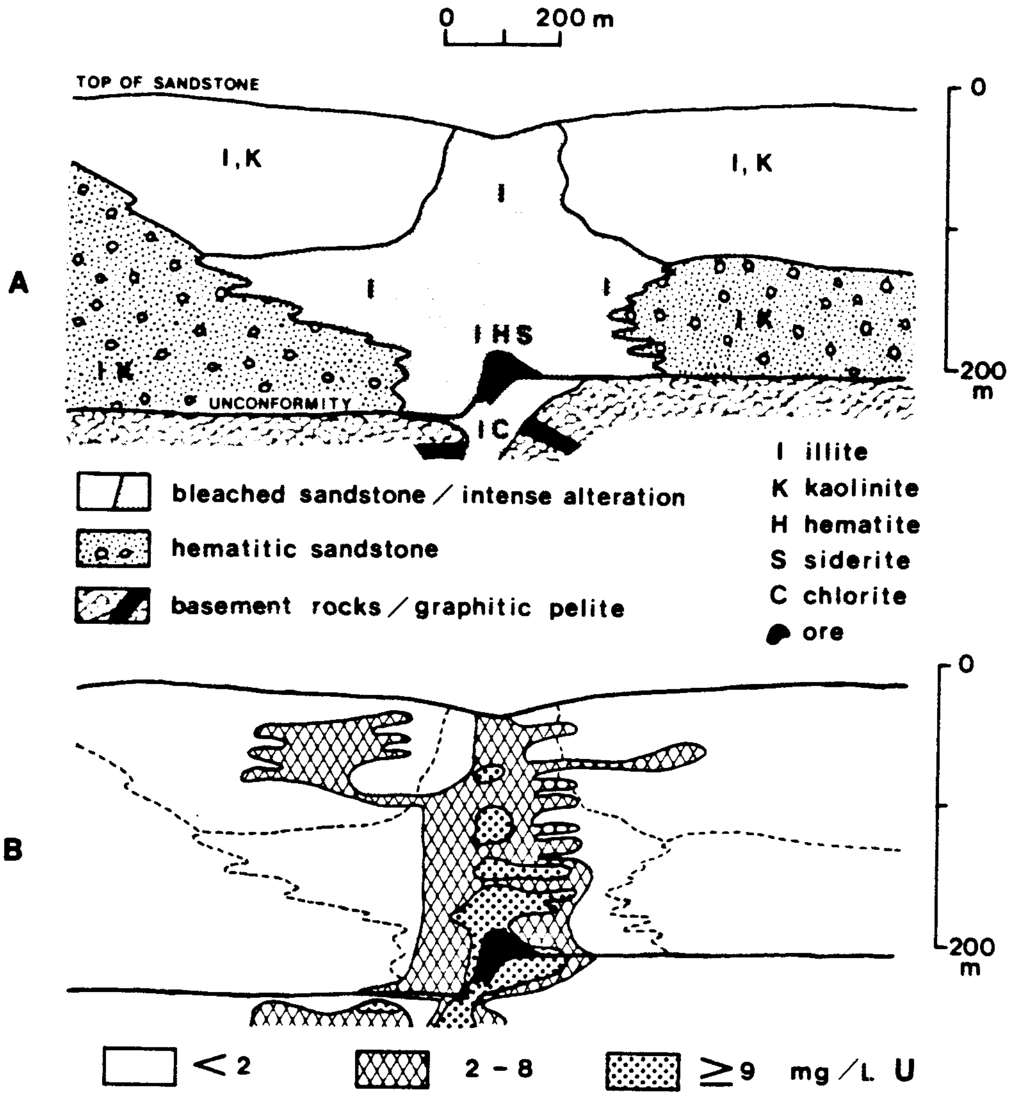


Figure 3. Typical cross section of an unconformity-type U deposit: Midwest Deposit (Sopuck et al., 1983): (A) geology, (B) U-distribution.

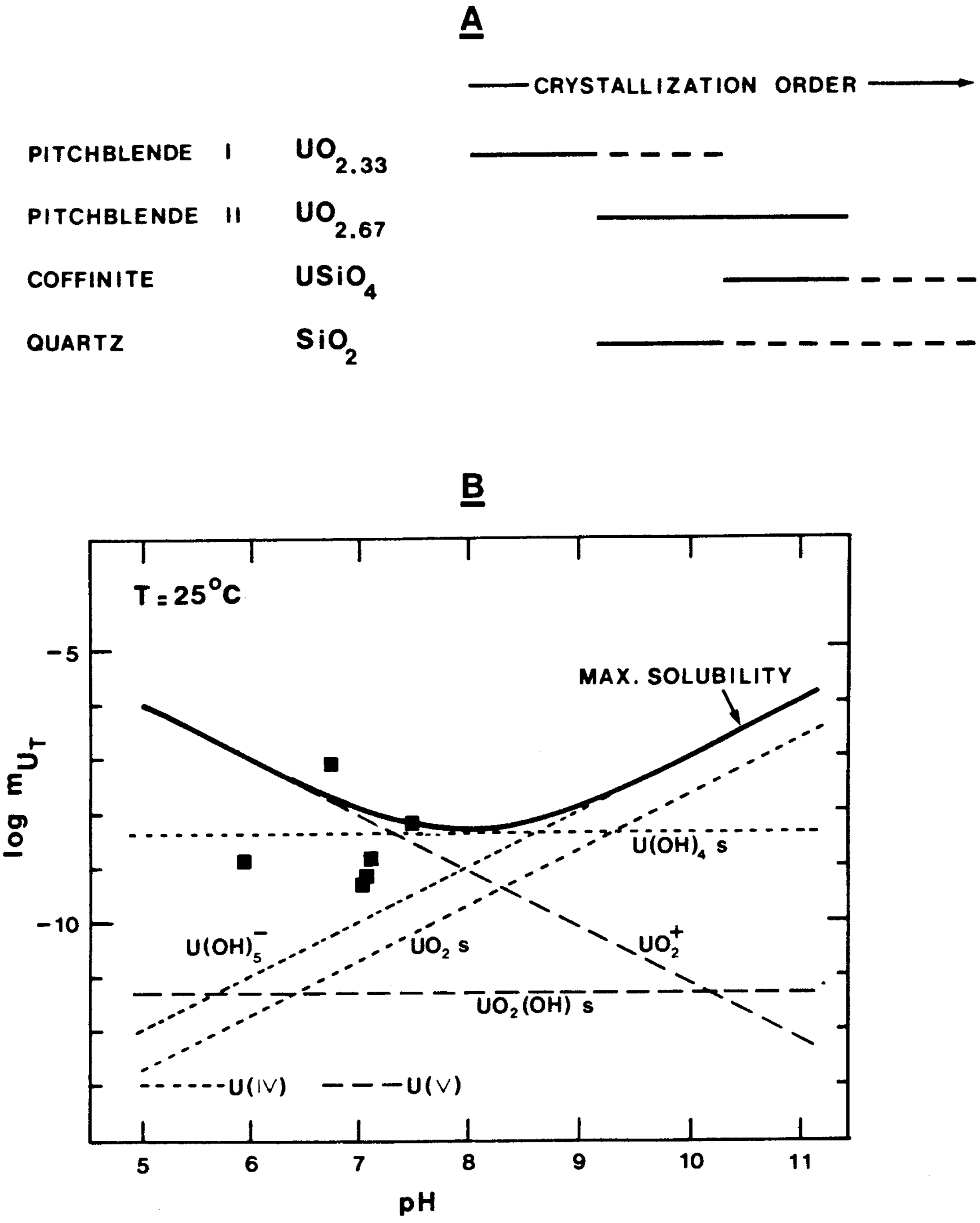
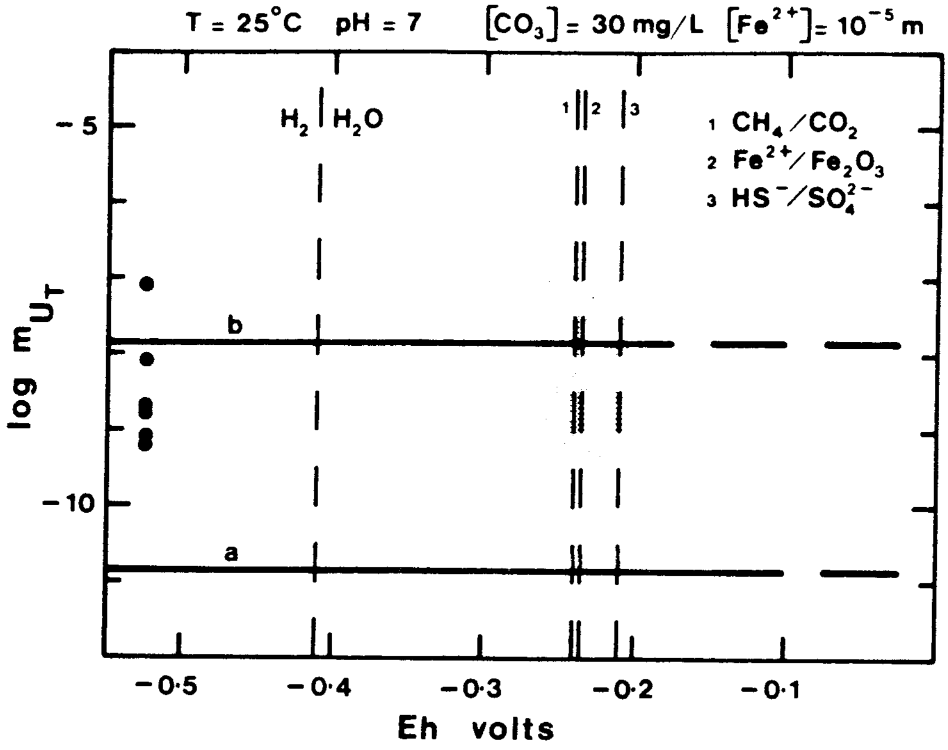


Figure 4. (A) Paragenesis of U-ore minerals and quartz in an unconformity-type U deposit (Dahlkamp, 1978).

(B) Uranium concentrations in reducing, carbonate-poor, groundwater as a function of pH. Sample points are groundwaters from the Dawn Lake Deposit (Table 1). (Solubility data from Allard, 1982).



Figur 5. Plot of U concentration versus Eh at pH = 7, showing solubility (solid lines) of crystalline uraninite (a), maximum solubility (b) from Figure 4(B), and Eh values for some important redox couples (dashed lines). The points on the left indicate the U values for the groundwater from Dawn Lake (Table 1), and the dashed field indicates the possible Eh values corresponding to those U values.

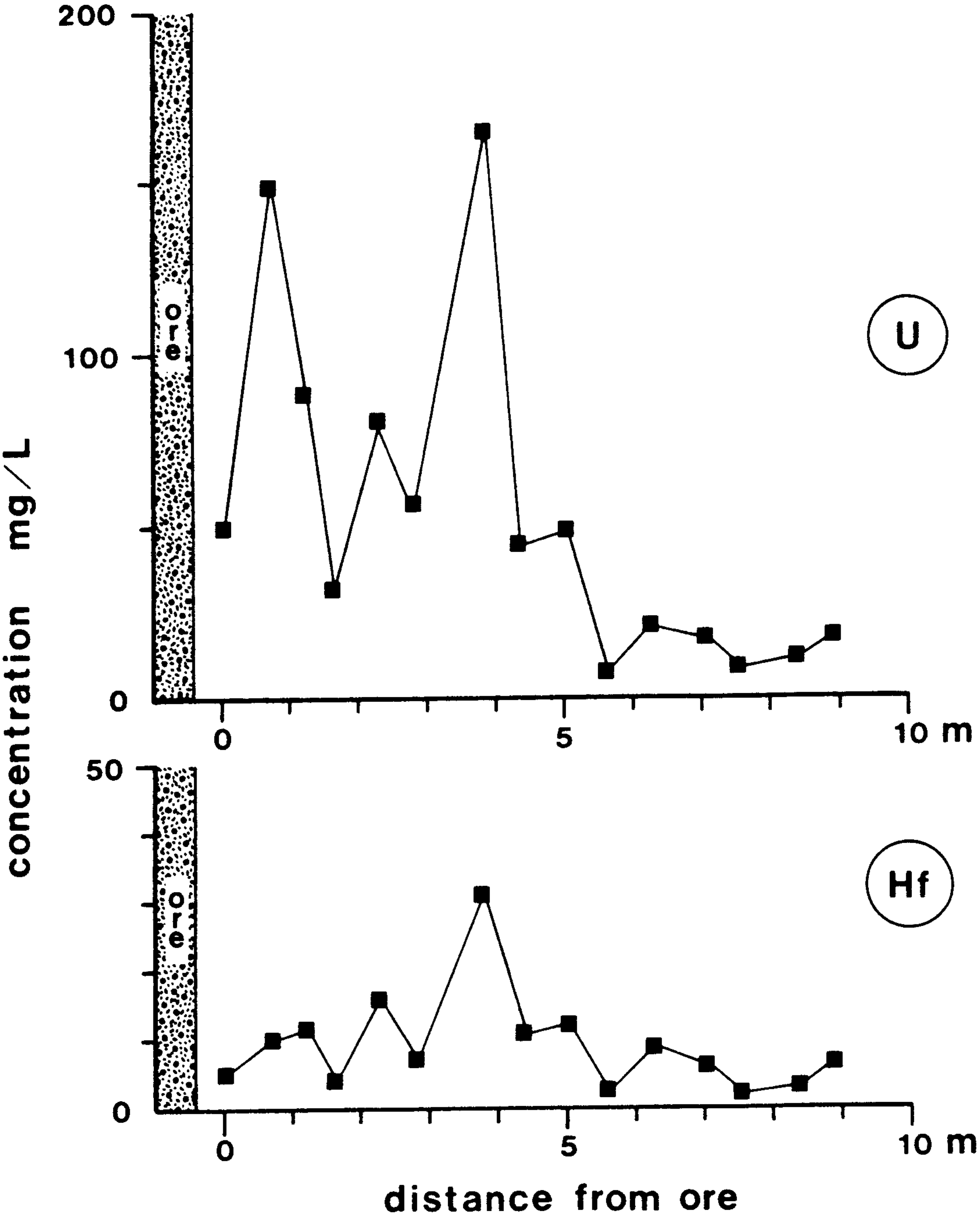


Figure 6. Profile through the clay-rich halo around an ore body at the Dawn Lake Deposit, showing the distribution of uranium and hafnium with respect to the distance from the ore.

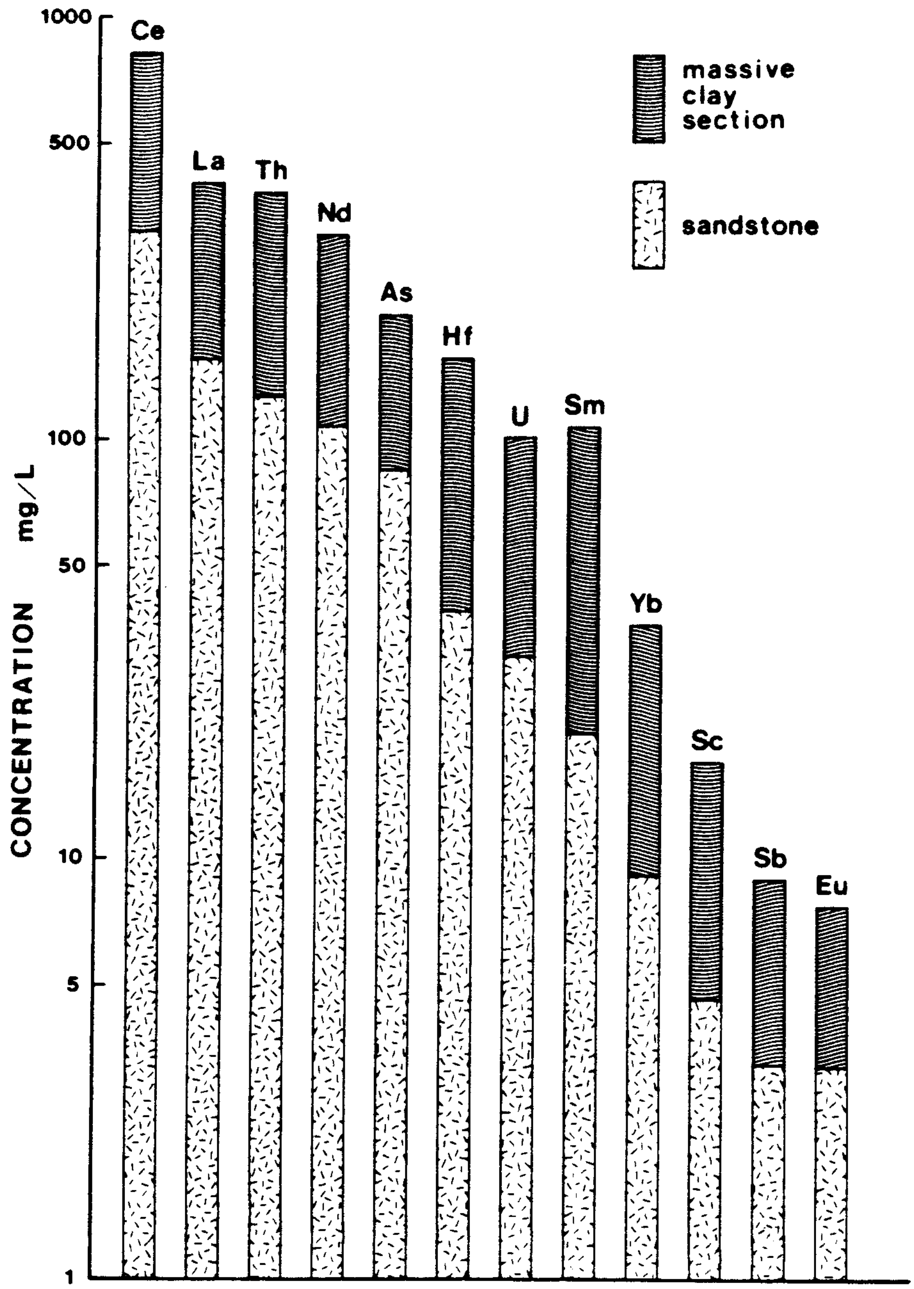


Figure 7. Concentrations for various trace elements in two intimately associated sections of one sample from the clay-rich halo around an ore body at the Dawn Lake Deposit. The top of each differently marked column-section gives the concentration for an element in the corresponding rock type. Elements are plotted in decreasing order of abundance.

GEOCHEMICAL CONTROLS ON ^{99}Tc TRANSPORT AND RETENTION

D.B. Curtis

Isotope Geochemistry Group, MS-J514, Los Alamos
National Laboratory, Los Alamos, New Mexico, 87545

ABSTRACT

Geologic systems are complex and diversified. Thus, to understand repository behavior one must divide a complex system of interacting phenomena into individual components. No study of a natural system is going to simulate the complex system of interacting phenomena associated with a geologic repository for high-level radioactive wastes. By discussing the geochemistry of technetium present at natural reactors, it is suggested that the study of natural systems in support of the design and assessment of repositories should be clearly focused on "individual components" of the complex system. Such focused research should contribute significantly to posing questions and providing answers regarding the hydrologic, thermal, mechanical and chemical interactions between a high-level waste repository and the geologic environment which encompasses it.

INTRODUCTION

Technetium-99 is a nuclide of primary concern in the disposal of radioactive wastes. It is a high yield fission product and thus a prominent component of the wastes. Because of its long half-life, 2.13×10^5 years, it will remain an important constituent of the waste package for more than a million years. The stability of the engineered waste package over such a long period of time cannot be evaluated with any degree of confidence. Consequently there must be a reasonable assurance that the geologic barrier will retain technetium for the length of time required for it to decay to innocuous levels. Technetium is extremely rare in the natural environment, therefore geochemical controls on its rate of transport are inferred from laboratory studies. Confirmation of the conclusions of such studies would provide assurances as to the effective long term storage of this element. Such assurances should be sought in geologic environments where natural technetium is or has been present as a detectable component. One such environment is the uraniferous rock at the Oklo mine in equatorial Africa that once sustained natural fission reactors. These fossils of nuclear reactors offer a unique opportunity to study the geochemistry of technetium.

TECHNETIUM-99 REDISTRIBUTION IN THE NATURAL REACTORS

The reactors at Oklo were critical two billion years ago. Criticality was sustained, perhaps intermitently, for a period between 10^5 and 10^6 years. Because of the extreme length of time since criticality, all the ^{99}Tc that was produced in the reactor has decayed to its stable daughter ^{99}Ru. Measurements of the isotope abundance of ^{99}Ru provide information about the geochemistry of technetium during its existence in the reactors two billion years ago. Nuclear fission produces four stable isotopes of ruthenium; ^{99}Ru, ^{101}Ru, ^{102}Ru, and ^{104}Ru. The latter three are produced instantaneously, i.e. their radioactive precursors are short lived relative to the rate of relevant geologic processes. However, because of the long half-life of its immediate precursor, ^{99}Tc, the rate of production of ^{99}Ru is much slower than it is for the other fissiogenic ruthenium isotopes. For a geologically significant period of time the fission produced isobars at mass 99 existed as two different chemical species; ruthenium and technetium. Fractionation of these two elements produced measurable excesses and deficiencies of ^{99}Ru relative to the other fissiogenic isotopes. The extent of such fractionation may be evaluated by comparing the measured ratio of ^{99}Ru/^{101}Ru + ^{102}Ru to the ratio of the fission yields is unity it signifies a closed system with respect to these two elements. If this value is greater than unity, the rock was enriched in technetium and a value less than unity signifies technetium depletion. Such normalized ratios in rocks from the reactor zones and their periphery are presented in Table 1.

Values in Table 1 range form 0.61 to 40.0. Only 9% of the 56 results have values of unity. There is no doubt that technetium and ruthenium were fractionated from each other during the period of nuclear criticality. With a few exceptions rocks from within the reactor zones and from the aureoles within about a meter of the reactor zones are deficient in technetium. In contrast, all the samples with very large excesses of technetium were taken from distances greater than a meter from the nearest reactor zone. Those with the largest excesses were carefully chosen at distances between 1 and 6 meters of the nearest exposure of reactor zone 9.

Technetium is a multivalent element. In a reduced environment it forms a highly insoluble tetravalent oxide. In an oxidized environment the hexavalent element takes the form of a soluble oxyanion. Redox controlled partitioning between these two valence states is beleived to control the rate of movement of technetium in the presence of a mobile aqueous phase. Uranium mines are considered to be strongly reduced environments. Figure 1 shows the Eh-pH conditions in uranium ores (Brookins, 1978). Included in the diagram are the stability fields of technetium species at 25°C (Brookins, 1978). The superposition of the uranium ore stability field and that of the tetravalent oxide suggests that technetium would have been insoluble and hence immobile in the uranium ores of Oklo. This is contrary to the abundant evidence of technetium redistribution around the natural reactors.

The almost universal deficiency of technetium in the reactor zones and the exclusive association of technetium excesses with rocks from the periphery of the reactors suggests that the element was transported out of the reactors and redeposited in nearby rocks. If this is the case, it can be concluded that the mobilization of technetium can be attributed to conditions established by the reactors themselves. Once technetium was transported into the ambient geologic environment, it was rendered immobile as would be expected from the redox considerations. In the jargon of the United States waste isolation program, mobilization of technetium at Oklo appears to be the result of near field conditions. Under far field conditions it was effectively immobilized.

The transport and retention of an element depends upon the equilibrium solubility of the element bearing mineral, the degree of saturation of the mobile phase with respect to the element, and its partitioning between mobile and immobile phases. The following discussion will consider three possible controls on the redistribution of ^{99}Tc in the natural reactors: The first deals with reactor produced alterations of the rocks that enclosed the reactors. The remainder of the discussion deals with speculations regarding changes in the chemical environment produced by increases in temperature and by the radiation fields associated with the reactors.

REACTOR PRODUCED ALTERATIONS

The reactor zones can be generally characterized as a reactor core where the sustained nuclear reactions actually occurred, and a series of aureoles extending for a distance of two metres from the reactor zone. Rocks that contain the remnants of the nuclear reactors and those that immediately surround them are anomalous compared to rest of the uranium rich statum in the Oklo mines. The chemistry and mineralogy of the reactor zones and their aureoles are probably direct manifestations of changes in the physical and chemical environment induced by the nuclear reactions (Weber, 1978). In this sandstone environment, the reactor zones exhibit few sedimentary features. The gangue of the ore in the reactor zones is characterized small portions of quartz and major quantities of clays. This is in sharp contrast to the surrounding sandstone where quartz is a major mineral and clays are generally accessary phases. Aureoles around the reactor zone are defined primarily by changing clay mineralogy. A detailed discussion the mineralogy and lithology of the reactors may be found in Gauthier-Lafaye and Weber (1978). Figure 2 is a generalized diagram taken from that paper to illustrate the alterations associated with the reactor zones. There are also chemical differences between rocks from the reactor zones and their aureoles which probably reflect differences in mineralogy in relation to the degree of radiation exposure. Rocks that sustained nuclear reactions have chemical properties that are distinct from those in samples which were not exposed to the nuclear reactions (Curtis and Gancarz, 1983). In Figure 4 the former are identified as chemical type 1 and the latter as chemical type 4. Minerals capable of concentrating technetium may have been unstable under conditions in the reactors and stable under conditions in the aureoles or the unaltered sandstone. Differences between the mineralogy of the reactor zones, the aureoles, and the unaltered host rock may have controlled the redistribution of technetium.

TEMPERATURE EFFECTS

The effects of reactor produced increases in temperature on the redox controlled solubility of technetium were considered by Curtis et al. (1981). Figure 3 is a diagram from that paper showing increases in the solubility of technetium increases as a function of increases of temperature. Superimposed on the temperature dependent variations in technetium solubility is an estimate of the concentration required to produce the observed deficiencies by transport in a mobile aqueous phase. The temperature dependence was calculated by determining the oxygen fugacity as a function of temperature in a system buffered by a mixture of hematite and magnetite. At temperatures between 100°C and 200°C, the redox controlled concentration of TcO_4^- is large enough to account for the observed deficiencies of technetium by transport with reasonable volumes of aqueous fluids. These higher temperatures are consistent with the thermal history of the reactors.

There are difficulties with this consideration: Magnetite is not found in the reactor bearing stratum and hematite is a sporadic minor constituent. It is unlikely that iron oxides controlled the oxygen fugacity in the Oklo ores. Such a model provides an explanation for the increase in solubility required to remove technetium from the reactors, but it cannot account for the observed fractionation between technetium and other elements. Despite the shortcomings, the study suggests that appropriate considerations of the temperature dependence of technetium solubility should be a part of any assessment of the effectiveness of geologic repositories.

RADIATION EFFECTS

Another study of the Oklo reactors indicates that radiation effects should be considered in evaluating the near field effects on the stability of multivalent elements. Shifts in the oxidation state of iron seem to correlate with chemical properties that reflect the degree of nuclear activity sustained by the samples. Iron in rocks from the heart of the reactor zones (chemical type 1) is largely in the reduced ferrous state. Samples that have sustained no nuclear reactions (chemical type 4) contain iron that is about equally distributed between the two oxidation states. These correlated changes are shown in Figure 4 (Curtis and Gancarz, 1983). The shifts in the oxidation state of iron might have been caused by localized changes in the redox potential caused by radiolysis of aqueous fluids in intimate contact with the reactor fuel.

Radiolysis is a common laboratory phenomenon that produces a variety of short lived chemical species by the interaction of radioactive emissions with water molecules. If intervening processes selectively remove some of the radiolysis products during their short lifetime, the effect is an increase in the concentration of other species in solution and a concomitant change in the chemical conditions. Shifts in the valence state of iron may reflect the preferential diffusion of radiolysis produced hydrogen into iron bearing minerals. The less mobile oxidizing species (O_2,H_2O_2) would have been concentrated in the aqueous phase and thus it would have been more oxidizing than if it were in equilibrium with the uraniferous sandstone of the reactor hosts or the phyllitic ores of the reactors themselves. The preferential movement of uranium from the reactor zone to the nearby host rock may have been the result of such radiolysis produced effects. Radiation induced shifts in the redox potential of the mobile phase would also have the effect of redistributing technetium by oxidizing it to the TcO_4^-. The retention of technetium in peripheral rocks may reflect the return to an environment where the redox state of the solution was controlled by the ambient geologic conditions.

CONCLUSION

"Developing a geologic repository for disposal of high-level radioactive waste requires careful definition of scientific and engineering questions to subdivide a large multidisciplinary problem into components that are resolvable. The difficulties in defining technical questions arise because many phenomena that contribute to overall repository behavior (e.g. hydrologic, thermal, mechanical and chemical responses) are closely coupled. Thus, to understand repository behavior, we must divide a complex system of interacting phenomena into individual components." (Duguid, 1981). Geologic systems are complex and diversified. No study of a natural system is going to simulate the "complex system of interacting phenomena" associated with a geologic repository for high-level radioactive wastes. As I have tried to demonstrate by the discussion of the geochemistry of technetium at the natural reactors, the study of natural systems in support of the design and assessment of repositories should be clearly focused on "individual components" of the complex system. Such focused research should contribute significantly to questions and answers regarding the hydrologic, thermal, mechanical and chemical interactions between a high-level waste repository and the geologic environment which encompasses it.

ACKNOWLEDGEMENTS

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Table I. Technetium-99 Deficiencies and Enrichments in Natural Reactors and Their Host Rocks.

Sample	Δ*
Reactor Zone 2	Reactor Zones
1408/4	0.91
1410/3	0.78
1413/3	0.81
1418	0.74
1421/5	1.14
1424/5	1.06
1425/1	1.00
1892	1.20
1897	0.88
1899/5	0.93
1901	1.00
3548	0.88
323	1.00
401/3	0.94
404/4	0.93
1177	0.81
1179	0.80
1181	0.95
1184	0.83
1187	0.94
Reactor Zone 3-4	
1763	0.88
1876	1.06
1844	1.06
1852	0.85
1856	0.99
1860	0.92
1864	1.00
1877	0.85
2223	0.80
Reactor Zone 9	
5	0.86
4	0.71
35	0.62
36	0.61
15	0.65
16	0.72
30	0.68
28	0.63

Table I. Technetium-99 Deficiencies and Enrichments in Natural Reactors and Their Host Rocks (Cont.).

Sample	Δ*
Zones 2 and 3-4	Peripheral Rocks
2650	2.5
2665	0.63
2669	0.87
2690	3.1
KN-258	0.92
2703	0.62
2197	0.99
2705	0.60
SCO-2252	2.7
Reactor Zone 9	
1-WR	4.1
2-L	39.
2-WR	23.
3-L	23.
3-WR	23.
6-L	0.87
6-WR	0.93
8-L	14.
C-L	38.
C3-L	39.

Data from Apt (1976), Cowan et al. (1975), Curtis et al. (1981), Gancarz et al. (1980), Hagemann et al. (1978), Maeck and Delmore (1982), Ruffenach (1978) and Ruffenach et al. (1975).

$$\Delta^* = \frac{\left[\dfrac{^{99}\mathrm{Ru}}{101 + 102_{\mathrm{Ru}}}\right]_{\text{Measured}}}{\left[\dfrac{^{99}\mathrm{Ru}}{101 + 102_{\mathrm{Ru}}}\right]_{\text{Fission Yield}}}$$

$\Delta^* > 1 \rightarrow$ ^{99}Tc Gain
$\Delta^* = 1 \rightarrow$ Closed System
$\Delta^* < 1 \rightarrow$ ^{99}Tc Loss

Figure 1

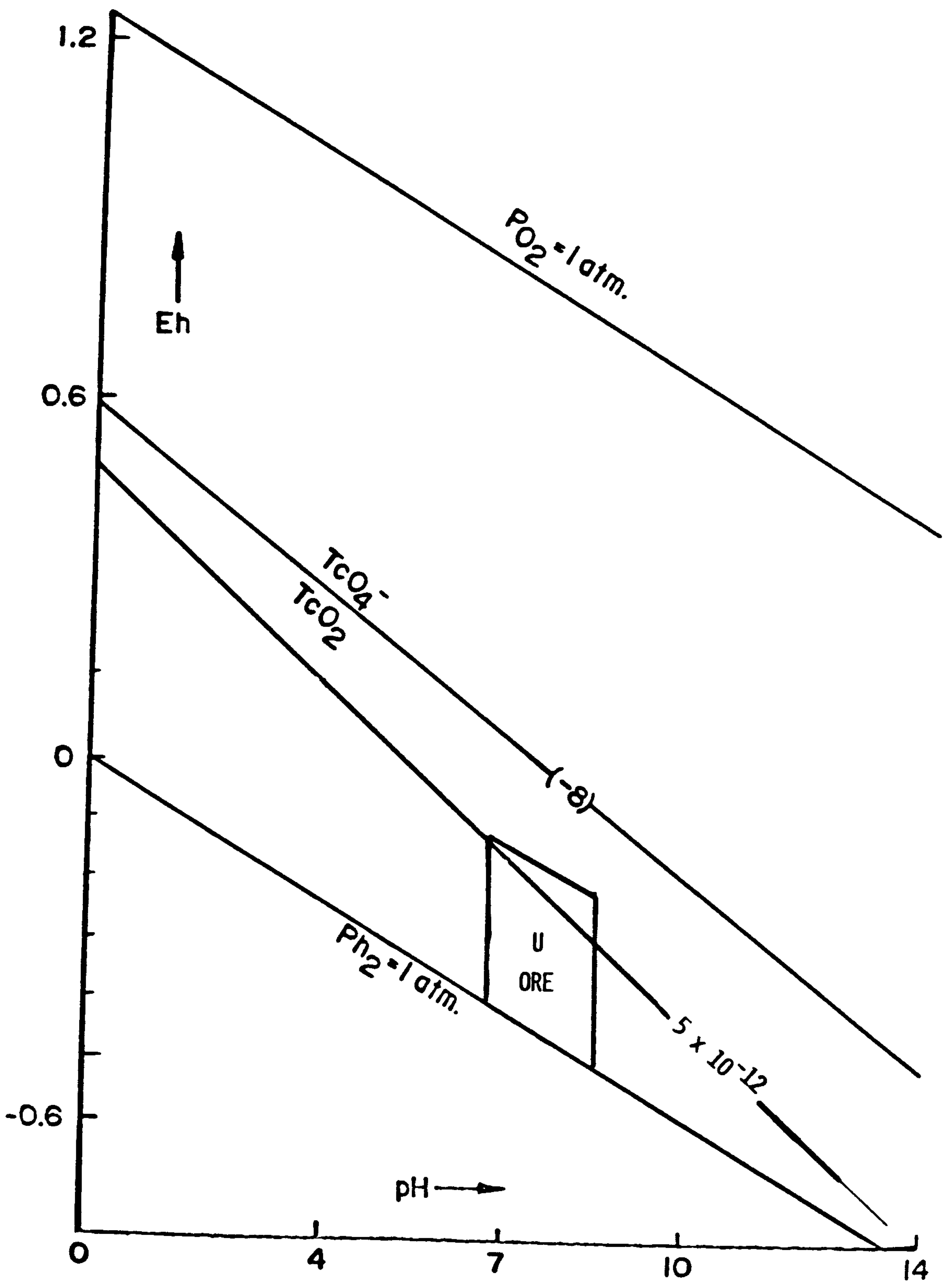

1.2
0.6
0
-0.6
Eh
P_{O_2}=1 atm.
TcO_4^-
TcO_2
(-8)
U
ORE
P_{H_2}=1 atm.
5 x 10^{-12}
pH
0
4
7
10
14

Figure 2

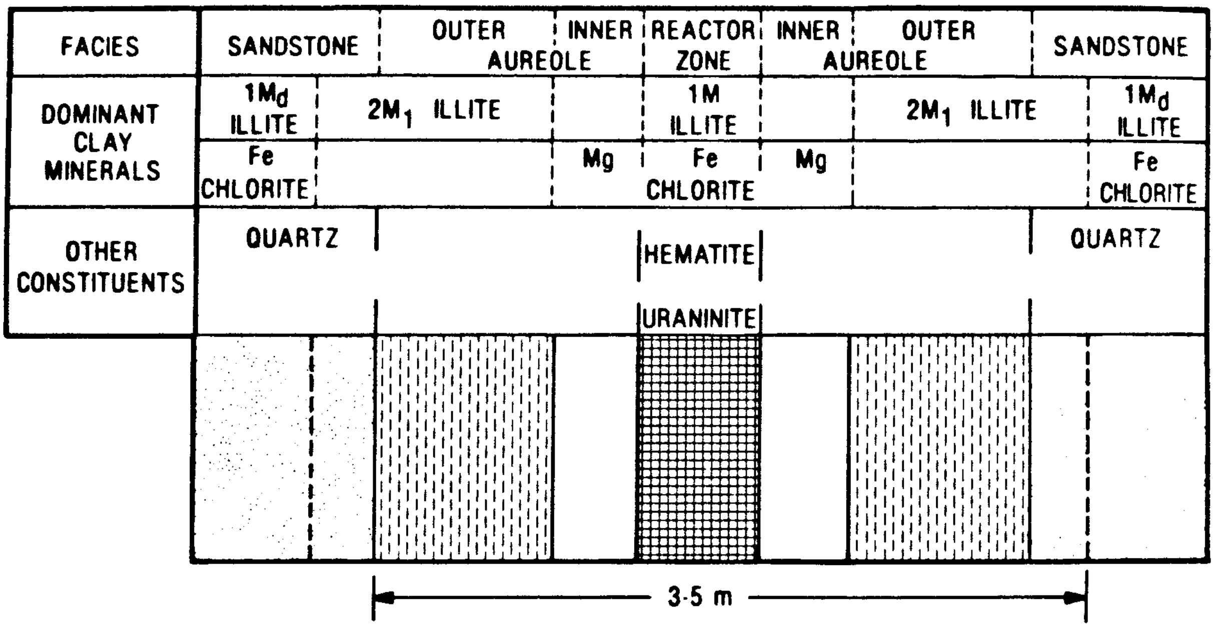
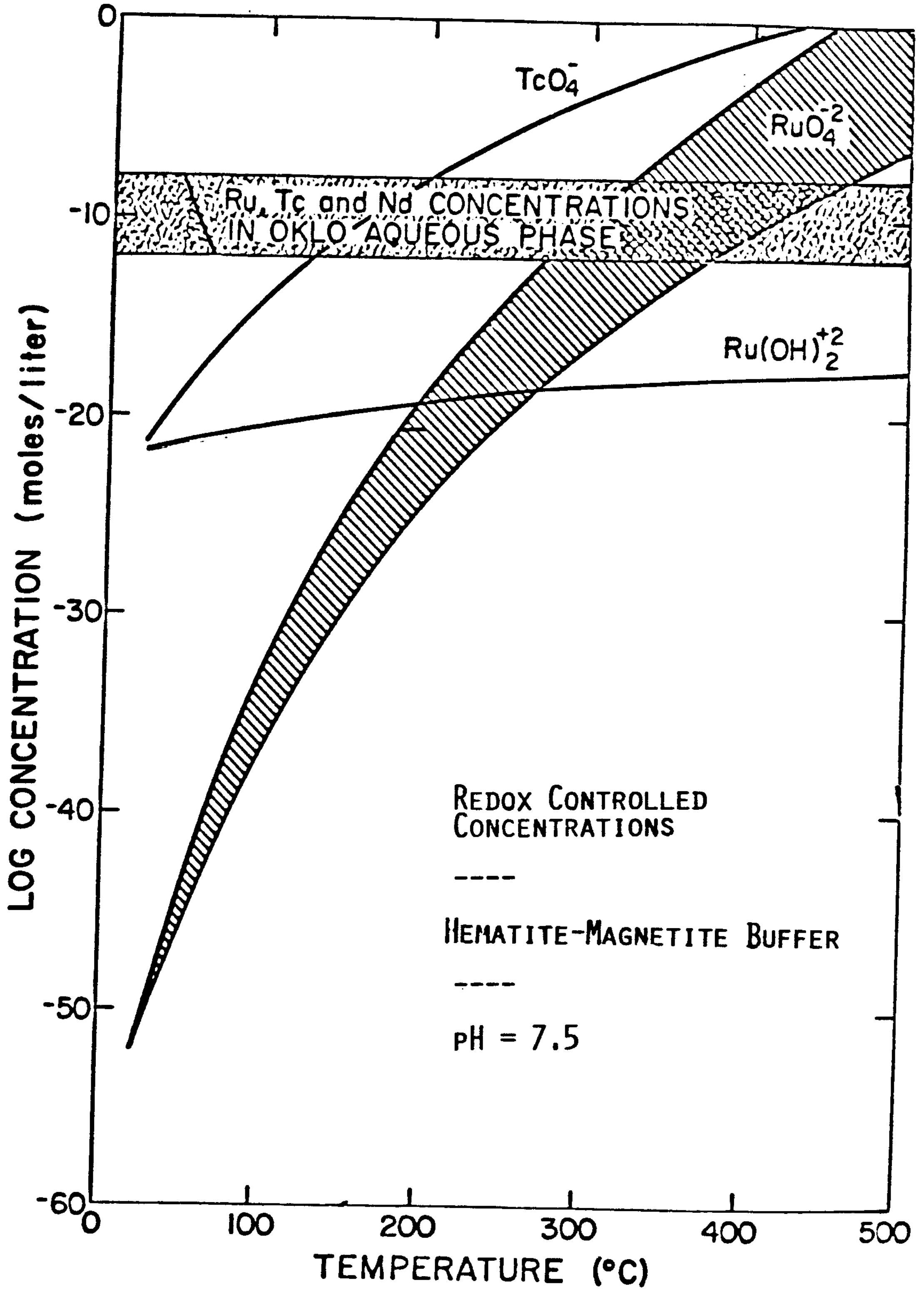
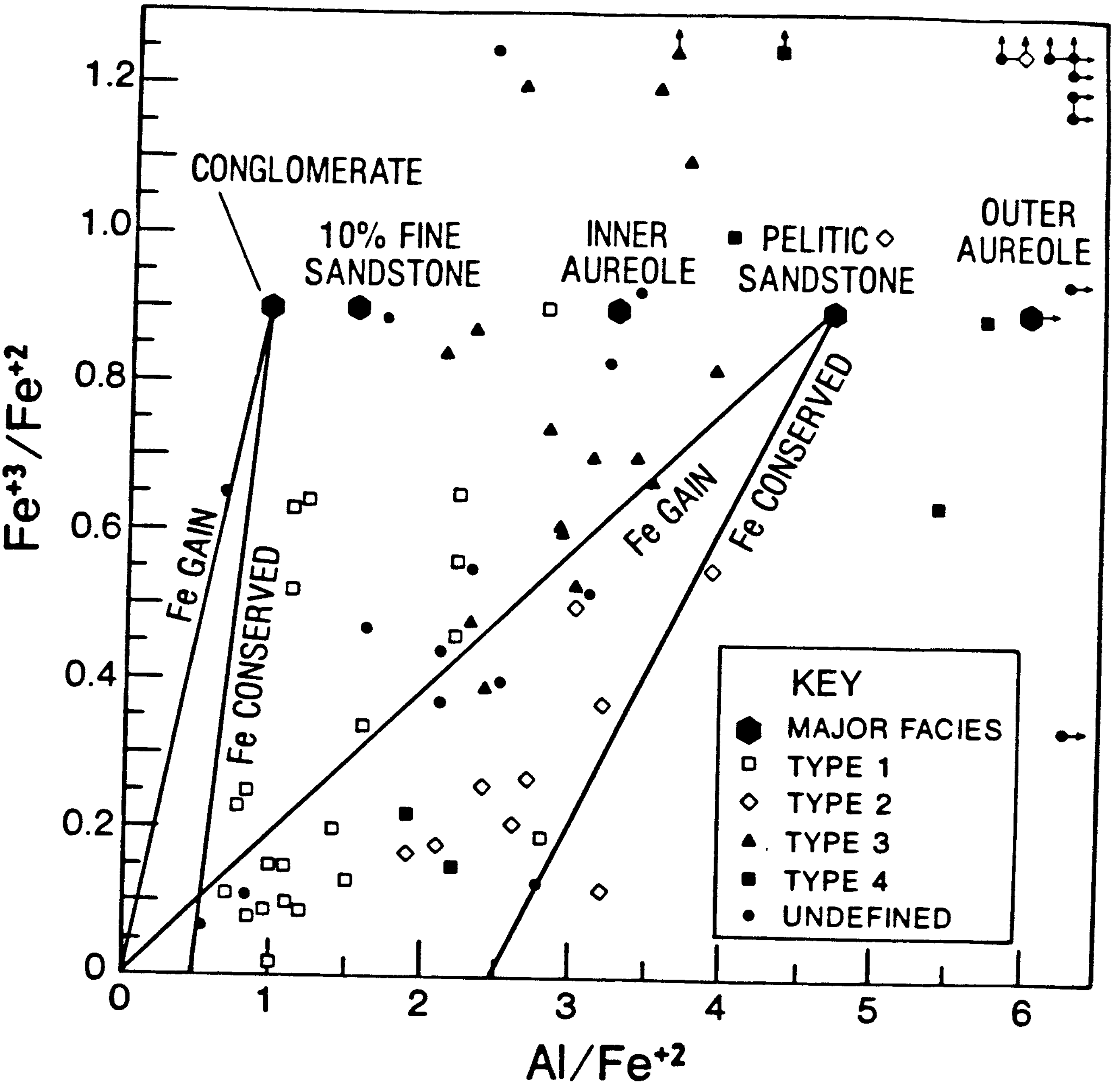

FACIES
SANDSTONE
OUTER AUREOLE
INNER AUREOLE
REACTOR ZONE
INNER AUREOLE
OUTER AUREOLE
SANDSTONE
DOMINANT CLAY MINERALS
1M$_d$ ILLITE
2M$_1$ ILLITE
1M ILLITE
2M$_1$ ILLITE
1M$_d$ ILLITE
Fe CHLORITE
Mg
Fe CHLORITE
Mg
Fe CHLORITE
OTHER CONSTITUENTS
QUARTZ
HEMATITE
URANINITE
QUARTZ
3·5 m

Figure 3


LOG CONCENTRATION (moles/liter)
0
-10
-20
-30
-40
-50
-60
0
100
200
300
400
500
TEMPERATURE (°C)
TcO$_4^-$
RuO$_4^{-2}$
Ru, Tc and Nd CONCENTRATIONS IN OKLO AQUEOUS PHASE
Ru(OH)$_2^{+2}$
REDOX CONTROLLED CONCENTRATIONS

HEMATITE-MAGNETITE BUFFER
----
pH = 7.5

Figure 4


1.2
1.0
0.8
0.6
0.4
0.2
0
0
1
2
3
4
5
6
Fe+3/Fe+2
Al/Fe+2
CONGLOMERATE
10% FINE SANDSTONE
INNER AUREOLE
■ PELITIC ◇ SANDSTONE
OUTER AUREOLE
Fe GAIN
Fe CONSERVED
Fe GAIN
Fe CONSERVED
KEY
MAJOR FACIES
TYPE 1
TYPE 2
TYPE 3
TYPE 4
UNDEFINED

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

J.A.T. Smellie1), A.B. MacKenzie2) and R.D. Scott2)

1) Swedish Geological Co., Box 1424, 751 44 Uppsala, Sweden.
2) Scottish Universities Research Reactor Centre, East Kilbride, Glasgow G75 0QU, Scotland

ABSTRACT

During far-field radionuclide transport along hydraulically connected fracture systems, radionuclides in solution will be subject to fluid-flow retardation mechanisms such as reversible and irreversible sorption into fractures and fissure mineral phases. In addition, rdionuclide diffusion into a water-saturated rock matrix could be an important factor. In an attempt to validate such processes use has been made of the uranium decay series in conjunction with REE and Fe^{2+}/Fe^{3+} analysis, alpha track autoradiography, fission-track analysis and detailed mineralogy. For this study drillcore lengths intersecting suitable water-conducting fracture zones were chosen from the Kråkemåla granite area in S.E. Sweden. The results show that: 1) naturally-occurring radionuclides have been mobilised and removed by rock/water interaction processes within the granite marginal to a water-conducting fracture zone at repository depths, 2) water/rock interaction has taken place under reducing conditions within measurable geological time, 3) isotopic movement has been mostly from the granite to the fracture zone, 4) sorption and isotopic fractionation of radionuclides has occurred at the fracture zone; the major source of these radionuclides is believed to be the groundwaters, although some may have originated from the granite during depletion, 5) some radonuclide movement may have taken place from the fracture zone (via groundwater) into the granite, 6) it is not known at the moment how these radionuclides have been moved.

INTRODUCTION

Safety assessment evaluations for the disposal of high-level radioactive waste characteristically assume a "worst case" situation. This usually means that progressive corrosion of the spent fuel metal container will occur, resulting in a slow release of radionuclide material into circulating meteoric waters present within the surrounding bedrock repository. It is highly probable that crystalline rocks at repository depths will be fractured, even prior to excavation, and that fracture permeability will be the dominant mode of flow. Thus, based on the premise that a cumulative failure of the near-field engineered barriers will occur, far-field retardation processes in the geosphere would appear to be qualitatively the most important factor in controlling releases of radionuclide material to the biosphere.

During far-field radionuclide transport along hydraulically connected fracture systems, radionuclides in solution will be subject to fluid-flow retardation mechanisms such as reversible and irreversible sorption into fracture and fissure mineral coating phases. In addition, radionuclide diffusion into a water-saturated rock matrix could be an important retardation factor. To date, much of the work and model derivation involving radionuclide migration has been experimentally based. An obvious means of validating the experimental data is to examine naturally occurring radionuclide migration (or lack of migration) within the bedrock environment of the chosen repository. Such an analogue study allows, most importantly, an appraisal of migration on the scale of geological time.

Naturally occurring uranium and thorium are of particular interest in radioactive wast disposal since they represent useful analogues of the actinides. Furthermore, the daughter nuclides in the ^{238}U and ^{232}Th decay chains show ranges of chemical properties and half-lives such that the degree of equilibrium between parent-daughter pairs can be used to provide information about rock-water interactions. Such studies can indicate the degree of radionuclide mobility and can provide information on the rates of processes occurring over time intervals of up to 1 Ma.

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 different hydrogeological environments; two in Switzerland (Böttstein and Grimsel) representing a gneiss and a granite respectively, and one in Sweden (Kråkemåla) representing a granite; this paper briefly describes studies from the Kråkemåla core section.

The Kråkemåla sample represents, in common with the other samples, a profile from the intersected fracture face into the bedrock. Sections cut from the profile are being investigated using the uranium decay series (^{238}U - ^{234}U - ^{230}Th - ^{226}Ra), in conjunction with REE and Fe^{2+}/Fe^{3+} analysis, alpha-track autoradiography, fission-track analysis and detailed mineralogy. Not all the results are yet available; these, together with the results from the other two locations, will be reported in due course.

To the extent that the uranium-series disequilibrium is a product of rock-water interaction, these measurements may help to evaluate the effective addition or removal of uranium within the near vicinity of an open, water-bearing fracture zone. Evidence of such a migration profile occurring into the bedrock under ambient temperatures, should lend or detract support to models involving far-field radionuclide retardation processes.

URANIUM-SERIES DISEQUILIBRIUM IN ROCKS

Studies of the uranium decay series have now become a fairly standard investigative method within the field of geochemistry. Pioneered by Cherdynstev (e.g. 1955, 1971) the methods have been subsequently improved and applied by many workers to a wide range of geological environments and their related problems; see, for example, Rosholt (1959, 1983), Thurber (1962), Rosholt et al. (1963, 1966), Koide and Goldberg (1965), Kighoshi (1971), Kronfeld (1974), Osmond and Cowart (1976, 1972) and Fleischer and Raabe (1978).

In closed geological systems the nuclides ^{238}U - ^{234}U - ^{230}Th attain radioactive equilibrium after about 1.7 Ma, i.e. the respective activity ratios $^{234}U/^{238}U$, $^{230}Th/^{234}U$ and $^{230}Th/^{238}U$ all equal unity. However, if the systems are exposed to weathering and groundwater circulation, and assuming that ^{230}Th is immobile under normal groundwater conditions, the different physico-chemical properties of ^{238}U and ^{234}U will result in their fractionation and thus isotopic disequilibrium. The respective activity ratios will therefore be greater or less than unity depending on whether there is an excess or deficiency of ^{238}U and/or ^{234}U. Fractionation of ^{234}U and ^{238}U arises from the radiogenically produced ^{234}U daughter which originates through the three-step alpha and beta decay from its ^{238}U parent:

$$^{238}U \xrightarrow[4.51 \times 10^{9}\ \text{yrs.}]{\alpha} {}^{234}Th \xrightarrow[24.1\ \text{days}]{\beta} {}^{234}Pa \xrightarrow[1.18\ \text{min.}]{\beta} {}^{234}U$$

In general, the isotopic variation of uranium has been recognized as being produced by two mechanisms: (1) selective leaching of ^{234}U itself, (2) the direct alpha recoil transfer of a ^{234}U precursor (i.e. ^{234}Th), and a combination of these processes. For selective leaching to occur, ^{234}U atoms must be more susceptible to leaching and removal than ^{238}U atoms. This is facilitated by lattice damage resulting from the radioactive decay of ^{238}U. The resultant daughter atoms will be located in weakly bonded or interstitial sites, and oxidation of the daughter (i.e. ^{234}U) to the 6+ valency state as a result of the recoil within the lattice, will render it more vulnerable to removal by water. Direct alpha recoil of ^{234}Th can occur from near the surface of a mineral grain into the intergranular pore water, whereupon it is trapped and further decays to ^{234}U. This results in the enrichment of ^{234}U in water and a ^{234}U depletion in the mineral (i.e. solid to solution ^{234}U recoil gain). An additional mechanism recognizes the process of daughter product emplacement from pore waters containing dissolved ^{238}U and ^{234}U. Subsequent decay of these radionuclides results in the recoiling nuclides of ^{230}Th, ^{234}Th, ^{234}Pa and ^{234}U being absorbed or embedded in particulate matter at the solid-liquid interface. After sufficient geological time, this mechanism results in solids which are enriched in ^{234}U and ^{230}Th relative to ^{238}U (i.e. solution to solid ^{234}U + ^{230}Th recoil gain).

For crystalline rocks, such as these described in this paper, the uranium decay system has been used as a sensitive indicator of recent uranium mobility (Zielinski et al., 1981; Schwartz et al., 1982; Rosholt, 1983; Gascoyne, 1983; Smellie and Rosholt, 1984). How recently this migration has occurred is determined from the half-life of the nuclide involved. In this present study the nuclides ^{238}U, ^{234}U and ^{230}Th have been measured; ^{226}Ra is in the process of being measured. Using the daughter/parent activity ratios ^{234}U/^{238}U, ^{230}Th/^{234}U and ^{226}Ra/^{230}Th, radionuclide migration over timescales of 1 million years, 300 000 years and 8 000 years respectively, can be detected.

SAMPLE LOCATION AND ANALYSIS

The Kråkemåla specimen was selected at a depth of approximately 381 m from one of three test holes drilled in the Götemar granite, located along the south-eastern coast of Sweden. The Kråkemåla area within the Götemar granite has been the focus of geological investigations as part of an earlier programme concerning the feasibility for the disposal of radioactive waste material in crystalline rocks (Scherman et al., 1977). The geology, geochemistry and geochronology of the Götemar granite has been previously described by Kresten and Chyssler (1976), Åberg (1978) and Smellie and Stuckless (1985).

The sample location level is characterized by the coarse-grained granite variety which is macroscopically homogeneous. The chosen core is traversed by a single, open fracture zone at 45° to the vertical drillcore length; from geophysical logging investigations (Magnusson and Duran, 1982) 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.

A drillcore length of 55 cm (diameter 56 mm) was selected and a thin rock slice was removed along the drillcore length for mineralogical, autoradiographic and fission-track studies. The 14 cm length nearest the fracture zone was cleaved into approximately 1 cm thick slices. One further sample was taken 45 cm from the fracture zone and the mineral coatings scraped from the inside surface of the fracture zone constituted another sample. The drillcore was cleaved to avoid possible removal of uranium in solution by sawing.

For uranium-series measurements samples of the powdered granite were spiked with ^{232}U in equilibrium with ^{228}Th and then digested with aqua regia and hydrofluoric acid. Soluble components were leached using 6 M hydrochloric acid and the small residue of insoluble material was further digested with nitric and hydrofluoric acids in a Parr high pressure digestion bomb. This process was repeated if necessary until the residue totally dissolved in 6 M hydrochloric acid. Uranium and thorium were recovered from half of the combined acid leachings by anion exchange techniques (Bacon and Rosholt, 1982) and were then electrodeposited onto stainless steel planchettes for alpha spectrometry measurements using silicon surface barrier detectors. The precision of the results is better than ± 5 % for the $^{234}U/^{238}U$ activity ratios and ± 10 % for the $^{230}Th/^{234}U$ and $^{230}Th/^{232}Th$ activity ratios.

^{226}Ra analyses were initially attempted on the remaining half of the acid leaching solution by the standard technique of collection and alpha counting of the daughter ^{222}Ra (Scott and MacKenzie, 1984; Scott and MacKenzie, 1985). Since there is no spike available to act as a yield tracer in this method, the process depends upon 100 % transfer of ^{226}Ra to the radon emanation vessel. Replicate analyses and analyses of samples to which a known quantity of ^{226}Ra was added indicated that the above condition was not being satisfied and that loss of ^{226}Ra was occurring before transfer to the emanation vessel. No satisfactory explanation is at present available for this loss but attempts at ^{226}Ra analysis by this method were abandoned in favour of direct counting of the 609 KeV peak in the gamma spectrum of ^{226}Ra decay products in a subsample of the untreated powdered granite. This peak, produced by ^{214}Bi decay, can only be used if ^{222}Ra does not escape to any significant extent from the sample and initial results appear to justify this assumption.

REE and total Fe analysis were carried out on 0.1 g samples using instrumental neutron activation analysis (INAA). This involved a six hour irradiation in a thermal neutron flux of 3×10^{12} neutrons cm^{-2} sec^{-1}. Gamma counting using co-axial and planar Ge (li) detectors was performed at approximately 3 days and 3 weeks after irradiation (MacKenzie et al., 1983). Fe^{2+} was analysed using standard wet chemical techniques.

Alpha tracks from polished thin sections of the granite were recorded on CR-39 plastic, and fision-track distributions were similarly recorded on polycarbonate by thermal neutron irradiation (MacKenzie et al., 1984).

MINERALOGY OF THE DRILLCORE

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. The plagioclase (An <10%) occurs mostly as enhedral to subhedral laths, as a matrix constituent, and included in potassium feldspar. Accessory minerals include interstitial amounts of magnetite, apatite, zircon, fluorite, sphene and monazite; isolated grains of galena, pyrite, and more rarely molybdenite, also occur. The non-sulphide accessory phases usually occur as intergranular aggregates sporadically dispersed throughout the rock, resulting in considerable inhomogeneity on the scale of a thin section.

Throughout the length of the drillcore sample the granite is weakly but uniformly altered; this is generally typical to the depths of maximum drilling in the massif (Smellie and Stuckless, 1985). In most sections the partial breakdown of the feldspars to muscovite/sericite with minor quartz occurs. Magnetite sporadically shows limited alteration to hematite, or partial to complete pseudomorphing by chlorite. Biotite is sometimes partly altered to chlorite, and muscovite, normally clear and unaltered, has occasionally altered to chlorite and less frequently to epidote and opaque phases (mostly Fe-Ti-oxides).

The fracture zone 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.

CHEMISTRY OF THE DRILLCORE

The drillcore contents and distributions of uranium and its daughter decay products, iron and the rare-earth elements (REE), are listed in Table I and illustrated in Figures 1 and 2. Other elements analysed but not illustrated include Na, K, Sc, Co, Rb, Cs and Ta.

The uranium contents range from 11.5 to 21.4 ppm (mean 14.4 ppm) and the thorium from 46 to 96 ppm (mean 68.9 ppm); the mean Th/U ratio is 4.8. These uranium and thorium values, which are roughly in agreement with the average values from the granite as a whole (Smellie and Stuckless, 1985), are still anomalously high when compared to either the average contents for world-wide granites (Rogers and Adams, 1969 a,b) or a compilation of 2,500 granites mainly from the U.S.A. (Stuckless and Van Trump, 1982). Furthermore, in crustal rocks the average Th/U ratio is 3.5 (Rogers and Adams, 1969), i.e. thorium concentrations usually correlate with uranium by a factor of 3. Thus the high Th/U ratio recorded from the Götemar granite would suggest a general removal of uranium, which has also been demonstrated isotopically by Smellie and Stuckless (1985).

From fission-track studies of the Götemar granite (Kresten and Chyssler, 1976; Smellie and Stuckless, 1985) 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 dispersion. Although no data are available for minor thorium, the distribution of monazite, which can contain up to 10 wt.% Th and perhaps as high as 26 wt.% Th (Frondel et al. 1967), almost certainly controls the thorium distributions in the Götemar granite.

The distribution of uranium and thorium along the drillcore from the fracture zone is shown in Figure 1. 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.

On the basis of mineralogy, the known geochemical behaviour of uranium and thorium and the similarity of the Th profile with those of the rare-earth elements (discussed below), these profiles suggest 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. As the first sample represents fracture-surface scrapings of mostly hematite, chlorite, clay minerals and FeOOH-oxides, the lower thorium value recorded here is perhaps not so surprising. 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. If the granite had remained a closed chemical system since crystallisation, then most of the uranium would be associated with primary resistate radioactive minerals (often together with thorium and REE) with more minor amounts along intergranular boundaries (Tieh et al., 1980). For the case in question therefore, the distribution of major uranium would be expected to be sympathetic to thorium which in turn would be a reflection of the monazite content in the rock, as suggested above. In fact 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 leaching is taking place.

Similar marginal increases in uranium have been reported in altered and fractured samples of granite from the Eye-Dashwa Lakes pluton, Ontario (Kamineni, this volume) which has been interpreted as preferential sorption or co-precipitation of uranium with hematite.

Uranium-series Disequilibrium

Plots of the activity ratios $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ are presented in Figure 1. The $^{234}U/^{238}U$ ratios indicate general disequilibrium within a 2 σ analytical error, with values ranging from a maximum of 2.29 at the fracture surface to a mean value of 0.859 for the major length of the drillcore. In contrast, most of the $^{230}Th/^{234}U$ ratios lie within 2 σ of secular equilibrium.

Considering the major length of the drillcore (i.e. excluding the fracture edge) the isotope data show deficiencies of both ^{234}U and ^{230}Th relative to ^{238}U. This indicates a significant ^{234}U loss (most likely by recoil processes) with little or no ^{238}U loss, followed by a requilibration of the ^{230}Th daughter with ^{234}U. In other words, throughout the granite represented by these samples, the loss of ^{234}U (probably continuous) has been occurring over the last one million years by solid to solution alpha-recoil of ^{234}U.

In strong contrast, the granite marginal to the fracture zone is characterised by enrichments of all three isotopes measured (Table I); these fall off rapidly over a distance of 1-3 cm into the granite. The $^{234}U/^{238}U$ ratios indicate the accumulation of ^{234}U which must be occurring sufficiently slowly to allow re-equilibration of the ^{230}Th daughter with ^{234}U; this could account for the isotopic equilibrium observed between ^{234}U and ^{230}Th.

The question now arises as to whether these observed isotopic values at the fracture/groundwater interface zone are due to continuous isotopic movement from the granite to the interface zone, followed by subsequent sorption and/or isotopic fractionation unto the fracture minerals or, if these isotopic products have been introduced from the groundwaters to the fracture face by direct sorption or through daughter emplacement processes (i.e. solution to solid ^{234}U + ^{230}Th recoil gain) as suggested by Rosholt (1983). At this stage in the investigation it is not possible to say if one or a combination of these two processes are responsible. In any case it underlines the importance of the physico-chemical properties of the fracture minerals in radionuclide retardation processes. The work of Airey (this volume) clearly illustrates that the subsequent immobility of the radionuclides after up-take from solution will largely depend on the isotopic fractionation between the fracture zone minerals. It was shown that uranium and thorium tend to concentrate principally on the iron phases, whilst radium seems to be more in association with the clay/quartz fraction where its activity exceeds that of its parent thorium. Furthermore, radionuclides taken up by crystalline iron phases such as geothite are believed to be inaccessible to removal by solution. Work by Kamineni (this volume) also records the importance of goethite to explain enrichments of thorium along fractured zones located in the Eye-Daswa pluton, Ontario.

Unfortunately there is no isotopic analysis of the groundwater in contact with the fracture zone that might indicate which uranium daughters are being removed fom or lost to the fracture surfaces. Groundwaters at the depth of the drillcore sample (approximately 381 m) should be reducing in character. According to secondary uranium accumulation processes as discussed by Osmond et al. (1983), the isotopic data from the fracture/groundwater interface sample indicates a position furthest down-flow whereupon the groundwater is strongly reducing and ^{234}U exceeds ^{238}U, as does ^{230}Th, its in-grown daughter. Furthermore, if a comparison is made with other granite areas in Sweden which are also anomalously enriched in uranium, for example the Stripa granite, the groundwaters should be characterised by an ^{234}U excess and appreciable ^{226}Ra and ^{222}Rn. At Stripa it was demonstrated by Andrews (1983) that the groundwater content of ^{226}Ra increased with increasing depth; excess ^{234}U was also recorded from all groundwaters sampled at depth. The source of ^{226}Ra and ^{234}U is believed to be through alpha-recoil processes from their respective parent isotopes which are located along fractures enriched in uranium, less so by thorium.

It would appear reasonable to assume, therefore, that the groundwaters at a depth of around 350-400 m at Kråkemåla are characterised by an excess of ^{234}U and are strongly reducing. Along the fracture surfaces sorption and/or co-precipitation of ^{234}U with iron oxides is taking place; solution to solid ^{234}U + ^{230}Th recoil gain processes may also be contributing. The continuous loss of ^{234}U indicated from the overall length of the drillcore suggests that there is also some radionuclide movement at the fracture edge and probably, mainly through recoil processes, to the groundwater. The degree of radionuclide retardation and retention from both processes will be dependent on the physico-chemical properties of the fracture zone minerals, which consists mostly of hematite, chlorite, hydroxy Fe-oxides and clay minerals.

Iron and $Fe^{2+}/Fe^{2+} + Fe^{3+}$ Oxidation States

Figure 1 illustrates the distribution of iron and the variation of $Fe^{2+}/(Fe^{2+} + Fe^{3+})$ oxidation ratio along the drillcore. Iron shows a slightly irregular but distinct increase towards the fracture face; this is apparent mineralogically by an increase of hydroxy Fe-oxide dispersions throughout the rock, together with the presence of chlorite and hematite at and near the fracture face. The similarity of the iron distribution pattern, excluding the fracture face, with that of thorium, is due to the presence of magnetite grains which often accompany the monazite aggregates in the granite.

An attempt to assess the extent of any oxidation effects in the rock was crudely made using whole-rock Fe^{2+} and Fe^{3+} analysis; the degree of oxidation is expressed as the ratio $Fe^{2+}/(Fe^{2+} + Fe^{3+})$. Towards the fracture face there is some suggestion of increased oxidation, although similarly low values are also evident well within the granite, even in the sample located furthest from the fracture face.

Rare-Earth Distribution

Plots of the REE (La, Ce, Nd, Sm, Eu, Lu and Hf), together with Ta are presented in Figure 2. From the general similarity of the element distribution patterns within the drillcore, and in comparison with Th (Fig. 1), it can be concluded that no obvious mobilisation of these elements has taken place, and that their distribution is a reflection of the occurrence of monazite in the granite.

SUMMARY AND CONCLUSIONS

A drillcore section traversing a water-conducting fracture zone has been investigated from the Kråkemåla area (Götemar granite) in S.E. Sweden. The core, sampled from a depth of approximately 380 m, has been examined using the uranium decay series together with the analysis of REE, Fe^{2+}/Fe^{3+} ratios, and other elements such as Na, K, Sc, Co, Rb, Cs, Ba and Ta. Although not all the data are available, eventually these analyses will be interpreted alongside alpha-track autoradiography, fission-track analysis and detailed mineralogy.

Preliminary mineralogical studies have shown that at some stage the core has been subject to a weak, pervasine alteration throughout its length. This is mostly apparent as feldspar sericitisation + minor oxidation of biotite and/or magnetite. A more intense alteration is evident within a marginal zone (3-5 cm wide) adjacent to the fracture zone. Here there is widespread alteration of feldspar and magnetite together with impregnations of hydroxy Fe-oxides. The mineral coatings on the fracture face have not been quantitatively determined, but appear to be composed of a mixture of hematite, chlorite, clay minerals and hydroxy Fe-oxides.

Of the elements measured, the variation of REE and thorium (together with Ta, Cs and Sc) appear to reflect the primary distribution of those radioactive refractory phases dominated by monazite. Uranium, on the other hand, shows evidence of mobilisation and leaching from monazite up to a distance of 8 cm from the fracture zone; for the remainder of the core length the uranium distribution is symphathetic with that of thorium and the REE. Work by Smellie and Stuckless (1985) showed a general loss of uranium in the Götemar granite as a result of large-scale hydrothermal alteration processes some 420 ± 171 Ma. These processes may have contributed to the breakdown and removal of uranium from the monazite phases marginal to the fracture zone.

The isotopic data show that along the length of the drillcore (excluding a marginal zone of some 1-3 cm adjacent to the fracture zone) there has been a uniform loss of ^{234}U over the last 1-2 Ma by recoil processes. This was followed by the re-equilibration of ^{230}Th with its parent ^{234}U. This isotopic behaviour shows that the granite represented by the drillcore section has been subject to rock/water interaction processes within recent geological time, and represents a second stage of alteration at ambient temperatures.

The fracture marginal zone, in contrast, indicates an accumulation of ^{234}U and possibly some ^{230}Th (from solution to solid ^{234}U + ^{230}Th recoil gain). These isotopic accumulations are considered to be mostly due to sorption and isotopic fractionation from the groundwaters which are assumed to be reducing and characterised by an excess of ^{234}U resulting from solid to solution recoil loss from along the fracture zones. However, as the isotopic data from the overall drillcore length shows a continuous depletion of ^{234}U there is also the possibility that this radionuclide movement from the core has contributed to some of the observed accumulations at the fracture zone. The degree and retention of radionuclide retardation and retention from both processes will be dependent on the physico-chemical properties of the fracture zone minerals.

Such natural analogue studies, as reported here from Kråkemåla, could play an important role in validating the importance of far-field radionuclide retardation mechanisms within the context of high-level radioactive waste disposal in a crystalline bedrock, whereupon fracture permeability will be the dominant mode of groundwater flow. Although the data are incomplete, the most important conclusion is that within recent geological time (i.e. from at least 0.5 Ma to the present time) radionuclides have been removed from the granite at depths approaching radioactive waste repository levels. Whether the removal of these radionuclides, which has been pervasive and fairly uniform, is by flow along structural weakness such as micro-fractures/fissures, or by matrix diffusion mechanisms, is as yet unclear. It is hoped that the alpha-track autoradiography and fission-track analysis may help to clarify such mechanisms.

In conclusion, the preliminary data show:

1) naturally-occurring radionuclides have been mobilised and removed by rock/water interaction processes within a normal compact granite marginal to a water-conducting fracture zone at repository depths.

2) Water/rock interaction has taken place under reducing conditions within measurable 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 fracture zone.

4) Sorption and isotopic fractionation of radionuclides has occurred at the fracture zone; the major source of these radionuclides is believed to be the groundwaters, although some may have originated from the granite during depletion. The fracture zone minerals (i.e. hematite, chlorite, clay minerals and hydroxy Fe-oxides) are particularly conductive to the retardation and retention of these radionuclides.

5) Some radionuclide movement may have taken place from the fracture zone (via the groundwater) into the granite. If this has occurred, the extent of penetration has been from 1-3 cm.

6) It is not known at the moment how these radionuclides have been moved (e.g. by fracture-flow or by matrix diffusion processes). Some indication may be obtained when the data are complete.

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Table 1: Isotopic and chemical analyses of uranium and thorium from drillcore K 1, Kråkemåla, Sweden.

Specimen	Distance from fracture face (cm)	Uranium[1] (ppm)	Thorium[1] (ppm)	Th/U	^{238}U	^{234}U	^{230}Th	$^{234}U/^{238}U$	$^{230}Th/^{234}U$	$^{230}Th/^{232}Th$
KIA-1	Surface scrapings	18.5	45±2		14.8	33.9	31.1	2.29	0.92	2.9
KIA-2	1	11.5	64±2		9.2	16.7	-	1.81	-	-
KIA-3	2	12.1	96±3		9.7	10.9	-	1.12	-	-
KIA-4	3	11.8	62±2		9.4	9.0	8.9	0.957	0.99	0.57
KIA-5	4	11.9	92±3		9.5	8.5	8.3	0.857	0.98	0.42
KIA-6	5	12.4	58±2		9.9	8.7	8.4	0.877	0.97	0.58
KIA-7	6	12.4	77±3		9.9	8.6	8.3	0.871	0.97	0.55
KIA-8	7	11.6	71±2		9.3	7.9	7.6	0.847	0.96	0.47
KIA-9	8	13.4	48±2		10.7	9.4	9.5	0.879	1.01	0.84
KIA-10	9	13.3	61±2		10.6	8.9	9.1	0.843	1.02	0.55
KIA-11	10	17.8	78±3		14.2	11.4	11.5	0.805	1.01	0.76
KIA-12	11	21.4	89±3		17.1	14.7	15.7	0.860	1.07	0.75
KIA-13	12	17.8	74±3		14.2	12.5	11.1	0.877	0.89	0.57
KIA-14	13	13.0	46±2		10.4	8.5	8.6	0.822	1.01	0.71
KIA-15	43	17.4	71±2		13.9	12.1	11.1	0.871	0.92	0.65

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1) Determined by radioisotope dilution and alpha spectrometry.

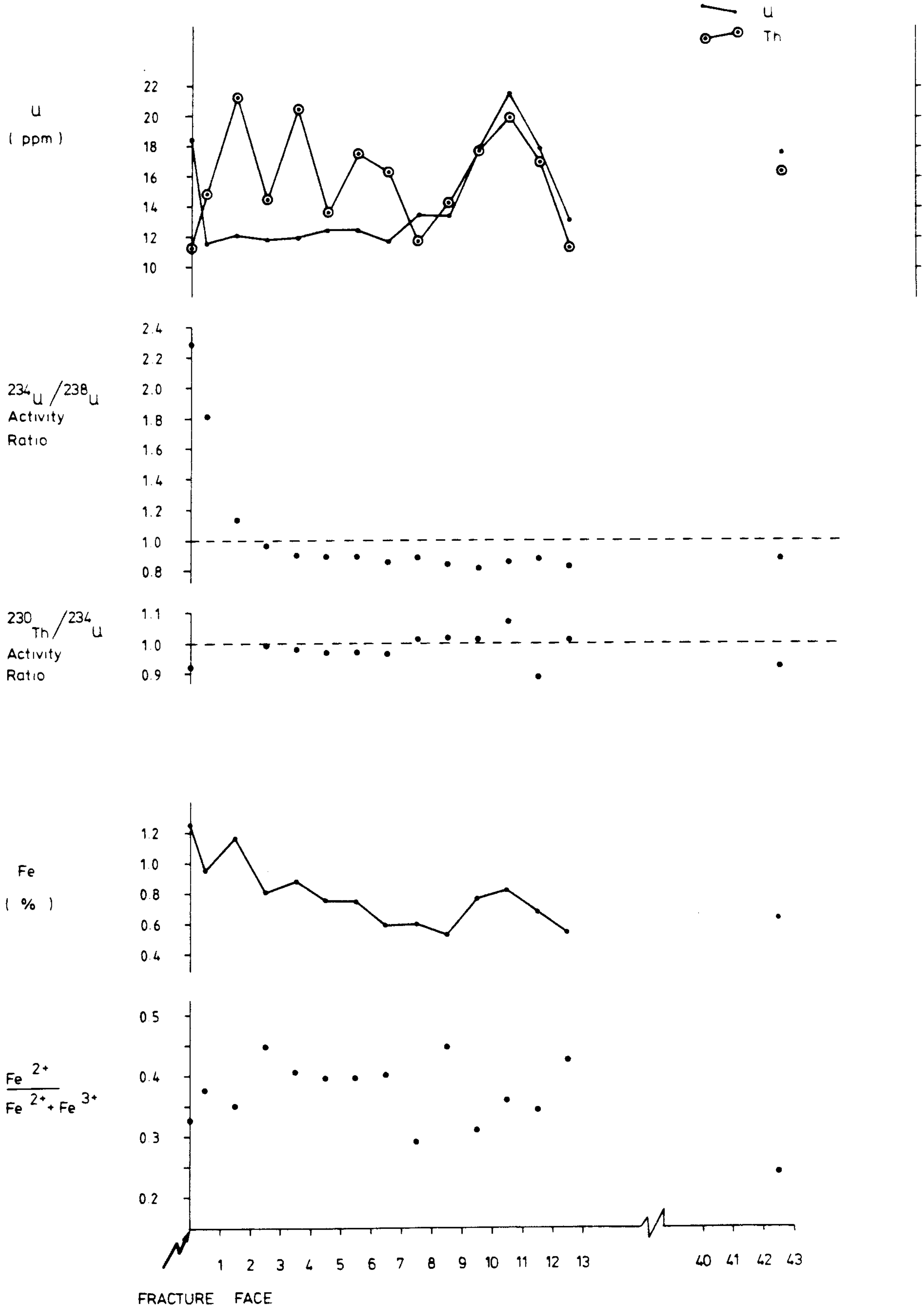

Figure 1. Radionuclide and elemental distributions from the Kråkemåla core sample.

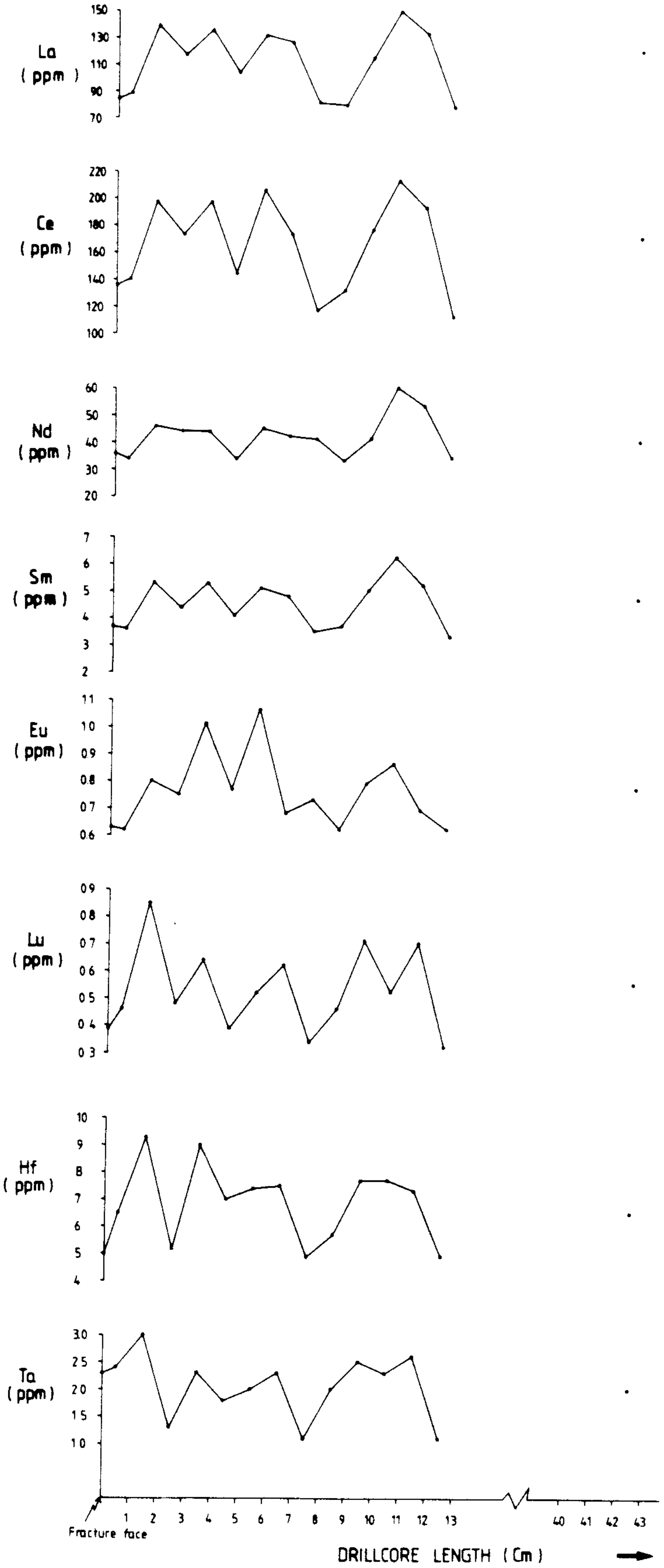

Figure 2. Trace-element distributions from the Kråkemåla core sample.

THE MARYSVALE NATURAL ANALOG STUDY: PRELIMINARY OXYGEN ISOTOPE RELATIONS

M. Shea[1] and K.A. Foland[2]

[1]Office of Crystalline Repository Development, Battelle Memorial Institute, 505 King Avenue, Columbus, Ohio 43201, USA.

[2]Department of Geology and Mineralogy, Ohio State University, 125 South Oval Mall, Columbus, Ohio 43210, USA.

ABSTRACT

The mass transport of various elements associated with hydrothermal uranium-molybdenum vein deposits near Marysvale, Utah, U.S.A., is being studied as a geological natural analog for radwaste isolation by the Office of Crystalline Repository Development for the U.S. Department of Energy. This report briefly outlines the analog study and presents some early results dealing with ^{18}O analyses of rock and water samples. Based on these preliminary data, it is clear that rocks of and around the Marysvale central mining area have experienced massive, subsolidus hydrothermal exchange with heated meteoric waters. Plutonic granitic rocks in the central mining area have $\delta^{18}O$ values ranging from +6.7 o/oo to as low as +0.1 o/oo. Quartz monzonite samples from surface exposures have, on the average ($\bar{x}$ = +2.9 o/oo), lower $\delta^{18}O$ values than subsurface samples ($\bar{x}$ = +4.3 o/oo). Within the limitations of present data, ^{18}O depletions of the intrusive rocks are not obviously correlated to proximity of known major fractures. The $\delta^{18}O$ data are consistent with hydrothermal modifications of normal igneous rocks, initially about +7 o/oo, by groundwater initially of −14 o/oo at temperatures on the order of 200 C. Preliminary estimates of integrated water/rock ratios range from less than 0.1 to about 1 for plutonic rocks. The hydrothermal solutions responsible for the mineralization were derived from meteoric water. Samples immediately adjacent to a quartz monzonite/granite contact show symmetrical ^{18}O depletion which may indicate that the contact was a feature allowing greater flow and/or residence time of the hydrothermal solution, and that the hydrothermal event apparently post-dates granite emplacement.

INTRODUCTION

This report briefly describes the Marysvale Natural Analog Study being conducted by the Office of Crystalline Repository Development for the U.S. Department of Energy. Preliminary oxygen isotope results are presented. They serve to place important constraints on the Marysvale hydrothermal activity and indicate the involvement of circulating heated meteoric waters.

Marysvale Natural Analog Study

The major focus of this study is the elucidation of the mass transport of nuclides in a hydrothermal system within "granitic" rock. The proper isolation of radioactive waste using an underground geologic repository is dependent upon the ability to understand and to predict natural phenomena which will likely impinge upon the waste form. Of particular concern are: (1) radionuclide migration by diffusion and/or fluid transport; (2) effects of fractures on the movement of groundwater and radionuclides; (3) absorption characteristics of the host rock and its constituent mineral phases; (4) possible complexing of radionuclides with groundwater and rock components; (5) precipitation/solubility of these various ligands; and (6) the effect upon rock strength and permeability by the interaction of heat, groundwater, and radionuclides. The objective is to quantify, or even qualify, these important factors which would be extremely helpful in selecting a suitable repository site that would avoid adverse conditions and/or take advantage of favorable ones.

Some, but certainly not all, of these parameters can be studied under laboratory conditions. Albeit that laboratory experiments have the ability to constrain the number of variables in an experiment, they suffer from the disadvantage that the experiments are only able to take place over very short periods of time and under relatively artificial and potentially misleading conditions. A geological analog study, although it may be complex, has the advantages of having taken place over a long, geological period of time, and in a natural, more realistic setting.

The type of geological analog that is being studied at Marysvale, Utah, is an inactive hydrothermal uranium/molybdenum ore deposit. A "fossil" hydrothermal system with significant mineralization can be considered analogous to a radwaste repository in which canisters have been breached and the interaction between groundwater, rock, and nuclides has taken place, initially at elevated temperatures. A uranium/molybdenum mineralized deposit is advantageous since it is likely to have present many of the nuclides expected in the radwaste. Thus, these ore deposit elements may be studied for migration characteristics and it is likely that certain other elements can proxy for given radwaste nuclides.

The objectives of the analog study are several and include determining the nature of the mineralizing hydrothermal system in terms of thermal, spatial, and temporal parameters as well as in terms of the composition and source of the hydrothermal fluids. Another is to determine the extent of the element/fluid migration and to identify the geochemical and geomechanical processes controlling this movement.

As presently conceived, the Marysvale Natural Analogy Study is divided into three phases. Phase I is concerned with the feasibility of various geochemical techniques to elucidate pertinent phenomena, as well as to characterize the setting and determine whether it can serve as an appropriate analog. Field work for this phase has been completed and laboratory studies have been initiated. Phase II will include a detailed follow up based upon the initial results and observations of Phase I. It will include revisiting the site, detailed sampling (including core), and detailed selected analytical work. Phase III will be devoted to interpretation of analytical data and field relations and to the development of final models, hypotheses, and conclusions.

The present report represents a first step in addressing the operational questions concerned with the nature of the hydrothermal deposit at Marysvale. Additional analyses are required and planned, including petrographic, microscopic, isotopic, chemical, and mechanical techniques.

Geological Setting and Previous Work at Marysvale

This natural analog study is being conducted in the district known as the "central mining area" near Marysvale, Utah, which is 260 kilometers south of Salt Lake City (Figure 1). The Marysvale area is a classic uranium locality. Although mining operations are now inactive, mining over the years has resulted in an extensive network of underground passages. Mining production in this area was principally from a network of hydrothermal uranium ore (uraninite-pyrite-fluorite) veins.

Previous geologic studies in the region include work by Kerr et al. (1957), El-Mahdy (1966), Cunningham and Steven (1979), Steven et al. (1979), Cunningham et al. (1982), and Steven et al. (1984). These studies were concerned with the general geology of the Marysvale area and surrounding region, and with the mineralogy and formation of the ores. They provide an invaluable source of "ground work" information.

The Marysvale area is toward the northeast terminus of an east-northeastwardly trending belt of Tertiary igneous rocks (Steven et al., 1979). This field is approximately 350 km in length (from central Utah to SE Nevada) and up to 100 km in width. It is situated at the intersection of the Colorado Plateau province and the Basin and Range province and is associated with other major volcanic areas which encircle the Colorado Plateau, including the San Juan, Mt. Taylor, Mogollon, and San Francisco Mountains volcanic areas. Making up the Marysvale igneous complex are flows, breccias, tuffs, diatremes, dikes, and intrusives. Included are distant ash flow sheets from the Great Basin commingling with the locally derived volcanics (Steven et al., 1979).

A simplified geologic history of the Marysvale region is shown schematically in Figure 2. Before volcanism began, the region comprised Mesozoic sedimentary rocks, including the Moenkopi and Navajo formations. Rocks of the Carmel Formation (upper Jurassic) were exposed and being eroded (Figure 2E). Between 35 and 22 mya (millions of years ago), local volcanic activity around Marysvale caused the accumulation of intermediate composition volcanic rocks, the Bullion Canyon Volcanics (Cunningham et al., 1982) (Figure 2D).

The Bullion Canyon volcanic activity was the harbinger of a quartz monzonite-monzonite intrusive (Tbi) locally known as the "central intrusive" (Figures 1 and 2C). Measured isotopic ages for this intrusion range between 27 and 17 mya, with 23 mya considered to be the best approximation (Steven et al., 1979; Cunningham et al., 1982). Alunitic alteration occurred in isolated areas within the region during the last stages of the Bullion Canyon volcanism, but is not associated with the uranium-molybdenum deposits of this study (Cunningham et al., 1984).

Beginning around 22-21 mya, the composition of the local volcanic rocks changed markedly from intermediate to silicic-alkalic (Cunningham et al., 1982). Two source areas produced a heterogeneous assemblage of tuffs, flows, domes, breccias, and local rhyolite-granite (fine-grained) intrusions (Figure 2B). About 19 mya calderas were formed at the two source areas: the major Mount Belknap caldera and the minor Red Hills caldera (Steven et al., 1984) (Figure 2A). The associated precaldera, intracaldera, and intercaldera (outflow) volcanics have all been designated the Mount Belknap Volcanics. Volcanic activity of this type ended about 14 mya (Cunningham et al., 1982). The fine-grained granite intrusives (Tmf) are consanguineous to the Mount Belknap Volcanics (Figures 1 and 2B). Since 18 mya, the Marysvale area has been relatively quiescent. Some nearby localities show evidence of inactive, as well as active geothermal systems (e.g., Monroe Hot Springs).

Mineralization (uranium-molybdenum-fluorine) occurred after the deposition of the Mount Belknap Volcanics, perhaps as little as 10 mya (Kerr et al., 1957, p. 61), although Cunningham et al. (1982) note the equivocal nature of that datum and suggest an age of mineralization close to the time (18-19 mya) of intrusion of glassy rhyolite dikes. This mineralizing event has been postulated to have arisen from the emplacement of a hidden stock beneath the central mining area (Cunningham and Steven, 1979). The duration of mineralization perhaps lasted on the order of 10,000 years (Cunningham, personal communication).

Of the rock units found in the central mining area, the quartz monzonite (Tbi) is the most affected by mineralization. Also of significance is a small stock of the fine-grained granite (Tmf). Much of the central mining is underlain by this granite, which also hosts major uranium mineralization. There is also some mineralization within the Red Hills Tuff (Tmr).

The Marysvale central mining area is highly faulted by both Basin and Range faults and a more local set of faults. Basin and Range faulting postdates the formation of the Mount Belknap Volcanics, and continues to the present. The local fault pattern has been postulated to reflect local distension imposed by an underlying magma chamber, and the mineralization was highly controlled by this local faulting (Cunningham and Steven, 1979).

The Tertiary intrusives of quartz monzonite (termed the "central intrusive") and granite, which generally host the hydrothermal mineralization, are of principal concern in this study. The quartz monzonite is medium grained and consists of calcic andesine, orthoclase, quartz, biotite, and in many specimens augite and hornblende. The principal accessory minerals include magnetite, apatite, sphene, zircon, rutile, and ilmenite. The granite is fine grained and porphyritic with phenocrysts of orthoclase and a groundmass consisting of plagioclase, biotite, orthoclase, and quartz. The granite bears accessory magnetite, apatite, and zircon. Major portions of the central intrusive show the effects of hydrothermal alteration, ranging from minor (or at least not obvious) to extreme. The granite is almost invariably highly altered.

The uranium veins and adjacent wallrock at Marysvale have previously been examined by Shea (1984) as a potential natural analog for radwaste isolation. This previous study concentrated on examining uranium distribution by fission track mapping with supportive scanning electron microscopy and cathodoluminescence. Briefly, the results indicated that: apparent diffusivities for U were orders of magnitude lower, and distribution constants for U were orders of magnitude higher, than those found in laboratory studies; and, U migration apparently extended a few centimeters into the wallrock.

ANALYTICAL METHODS

As part of Phase I fieldwork, rock samples were removed from outcrops both at the surface and underground in the mine workings.

All the samples reported on here were fresh, trimmed, and cleaned in the field and laboratory as necessary. Several water samples were also collected in order to determine the local water chemical and isotopic relationships. All water samples were untreated and unfiltered.

The oxygen isotope measurements were made using established analytical techniques at the Department of Earth Sciences at the University of California at Riverside. For the whole-rock samples, the techniques of Clayton and Mayeda (1963) of reaction with BrF_5 were used to extract O_2 gas from the sample. The extractions were done in Ni vessels heated at approximately 580°C for 12 to 14 hours. The oxygen was then converted to CO_2 by reaction with platinium catalyzed graphite rods heated by an external resistance furnace to a temperature of approximately 580°C. Two-sigma analytical uncertainties for the whole-rock analyses are ±0.3 o/oo.

For the water samples, the technique of Epstein and Mayeda (1953) of equilibrium of H_2O and CO_2 gas was used. The equilibrium temperature was 25°C (±0.25°) and known volumes of water and laboratory standard CO_2 gas were used. Sample aliquots were taken at different times (4, 5, and 6 days) to track the approach to equilibrium. The two-sigma analytical uncertainty of these measurements is ±0.1 o/oo.

The oxygen isotope results are reported in conventional ^{18}O notation relative to Standard Mean Ocean Water (specifically, V-SMOW). Standards used for calibration include NBS-19, PDB-4 and NBS-28, plus various intralaboratory standards. Calculated $\delta^{18}O$ values for all samples are adjusted such that standard sample values conform with those of Coplan et al. (1983).

RESULTS

The $\delta^{18}O$ analytical data are given in Tables 1 and 2. The $\delta^{18}O$ values for quartz monzonite and granite whole-rock samples are shown in histogram form in Figure 3. Overall, the range of ^{18}O for rock samples is from +0.1 to +9.1 o/oo. $\delta^{18}O$ is defined in the normal manner:

$$\delta^{18}O = \left[\frac{(^{18}O/^{16}O)\ \text{Sample}}{(^{18}O/^{16}O)\ \text{SMOW}} - 1\right] \times 10^3 \qquad \text{(Equation 1)}$$

Water Samples

The $\delta^{18}O$ values for the water samples (Table 1) range from -9.3 to -16.7 o/oo. The collection of these samples is as follows: MV-

W01 was taken from some shallow marshes and springs about 2 km southwest of the Marysvale central mining area; MV-W02 was taken from a spring ("Lemonade Spring") at Big Rock Candy Mountain, which is a highly altered tuffaceous deposit approximately 3 km west of the central mining area; MV-W03 is a sample from the Sevier River, where it flows along the western edge of the study area about 2 km west of the central mining area; MW-W04 is a sample of mine seep water obtained in underground workings in the central mining area by placing a polyethylene container such that it could catch drops of water, approximately one drop per minute, over a four-day period; and, MV-W05 is a water sample from the Monroe Hot Springs which is approximately 16 km northeast of the study area (this sample is probably highly diluted with substantial amounts of recent rainwater).

Whole-Rock Samples

The whole-rock $\delta^{18}O$ values (Table 2) within and among rock types show substantial variation. The quartz monzonite ranges from +1.4 to +6.7 o/oo with an average of 3.8 o/oo for 33 samples (Figures, 3a, b, and c). The average of five granite samples is +1.6 o/oo with values ranging from +0.1 to +3.6 o/oo (Figure 3d). With the exception of a few quartz monzonite samples with $\delta^{18}O$ of about +6 o/oo or higher, all these plutonic rocks are abnormally low in $\delta^{18}O$ compared to normal granitic rocks (Taylor, 1974).

Samples MVF-66 and MVF-68 with $\delta^{18}O$ values of 6.2 and 6.7 o/oo, respectively, are quartz monzonites from the subsurface. In hand sample, these rocks seem to be fresh with little or no hydrothermal alteration. In thin-section, however, these two rock samples do show evidence of alteration. Whether this is due to deuteric processes has as yet not been determined. Albeit there is some microscopic alteration, the oxygen isotopic compositions of these two samples are within the range of those for normal igneous rocks of this composition which have not experienced hydrothermal modification (Taylor, 1974).

MVF-50 is a sample taken across the quartz monzonite-granite contact as exposed underground. The $\delta^{18}O$ values for four subsamples are shown in Figure 4, which schematically illustrates the sampling geometry. Four subsamples were prepared by sawing approximately parallel to the contact, which is somewhat irregular. Two granite samples give +1.5 and +3.6 o/oo, respectively, for 0.3 to 1.3 cm and 3 to 4 cm from the contact; the quartz monzonite samples gave $\delta^{18}O$ values of +1.9 and +3.8 o/oo, respectively, for 0.3 to 1.3 cm and 3 to 4 cm from the contact.

Results obtained thus far on other rock types and materials at Marysvale are limited. A sample of vein quartz (MVF-40) associated with an ore vein gave +1.1 o/oo. A sample of the Red Hills tuff gave +9.1 o/oo.

DISCUSSION

The effects of hydrothermally circulated meteoric water upon the $\delta^{18}O$ of igeneous rock complexes have been described by various workers for many world-wide occurrences, and are common to those epizonally emplaced.

Examples of such localities include: Isle of Skye, Scotland (Taylor and Forester, 1971; Dickin et al., 1980); Skaergaard, Greeland (Taylor and Forester, 1979); Stony Mountain, Colorado (Crowley and Giletti, 1983); Western Cascades, Oregon (Taylor, 1971); and, the Casto Ring Zone, Idaho (Criss et al., 1984). These studies show that, although there may have been varying proportions of other types of waters (e.g., magmatic, connate, etc.), the most significant apparent source of hydrothermal water is meteoric. Water/rock ratios and hydrothermal fluid temperatures, assuming equilibrium, have also been calculated for many such occurrences. Below is described the preliminary results of similar exercises for Marysvale.

Initial Water $\delta^{18}O$

The water which circulated within the Marysville hydrothermal system was meteoric in origin. This water must have had a meteoric origin because meteoric water constitutes essentially the only source which could facilitate significant ^{18}O depletion of the rock.

Water analyses suggest a value of about -14 o/oo for meteoric water in the Marysvale area. This is an expected value for meteoric water of this geographic location, using δD values of recent and Tertiary clays (Sheppard et al., 1969; Taylor, 1974) to obtain $\delta^{18}O$ values (~ -16 and -11, respectively) via a meteoric line equation of $\delta D = 8\delta^{18}O + 10$ (Craig, 1961). The initial water $\delta^{18}O$ is assumed to be equivalent to the observed present-day value. At the time of hydrothermal activity in the Tertiary (~18 m.y. ago), the geography of western North America was basically as today so that this value is probably appropriate. The somewhat higher value of about -9 o/oo for the mine seep water may indicate some oxygen exchange or modification of the meteoric water as it passes through at least 150 meters of silicate bedrock (quartz monzonite).

Initial Rock $\delta^{18}O$

The $\delta^{18}O$ values of whole-rock samples from this study range from about normal for granitic rocks (~ +6 to 7 o/oo) to extremely depleted (~0 o/oo) in ^{18}O. The samples with $\delta^{18}O$ above +6 o/oo appear to be relatively unaltered. In contrast, most of the other sampled plutonic rocks show significant alteration. ^{18}O depleted igneous rocks such as these are characteristic of igneous rocks which have interacted at elevated temperatures with meteoric waters. Thus, the low $\delta^{18}O$ values and the observed range of values, coupled with field and petrographic observations, indicate that the plutonic rocks near Marysvale have been hydrothermally affected by O-isotope exchange with heated meteoric waters.

Further, these relationships indicate that the quartz monzonite was emplaced as a magma with essentially normal $\delta^{18}O$ and that the ^{18}O depletion observed is the result of subsolidus exchange with hydrothermal waters. Thus, the initial rock $\delta^{18}O$ is assumed to be +7 o/oo for the quartz monzonite, slightly higher than the highest observed value. The analyzed granites all show large ^{18}O depletions, consistent with the high degree of alteration seen in feldspars and ferro-magnesian minerals nearly ubiquitous to the granite. Due to the pervasive nature of this alteration, it is not possible to similarly assign an initial $\delta^{18}O$ value for the granite.

In terms of the low $\delta^{18}O$ values and their ranges, as well as the petrographic character of the rocks, the Marysvale plutonic rocks highly resemble those from other well-known localities which have experienced subsolidus modification by meteoric waters. The geologic setting of Marysvale by analogy fits well with this conclusion. The highly faulted bedrock, the shallow crustal emplacement, the repeated episodes of igneous activity supplying heat, and the relatively permeable overlying volcanics would all tend to promote hydrothermal circulation which indeed appears to have taken place at Marysvale. In contrast to the low $\delta^{18}O$ values for the plutonic rocks, the Red Hills volcanics appear to be higher in ^{18}O relative to normal igneous rocks of this composition. The high $\delta^{18}O$ value of +9.1 o/oo for this rock could indicate that it escaped hydrothermal modification. It could also indicate hydrothermal exchange. However, this exchange must have taken place with relatively ^{18}O-enriched waters (which had previously exchanged with bedrock), occurred at substantially lower temperatures, or a combination of these two factors.

Spatial Relationships of Hydrothermal Alteration

The $\delta^{18}O$ values (see Figure 1) for surface samples do not show a simple geometric distribution. Many similarly affected plutons, several with economic ore deposits (e.g., Taylor, 1974), display a "bull's-eye" pattern of inwardly decreasing $\delta^{18}O$ values. Such a pattern is not apparent with present data. Whether the circulation pattern and temperature gradients were inappropriate to the development of such a pattern is not clear. Additionally, the area of sample coverage may be too restricted to bring out a larger scale pattern even though surface quartz monzonites vary from +5.5 to +1.4 o/oo.

Focusing of circulation along the well-developed series of joints, faults, and veins quite likely has been important in hydrothermal modification, consistent with the expectation that these features provide the principal circulation paths. Indeed, as noted earlier, ore mineralization in the central mining area was highly controlled by fault planes. As documented at similar localities (Dickin et al., 1980), such control is likely at Marysvale. However, the oxygen isotope results do not unequivocally confirm this hypothesis. $\delta^{18}O$ of surface quartz monzonite is not well correlated with proximity to mapped faults. Likewise, $\delta^{18}O$ depletions in subsurface samples are not well correlated with proximity to the major ore-bearing veins (Figure 5).

The $\delta^{18}O$ values for subsurface quartz monzonite samples compared to those collected at the surface show substantial overlap in range but, on the average, the subsurface samples (+4.3 o/oo) are slightly more ^{18}O enriched than the surface samples (+2.9 o/oo). The difference could be due to a number of factors including: differences in grain size, different water/rock ratios, different temperatures of hydrothermal exchange, and a bias in sampling. The full definition of this difference awaits more detailed study, but at this stage it seems unlikely that it is due to sampling.

It is quite possible, in view of the number and time span of igneous events in the Marysvale region, that the study area was affected by more than one hydrothermal event. The lack of clear spatial patterns could be due to overlapping convective systems with differing geographic distributions. Much more study is needed to answer this question. At this preliminary stage, hydrothermal alteration by meteoric waters is assumed to have taken place during a single episode.

Temperature of Hydrothermal Fluid

The single analysis of quartz (+1.1 o/oo) from an ore vein provides important, even if preliminary, information. There is no information about whether this quartz is isotopically homogeneous or zoned. Taken at face value, this analysis can yield the temperature of precipitation or the $\delta^{18}O$ of the hydrothermal solution. Equilibrium isotopic fraction between a mineral phase may be described by:

$$\delta^{18}O_m - \delta^{18}O_w \approx A(10^6\ T^{-2}) + B; \qquad \text{(Equation 2)}$$

where the subscripts m and w refer to mineral and water, respectively, T is absolute temperature, and A and B are constants for the specific mineral. For quartz-water equilibrium, A = +3.38

and B = 3.40 (Clayton et al., 1972). Since meteoric water was involved at Marysvale, $\delta^{18}O$ may be estimated as -14 o/oo. The +1.1 o/oo value for quartz then yields a temperature of approximately 160°C. This temperature is similar to the 200°C estimate by Cunningham and Steven (1979). Note that the composition of the hydrothermal water is likely to have been somewhat higher than -14 o/oo due to prior exchange with country rock and thus the temperature would be correspondingly higher. The quartz $\delta^{18}O$ value would indicate $\delta^{18}O$ for water of -10.6 and -5.8 o/oo at assumed temperatures of 200°C and 300°C, respectively. Since a temperature on the order of 200°C is a reasonable estimate for ore formation, the mineralizing hydrothermal solutions must have been derived ultimately from groundwater of meteoric origin.

Apparent Water/Rock Ratios

An idea of the amounts of meteoric water involved in the hydrothermal alteration may be gained by calculating water/rock ratios in the manner outlined by Taylor (1979). The ratio of water to rock may be calculated for two simplified and extreme cases: open system and closed system. Such calculations yield integrated water/rock ratios which are minimum values because rock-water equilibration is assumed and significant volumes of water may pass through the rocks without equilibrating.

For the closed system case, continuous cyclic recirculation and requilibration of the fluid is assumed. In this limit (Taylor, 1979),

$$\frac{W}{R} = \frac{\delta^{f}_{r} - \delta^{i}_{r}}{\delta^{i}_{w} - (\delta^{f}_{r} - \Delta)} \qquad \text{(Equation 3)}$$

where $\frac{W}{R}$ is the atomic ratio of oxygen in water relative to rock, the subscripts r and w refer to rock and water, respectively, the superscripts f and i refer to final and initial values, respectively, the δ values are as defined in Equation 1, and $\Delta = \delta^{f}_{r} - \delta^{f}_{w}$ which represents the equilibrium isotope fractionation between rock and water and is a function only of rock composition and temperature.

For the open system model, water is assumed not to recycle but rather passes through the system only a single time. In this extreme case (Taylor, 1979),

$$\frac{W}{R} = \ln \frac{\delta^{i}_{w} + \Delta - \delta^{i}_{r}}{\delta^{i}_{w} - (\delta^{f}_{r} - \Delta)} \qquad \text{(Equation 4)}$$

where the notation is as given above.

These models have been used to calculate apparent water/rock ratios appropriate for the Marysvale central intrusive and the results are shown diagrammatically in Figure 6. As stated previously, the initial rock is assumed to be +7 o/oo in $\delta^{18}O$, and the initial water is assigned $\delta^{18}O$ of -14 o/oo. In the absence of detailed mineralogic data, the isotopic fractionation between rock and water is assumed to be that for plagioclase of An_{30} composition. Such an approximation seems reasonable since andesine feldspar is the dominant mineral phase and other phases such as quartz and mafic minerals have isotopic fractionations straddling the feldspar fractionation. Δ is determined from Equation 2 where $A = +2.68$ and $B = -0.353$ for An_{30} plagioclase (O'Neil and Taylor, 1967) for the appropriate temperatures.

The water/rock ratios were calculated for 200°C, as well as for 100°C and 300°C which are probable limits for the temperature of hydrothermal activity. For 200°C, apparent ratios (in terms of atom o/o of oxygen) for the quartz monzonite range from less than 0.1 to about 1. These simplified models clearly indicate large amounts of circulating meteoric water where involved. Note that an atomic value of 1 corresponds to a ratio by weight of 0.5.

Noting the spatial variations in $\delta^{18}O$, the apparent water/rock ratios show large variations over short distances. This suggests nonuniform flow of hydrothermal solutions probably controlled by fractures.

Timing of Hydrothermal alteration

The timing of rock/meteoric water interaction is not known at this point, but some limitations are suggested from the results on sample MVF-50 (Figure 4). Analyses of the granite and quartz monzonite adjacent to the contact show nearly symmetrical ^{18}O depletion on both sides of the contact. It is interpreted here that the contact served as a preferential conduit for circulation since larger depletions are seen adjacent to it. Assuming this to be the case, it then follows that the granite and quartz monzonite behaved similarly in terms of oxygen exchange. The granites are about 0.3 o/oo lower than the corresponding quartz monzonites, but this difference is not significant in view of the sampling accuracy and irregular contact surface, especially since the analyses imply a substantial gradient in $\delta^{18}O$. It follows that the hydrothermal alteration of both intrusive phases post-dates the emplacement of the granite. Since uranium mineralization also post-dates granite formation (Cunningham et al., 1982), all the ^{18}O depletions could be the result of a single event hosted by previously unaltered plutonic rocks and culminating in the formation of the uraniferous ores.

CONCLUSIONS

Based upon the preliminary results, it is concluded that: (1) the rocks of and around the central mining area at Marysvale, Utah, experienced massive, subsolidus hydrothermal exchange with circulating meteoric waters; (2) the initial $\delta^{18}O$ of the hydrothermal water in the central mining area was approximately -14.0 o/oo, and the initial $\delta^{18}O$ of the quartz monzonite was approximately +7.0 o/oo; (3) surface quartz monzonite samples on the average have lower $\delta^{18}O$ values than subsurface quartz monzonite samples; (4) model calculations indicate that for quartz monzonite at about 200°C, the integrated apparent W/R ratio was between 0.1 and 1; (5) the quartz monzonite/granite contact apparently allowed for enhanced passage of hydrothermal water, causing preferential $\delta^{18}O$ depletion at the interface; (6) the hydrothermal event apparently post-dates granite emplacement; and, (7) the hydrothermal solutions responsible for the mineralization were derived from meteoric water.

The results of this report are preliminary and, therefore, the conclusions are tentative. Much more work is needed to help better understand the processes operative at Marysvale, especially in regards to their influence on elemental migration.

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TABLE 1. $\delta^{18}O$ VALUES FOR WATER SAMPLES

MV-WO1	-12.9	Marsh Water
MV-WO2	-13.6	Big Rock Candy Mtn Spring
MV-WO3	-14.3	Sevier River
MV-WO4	-9.4	Mine Seep Water
MV-WO5	-16.7	Monroe Hot Springs

TABLE 2. $\delta^{18}O$ VALUES AND STATISTICS FOR WHOLE ROCK SAMPLES

Quartz Monzonite (Tbi)				Granite (Tmf)		Volcanics	
At Surface		Subsurface		At Surface		Red Hills Tuff (Tmr)	
Sample	$\delta^{18}O$						
MVF – 17	+1.4	MVF – 1	+2.3	MVF – 84	+0.8	MVF – 32	+9.1
26	1.5	4a	4.4				
31	1.7	4b	3.6	Subsurface			
46	4.3	5	4.7	MVF – 33	+1.3		
81	3.1	6	3.3	38	0.1		
82	2.6	7	4.5	50-1	1.5		
86	4.2	8	5.8	50-2	3.6		
101	3.9	10	5.0				
106	2.5	12	4.5	n = 4		Ore Material	
126	5.5	13	5.0	$\bar{x}$ = 1.6		Vein Quartz	
128	1.9/1.7	14	4.9	σ_{n-1} = 1.5			
131	3.3	50-3	1.9			MVF – 40	+1.1
		50-4	3.8				
n = 13		54	3.5				
$\bar{x}$ = 2.9		55	4.3				
σ_{n-1} = 1.3		59	3.7				
max = 5.5		60	4.9				
min = 1.4		66	6.2				
		68	6.7				
		78	3.1				
		n = 20					
		$\bar{x}$ = 4.3					
		σ_{n-1} = 1.2					
		max = 6.7					
		min = 1.9					

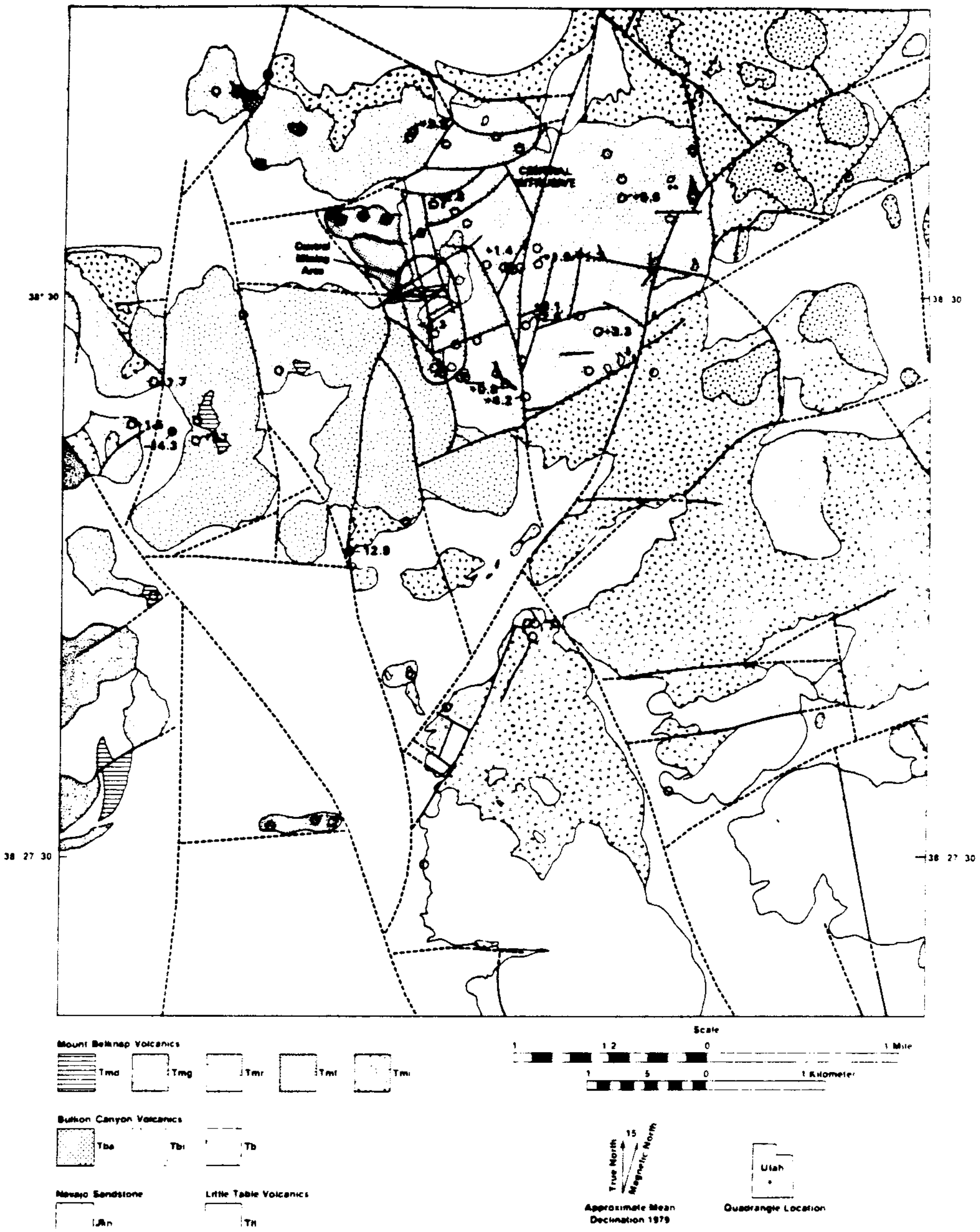

Figure 1. A simplified geologic map (after Cunningham and Steven, 1979) showing the locations of all Marysvale natural analog study Phase I surface samples. Preliminary $\delta^{18}O$ values are given in o/oo. Open circles are rock samples; closed circles are water samples. TMD = dikes and small stocks of aphanitic rhyolite. TMG = Gray Hill rhyolite member. TMR = Red Hills tuff member. TMF = fine-grained granite. TMI = porphyritic rhyolite stocks and lava domes. TBA = aplite plugs and dikes. TBI = intermediate-composition intrusive rock, including quartz monzonite, monzonite and granodiorite. TB = heterogeneous lava flows and breccias. JTRN = Navajo sandstone. TLT = little table volcanics.

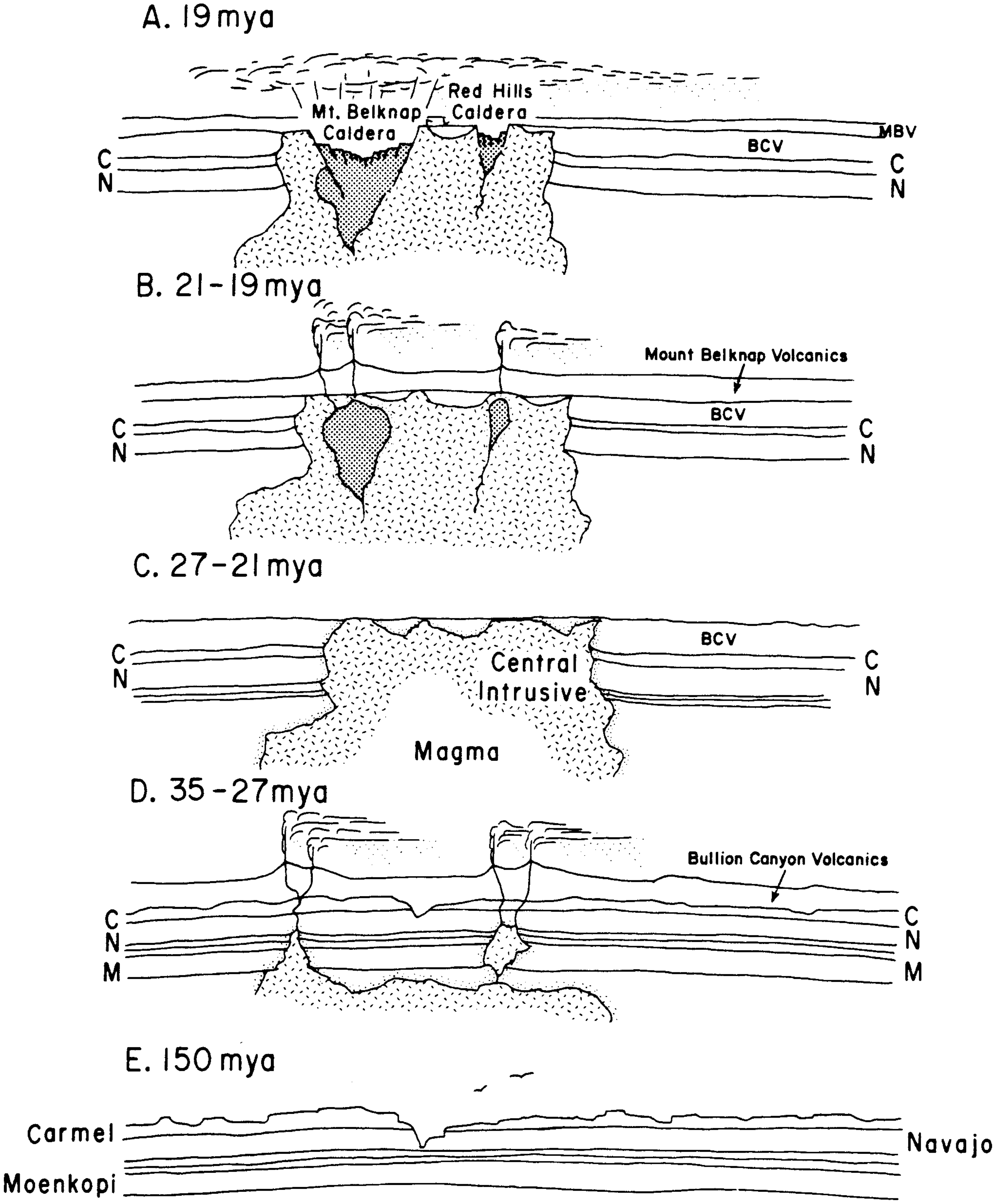

Figure 2. Schematic diagram of a simplified geologic history of the Marysvale area. See text for explanation.

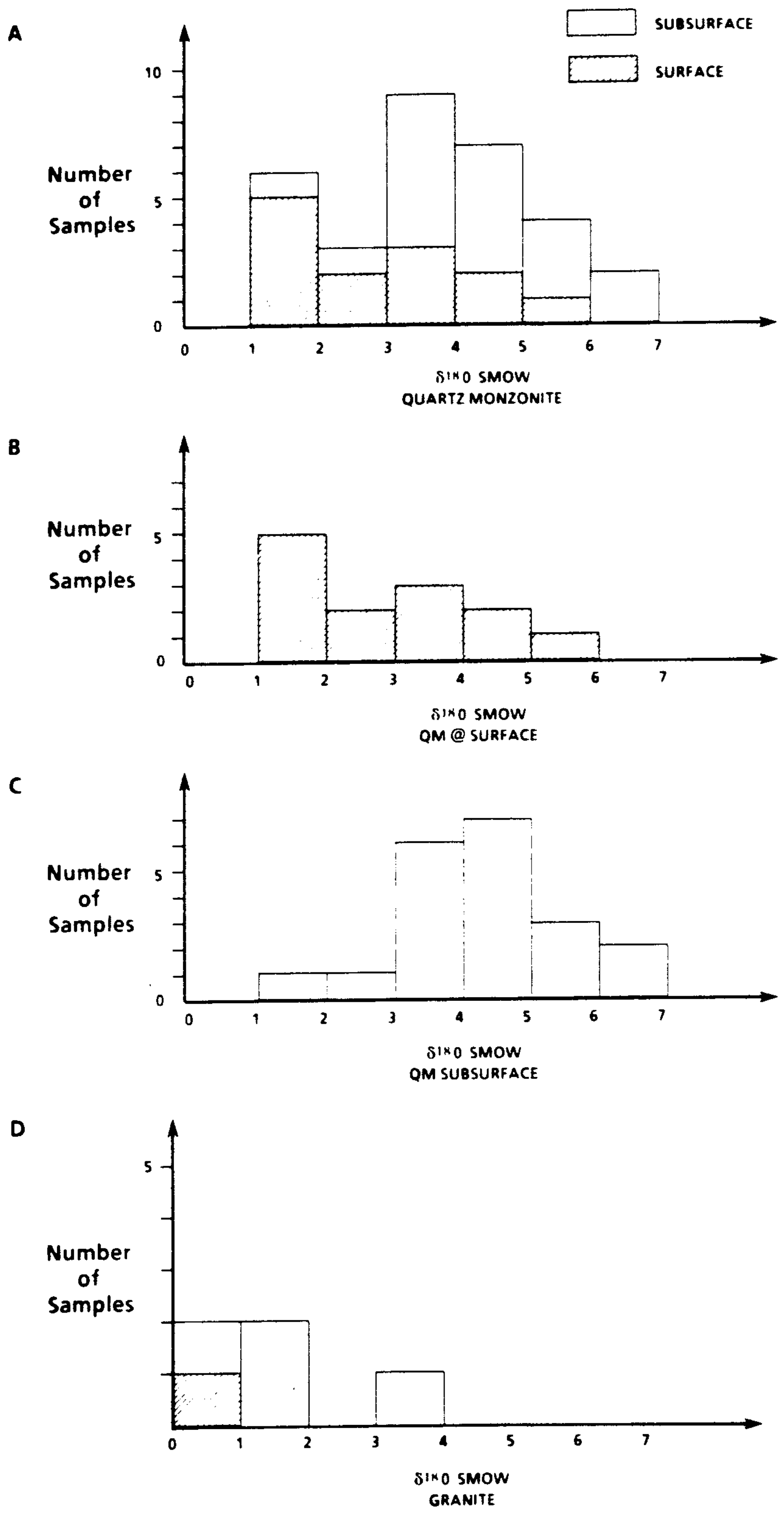

Figure 3. (a), (b), (c); histograms of $\delta^{18}O$ values of quartz monzonite (QM) from the Marysvale study area. Surface samples are slightly more depleted on the average than subsurface samples. (d) histogram of $\delta^{18}O$ values for granite found in the Marysvale central mining area.

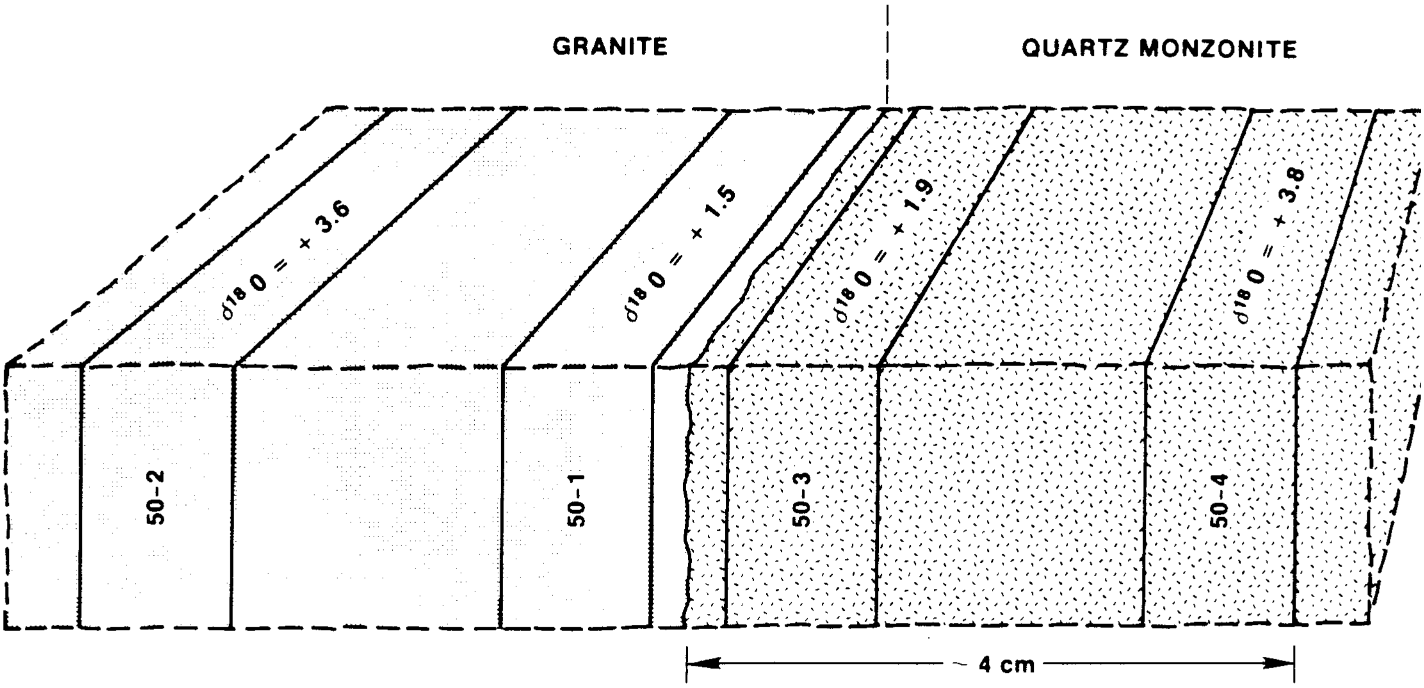

Figure 4. Schematic representation of sample MVF-50, showing the relationship of the subsamples to the irregular granite/quartz monzonite contact, with $\delta^{18}O$ values in o/oo.

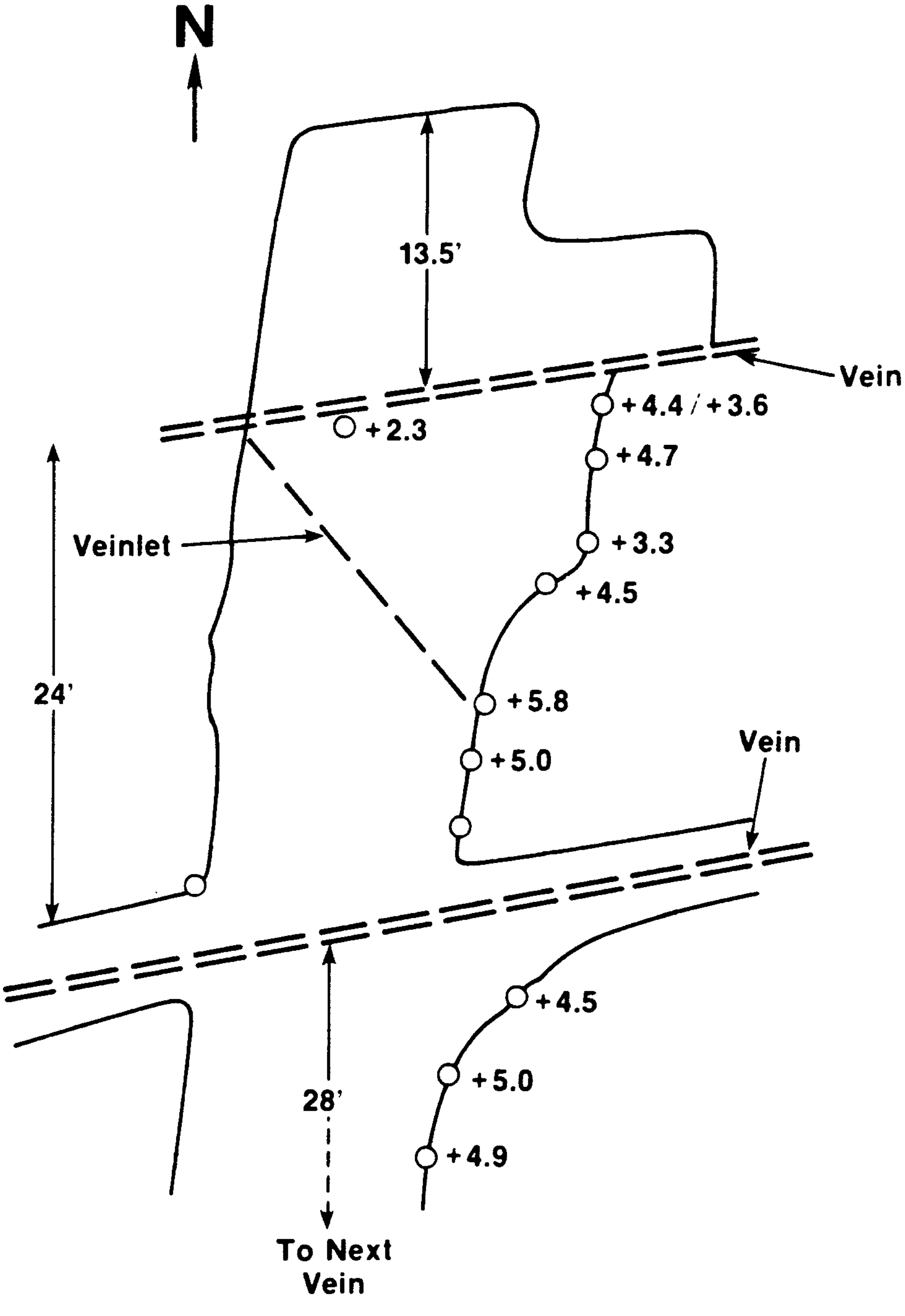

Figure 5. Diagrammatic sketch of the terminus of the VCA cross-cut, where it intercepts the freedom no. 2 veins, which is within quartz monzonite. Sample locations are noted by open circles. $\delta^{18}O$ values (o/oo) for analyzed samples are also shown.

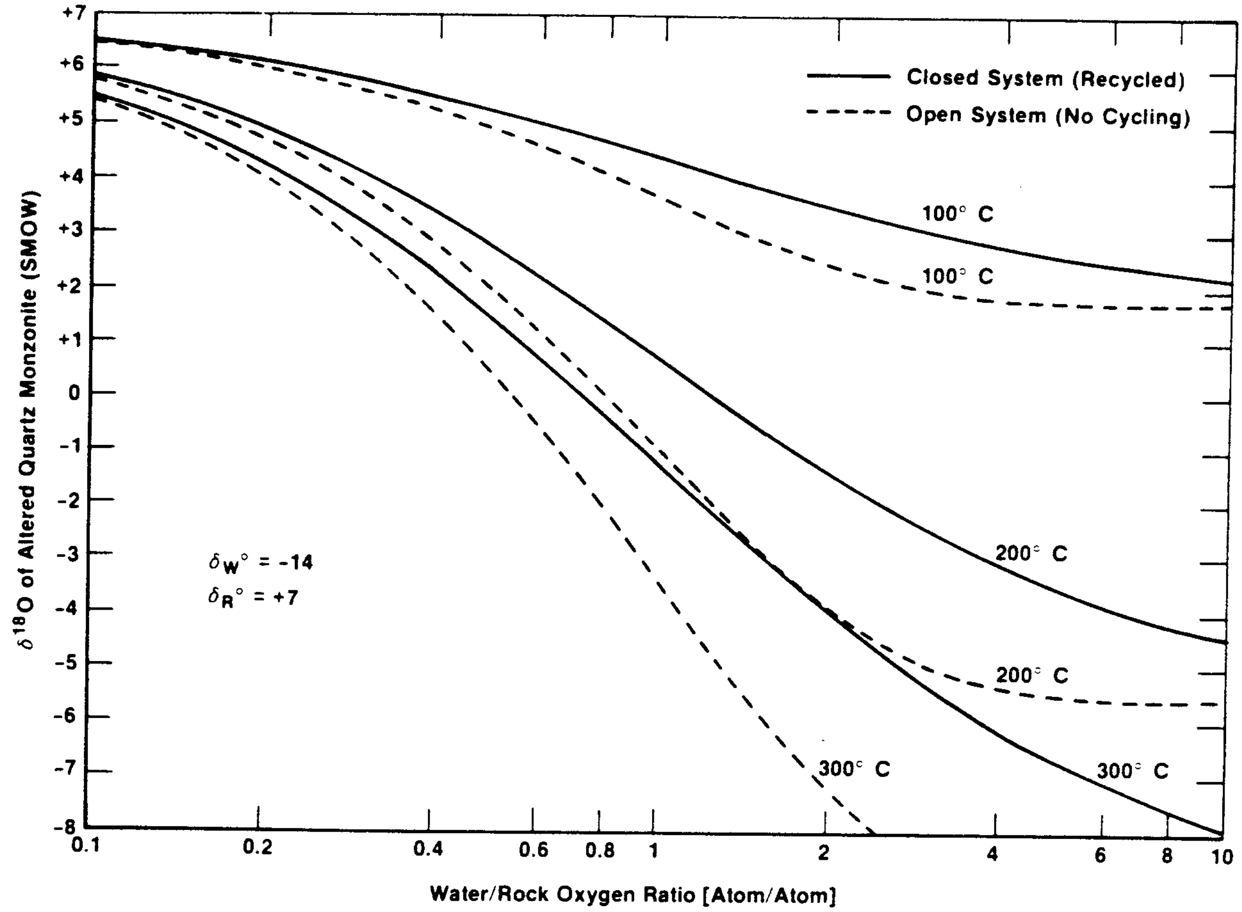

Figure 6. Model relationships between final rock $\delta^{18}O$ (δ_R^f) and water/rock ratio, for both open and closed systems, using equations 2 and 3 of the text. Initial water $\delta^{18}O$ (δ_W^i) is assumed to be equal to -14 o/oo and initial rock $\delta^{18}O$ (δ_R^i) is assumed to be equal to +7 o/oo.

SESSION E

HYDROTHERMAL/GEOTHERMAL ANALOGUE SYSTEMS

Chairman: Jan J. Cramer

CONTACT ZONES AND HYDROTHERMAL SYSTEMS AS ANALOGUES TO REPOSITORY CONDITIONS

H.A. Wollenberg and S. Flexser

Earth Sciences Division, Lawrence Berkeley Laboratory, University of California, Berkeley, CA. 94720, USA

ABSTRACT

Radioactive waste isolation efforts in the U.S. are currently focused on examining basalt, tuff, salt, and crystalline rock as candidate rock types to encompass waste repositories. As analogues to near-field conditions, the distributions of radio- and trace-elements have been examined across contacts between these rocks and dikes and stocks that have intruded them. The intensive study of the Stripa quartz monzonite has also offered the opportunity of observe the distribution of uranium and its daughters in groundwater and its relationship to U associated with fracture-filling and alteration minerals.

Investigations of intrusive contact zones to date have included 1) a Tertiary stock into Precambrian gneiss, 2) a stock into ash flow tuff, 3) a rhyodacite dike into Columbia River basalt, and 4) a kimberlite dike into salt. With respect to temperature and pressure, these contact zones may be considered "worst-case scenario" analogues. Results indicate that there has been no appreciable migration of radioelements from the more radioactive intrusives into the less radioactive country rocks, either in response to the intrusions or in the fracture-controlled hydrological systems that developed folowing emplacement. In many cases, the radioelements are locked up in accessory minerals, suggesting that artificial analogues to these would make ideal waste forms.

Emphasis should now shift to examination of active hydrothermal systems, studying the distribution of key elements in water, fractures, and alteration minerals under pressure and temperature conditions most similar to those expected in the near-field environment of a repository.

INTRODUCTION

Evidence for natural occurrences in candidate rock types can help to predict the long-term performance of nuclear waste repositories. Investigations of natural analogues are significant in determining the capability of radioelements to migrate into and through the near-field rock and into the hydrologic systems encompassing the repositories.

Occurrences reported here include those where intrusive rocks with relatively high concentrations of radioelements are in contact with some host-rock types presently considered candidates for repositories: plutonic rock and high-grade metamorphics, tuff, basalt, and salt. The conditions of intrusion have generally resulted in temperatures considerably higher than those expected in a repository. However, at stages in their cooling history the temperatures in intrusive-contact zones reach the range expected in the near-field, and during and following cooling, hydrologic systems are established that last for periods comparable to those of concern for repository environments.

Also of concern is the movement of radioelements and changes in mineralogy of near-field rock in response to the thermal-hydrologic effects of the introduction of the radioactive waste. A geologic analogue of this type has been investigated at Stripa, Sweden by mineralogic and radioelement measurements of the quartz monzonite following full-scale heater tests. Investigations of present-day active hydrothermal systems, where temperatures (100 to over 250 ^{o}C) are similar to those expected in rock close to the waste canisters, will also provide appraisals of radioelement movement and the effects of alteration mineralogy.

In this paper we describe analogue investigations of intrusive - country rock contact zones of contrasting character: one where there was no apparent hydrothermal system in response to the intrusion, and the other where a strong circulating hydrothermal system accompanied intrusion. Studies of contacts between relatively radioactive dikes cutting basalt and salt are briefly described, as are results of mineralogical and radioelement investigations of the Stripa pluton and preliminary findings at a present-day circulating hydrothermal system in basalt.

THE ELDORA STOCK - IDAHO SPRINGS FORMATION CONTACT ZONE: A CONDUCTIVE THERMAL REGIME

Samples were obtained from the contact zone between the 58-million-year-old Eldora Stock and Precambrian gneiss of the Idaho Springs Formation, Colorado, where previous geochronologic, mineralogic, geochemical and heat-flow modeling studies were well documented (Hart et al., 1968). The samples were collected from the stock and from the Idaho Springs Formation at the contact and at increasing distances to 7.5 km from the contact, (Figure 1) following a traverse essentially identical to that used by Hart et al. (1968).

The fresh stock rocks range in composition from monzonite to granodiorite. As described by Hart et al. (1968), the stock crystallized from a magma temperature of 780 °C and the rocks now exposed were probably never at depths greater than 1 km. The Idaho Springs Formation consists predominantly of alternating felsic- and mafic rich plagioclase-hornblende gneiss with occasional secretion pegmatites. Its age is 1.5-1.6 billion years, and the rocks were regionally metamorphosed approximately 1.4 billion years ago, at which time the pegmatites were injected. These "sweat" pegmatites filled the fractures and formed the veinlets that appear in the gneiss. Elemental variations due to pre-stock emplacement thermal events in the gneiss must then be carefully deciphered before attempting to interpret the stock-induced effects at 58 million years ago.

Samples from the stock, and of felsic, mafic and pegmatitic phases of the Idaho Springs Formation, were taken along the aforementioned traverse and from another site near Antelope Creek, Colorado (southwest portion of Figure 1). Splits of the samples were used for thin section preparation, laboratory gamma spectrometry, fission-track radiography, Rb-Sr and K-Ar geochronology, neutron activation analysis (NAA), and for stable oxygen isotopic analysis.

Rb-Sr, K-Ar, U, and Th-Pb radiometric ages and other data (Simmons and Hedge, 1978; Hart et al., 1968) allow heat models for the Eldora stock to be calculated. The stock is considered to have steep-to-vertical sides; the heat distribution about the stock was fairly uniform based on radiogenic Ar, Sr and Pb behavior in minerals, and the isotherm corresponding to the orthoclase-microcline transition (a maximum of 400 °C) is considered to be 300-800 m from the contact. The model advocated is that of a "brick" with large vertical extent downwards, its thickness equal to the average E-W outcrop extent of the stock and its length equal to the average N-S extent of the stock. The model is based on the assumption that cooling was solely by conduction and best explains the isotopic variations as a function of distance from the contact.

The loss of radiogenic ^{40}Ar from minerals as a function of distance in the gneiss from the contact was well documented by Hart et al. (1968), who also related estimated temperatures and apparent radiometric ages to distance from the contact. These apparent whole-rock ages were corroborated by K-Ar determinations on biotite, hornblende and feldspar from varying distances, and it was confirmed that the ages of minerals from various whole-rock samples are more thoroughly reset near the contact than away from it (Brookins et al., 1981). In addition, Rb-Sr whole-rock ages were determined on samples obtained at, near, and removed from the contact. The whole-rock isochron age is 1.5 ± 0.1 billion years, in close agreement with earlier work by Simmons and Hedge (1978). The Rb and Sr analyses also indicated that there was no gain of these elements in the Idaho Springs Formation from the Eldora stock except possibly within the 1-to-3 m contact zone where some mixing of magmatic fluids with the metamorphic rocks occurred.

To further investigate the matter of closed versus open system conditions, as well as to address the problem of conductive versus convective cooling, trace element and stable isotopic analyses of the samples used for Rb-Sr whole-rock geochronology were carried out. The rare earth/chondrite ratio versus rare-earth atomic number distribution plot is shown in Figure 2. Samples 1a and 1b are from stock material and samples 2 and 3 from stock-plus-metamorphic rocks in the 1- to 3 m contact zone. These four curves are all similar and show pronounced enrichment of the light rare earth elements (LREE). Curves 5a and 6a are from mafic units of the Idaho Srpings Formation, whereas curves 5b, 6b-1 and 6b-2 are from felsic units. The LREE are depleted in the mafic units but enriched in the felsic units; this behavior is noted not only in these samples taken 20-to-25 m from the contact (nos. 5, 6), but also in samples taken 2.5 km from the contact. It is apparent that some REE partitioning between mafic and felsic rocks took place during the Precambrian regional metamorphism, with open system conditions prevailing, as evidenced by the formation of secretion pegmatites.

The stable oxygen isotopic data (Figure 3) show a distinct contrast between the Eldora stock and the Idaho Springs Formation. Del ^{18}O values for the stock and stock-metamorphic mixes (in the contact zone) are confined to a relatively narrow range (+ 8.0 - 9.0 o/oo) compared with those of the Idaho Springs Formation (+7.5 - 11.5 o/oo). This indicates essentially closed system conditions for oxygen in the intruded rocks and no exchange of oxygen between the stock and the Idaho Springs Formation. In turn, this implies a lack of hydrothermal convective cooling, usually accompanied by hydrothermal solutions, (Parmentier and Schedl, 1981) and cooling by conduction appears most likely.

The location and abundance of uranium near and away from the contact were determined by fission-track radiography and gamma spectrometry (Flexser and Wollenberg, 1981). It was found that the occurrence of uranium is controlled predominantly by primary accessory minerals, both in the stock and in the Idaho Springs Formation: zircon, sphene, monazite, allanite, opaque minerals, and an unidentified highly uraniferous mineral present only in the Eldora intrusive (Figure 4). Secondary migration of uranium due to the intrusion of the stock has occurred, but on a small scale and only within a few meters of the contact. There is no indication of systematic enrichment or depletion in uranium, in either country rock or stock, as a function of distance from the contact. Migration of uranium is probably due to local redistribution from the accessory minerals by diffusion; there is no evidence to suggest that transport of uranium by circulating hydrothermal solutions in fractures played a significant role.

In summary, at the time of intrusion of the Eldora Stock and following its intrusion, the rocks of the Idaho Springs Formation were of low porosity and permeability, and the numerous fracture fillings and veinlets are prestock in age. In the 0.3 m zone at the contact, there was mixing of some fluids from the Eldora stock due to infiltration into cracked and deformed parts of the Idaho Springs Formation accompanying emplacement. With the exception of this zone, closed system conditions, over the 10^5 to 10^6 years of stock crystallization and cooling, are demonstrated by the geochemical data. The data also indicate that subsequent to intrusion and cooling of the stock, there has been no appreciable migration or redistribution of elements within the gneiss over the zone investigated.

THE ALAMOSA RIVER STOCK - LA JARA TUFF CONTACT ZONE: A CONVECTIVE THERMAL REGIME

In contrast to the Eldora occurrence, the presence of strong hydrothermal circulation in tuffaceous rock in response to the intrusion of the Alamosa river stock near Platoro, Colorado was evident from oxygen isotope ratios measured by Williams (1980) on samples collected over a broad region. Based on this evidence, the contact zone and areas away from the contact between the stock and the intruded rocks - the La Jara member of the Treasure Mountain tuff, and the Summitville andesite - were investigated, primarily to determine if radioelements and fission-product-analogue trace elements moved from the monzonite into the tuff or andesite, or moved within the tuff, in response to the circulating hydrothermal system.

The Alamosa River stock, of monzonitic composition, was emplaced at 29.1 ± 1.2 MYBP into predominantly andesitic volcanics forming and filling caldera structures (Lipman, 1975). The La Jara is predominantly a densely welded and devitrified ash flow tuff primarily of phenocryst rich quartz latite, ejected by an explosive event at 29.8 ± 1.2 MYBP.

Based on analyses of oxygen isotope ratios in 260 minerals and whole rock samples from the Alamosa River stock region, Williams (1980) suggested that the heat from the stock and other small intrusions, which range in age from 28 to 22.8 MY (Lipman, 1975), initiated extensive hydrothermal circulation. A roughly concentric aureole of $\delta^{18}O$ depletion was noted around the south and east margins of the stock, with depletion enhanced along two major faults, attesting to the importance of fracture permeability in the circulation of this system. Temperatures of the hydrothermal system were estimated by Williams (1980) to have been in the range 250-370 ^{o}C.

For our studies, samples from the Alamosa River stock area were collected at several locations as shown in Figure 5. A detailed traverse was made across the intrusive-tuff contact, as well as regional traverses in the tuff and in the andesite away from the stock, and samples were analyzed by neutron activation and fission-track methods to determine the distribution of radio- and trace elements.

Thin-section petrography shows that alteration of the tuff related to the monzonite contact has affected both the phenocrysts and the interstitial matrix. The progression of alteration starts within 60 m of the contact with the development of calcite, intergrown with the fine quartz-feldspar mosaic of the matrix. Within 40 m of the contact chlorite and sericite appear in the matrix, as well as stringers and over-growths of quartz which increase in abundance and coarseness toward the contact. Epidote also becomes a common matrix alteration within 12 m of the contact. Phenocryst alteration in the tuff more than 60 m from the contact is mainly confined to biotite, which is partly altered to fine opaque grains and sphene. Closer to the contact, pyroxene grains are altered to an opaque mineral, probably magnetite, and within 30 m of the contact biotite grains have been reduced to mere streaks of fine opaque grains, with associated epidote and sphene.

The distribution of uranium in rocks of this contact zone, represented by a traverse at Telluride Mountain (Figure 5), was examined by fission-track radiography. Uranium in the monzonite is mainly confined to minute accessory grains (probably zircon) which occur most typically in grains of potassium feldspar. Uranium also occurs, though more rarely, with altered mafic grains in monzonite close to the contact, and is probably associated there with very fine sphene. In contrast to the monzonite, the tuff rarely contains uranium-bearing accessory grains. Instead, U in the tuff usually occurs in low concentrations in the fine feldspar-quartz intergrowth comprising the matrix between phenocryst grains. The actual contact between monzonite and tuff, identifiable in thin sections, is marked by a dense intergrowth of epidote and lesser sphene. Uranium is often associated there with sphene, but is otherwise absent from the contact. The contact is also cut by fine hematite-filled fractures extending into adjacent tuff and monzonite. Uranium does not appear to be associated with these fractures within the immediate contact zone or on either side of the contact.

Results of neutron activation analyses of some trace elements in samples of monzonite and tuff from the meter-scale traverse across the contact at Telluride Mountain comprise Figure 6. Strong contrasts between monzonite and tuff are evident, with higher contents of Cs, Rb, Sc, V, Fe, Th, U and Co in the monzonite. On the 10-meter scale of sampling, there are suggestions of gradients in Cs, Th and Co in the tuff, with abundances of these elements increasing towards the contact. In general, the elements studied with the exception of Cs, Th and Co, show no evidence for migration between the stock and intruded rocks. These observations, together with petrographic investigation (Wollenberg et al., 1983), indicate that elemental distributions in the rocks appear to be mineralogically controlled, and local whole-rock chemical variations reflect mineralogical variations. On a broader scale, analyses of samples from a regional traverse (Figure 7), extending several kilometers from the contact, indicate that there are no apparent chemical gradients to match the regional gradients in whole-rock $\delta^{18}O$ in the La Jara tuff.

The effects of alteration on trace element abundances were investigated. Strongly altered tuff is enriched in Cs, Sr, and Rb and depleted in La and Fe, relative to the less altered tuff. Alteration effects are less apparent in the monzonite, though altered samples are high in Th and relatively low in La and Fe. The general high degree of correlation between U and Th, (Figure 8) irrespective of degree of alteration and distance from the contact, contrasts with the lack of correlations between Th and both Sr and Cs. Weak correlations with Th hold (in all but the strongly altered samples) for Rb and La, and for Fe in tuff and monzonite. These observations suggest that Sr and Cs were relatively mobile in response to alteration, while La, Rb, and Fe were less affected, and U and Th were essentially unaffected by alteration, and thus were relatively immobile.

Oxygen isotope data, obtained for samples from the Telluride Mountain traverse show a broad variation of $\delta^{18}O$ values of the tuff, ranging from + 0.8 o/oo to 3.6 o/oo in the zone within 60 m of the contact. Values in the monzonite within 10 m of the contact are +2 o/oo. The general degree of depletion in the monzonite and in the tuff is consistent with previous data (Williams, 1980). However, the $\delta^{18}O$ depletion does not, on the scale examined in the Telluride Mountain traverse, show any consistent gradient away from the intrusive in the tuff. Local fracture permeability variations appear to control the variations observations observed in the $\delta^{18}O$ depletion of any specific sample. Although rock samples from the Telluride Mountain traverse are quite variable in $\delta^{18}O$, they are all significantly depleted relative to normal igneous rock. Water-rock mass ratios greater than 0.1 are implied for even the least $\delta^{18}O$-depleted samples. The samples lowest in $\delta^{18}O$ indicate water/rock values greater than 0.3.

In summary, at Platoro:

- A strong convective hydrothermal system accompanied intrusion of Alamosa River Stock.

- The distributions of U, Th, REE, V, K, and Ti in the monzonite and tuff are apparently unaffected by the intrusion or are the result of complete homogenization by the hydrothermal circulation. This is true also for Rb, Sr, and other elements, although for some of these elements there is no strong chemical gradient between the rocks. U and Th are essentially immobile with alteration, in comparison with other trace elements.

- Within ten meters of the contact, some elements show evidence for contact zone mobility.

- Both monzonite and tuff have essentially retained their bulk chemistry during and after intrusion.

A RHYODACITE DIKE BASALT CONTACT ZONE

A contact zone between a rhyodacite dike and the Wanapum Basalt of the Grande Ronde Formation is exposed in a quarry on the Hood River, Oregon. Investigation of this contact showed that chemical gradients between the dike and the basalt are pronounced, permitting assessment of element migration during intrusion of the dike as well as during and after its cooling. In this study, radioelement contents and Sr isotope ratios were determined from a sampling traverse encompassing the dike and extending several meters into the basalt. If chemical and/or isotopic exchange has occurred between such contrasting rock types, mixing should be apparent in analyses of these samples.

The distributions of radioelement contents and Sr isotope ratios are plotted in Figure 9. The sharp contrast between the uranium and thorium contents of the rhyodacite and the basalt is evident, as is the strong contrast in $^{87}Sr/^{86}Sr$. Uranium in the rhyodacite averages 4.3 ppm; thorium, 13.2 ppm; potassium, 3.1%; and $^{87}Sr/^{86}Sr$ 0.7041. Corresponding average values for basalt are: U, 1.05 ppm: Th, 3.95 ppm; K, 0.9%, and $^{87}Sr/^{86}Sr$, 0.7052. These data argue against any transfer of radioelements or Sr from one rock into the other, either during intrusion of the dike or through fractures formed in the basalt after the dike had cooled.

It is concluded from this occurrence that

- The strontium isotopic characteristics of both the intrusive and intruded rocks are preserved. There is no evidence for Sr isotopic disturbance or redistribution due to the emplacement of the rhyodacite dike in the Wanapum Basalt.

- The distribution of radioelements, with pronounced gradients in U, Th, and K between the rhyodacite and basalt, shows that no radioelements have been transferred across the contact.

- Consideration of the rhyodacite as a heat engine, and therefore as an analogue for buried radioactive waste in basalt, indicates that radionuclide migration into the host rock is unlikely under the conditions of dike intrusion.

CONTACTS BETWEEN DIKES AND BEDDED SALT

The migration of radio- and trace elements into salt in response to intrusion of a dike and over long time periods following its cooling may be analogous to migration of radionuclides in the near-field of a breached canister in a salt repository. Investigation of the abundance and contents of fluid inclusions in the salt may also be definitive in assessing the thermal and chemical effects of the dike. Potential analogue occurrences include a lamprophyre dike cutting the evaporite sequence of the Delaware Basin in southeastern New Mexico, a basaltic dike transecting salt of the Zechstein, West Germany, and Permain kimberlitic dikes cutting upper Silurian salt beds of Salina Basin in northwestern New York.

Gamma spectrometric measurements of a set of samples obtained of the basaltic dike, of Miocene age, and salt of the Zechstein indicated appreciable radioelement contents of the dike (U = 2.1 ppm, Th = 7.6 ppm), while radioelement contents of the salt at and away from the contact are below detectability limits. A similar situation was observed in a set of samples of kimberlite dikes (U = 1.5 - 1.9 ppm, Th = 11.7 - 12.6 ppm) and salt obtained from underground exposure at the Cayuga mine, New York. Preliminary investigation of fluid inclusions in salt samples from the Cayuga mine by D.K. Smith (1983) indicates that their homogenization temperatures exceeded 380 ^{o}C.

The Cayuga set remains to be examined in more detail petrographically, and selected samples of salt and dike analyzed for trace elements. Examination of fluid inclusions, their abundance, configuration, and analyses of their contents are also required.

Preliminary data then suggest that U and Th have not migrated appreciably from the dikes into salt, either in response to injection of the dikes or over the tens to hundreds of millions of years subsequent to their cooling.

INVESTIGATIONS AT STRIPA, SWEDEN

At the Stripa experimental facility in an inactive iron mine in central Sweden (Witherspoon et al., 1981) radiogeologic studies included gamma-spectrometric surveys on the surface and underground of the U, Th and K contents of the quartz monzonite pluton encompassing the experiments, high-grade metamorphic rocks surrounding the pluton, and neighboring larger granitic plutons (Wollenberg et al., 1982). A geological cross section through the experimental workings comprises Figure 10.

Sampling at Stripa over a vertical extent of nearly 900 m was afforded by continuously-cored inclided holes drilled from the surface, excellent access to underground workings, and core from a vertical hole drilled underground from a depth of 410 to 899 m (Figure 10). The abundances of U, Th, and K were measured by laboratory gamma spectrometry of core and hand specimens and by field measurements, on the surface and underground, using a portable gamma-ray spectrometer. The field gamma spectral measurements were calibrated by the laboratory analyses, permitting calculations of radioelement concentrations from field counting rates. Laboratory analyses indicated that the daughter products in the U and Th decay series were in secular equilibrium with their parents in the granitic rocks studied.

The Stripa quartz monzonite is unique in its radioelement content, both in the abundance of radioelements and in their ratios, as summarized in Table 1. The relatively high U contents of the quartz monzonite contrast with those of the other granitic rocks in the region and with the neighboring metamorphic rocks. The Th/U ratio of the Stripa quartz monzonite (~1) is considerably lower than in the other plutons (2.4), leptite (3.8), and regional metamorphic rocks (2.6), and is considerably lower than the average for granitic rocks in general. The relatively low Th/U ratio in the quartz monzonite suggests that U and Th are not in their usual association with accessory minerals, a fact confirmed by alpha- and fission-tract radiography (Wollenberg et al., 1982).

Inspection of the plot of U and Th versus depth in the quartz monzonite (Figure 11) indicates that U is depleted in surface exposures relative to its abundance underground. However, U in groundwater (also shown in Figure 11) increases markedly to a depth of 150 - 200 m, then decreases steadily with depth in samples from the deep vertical drill hole. An explanation for these distributions based on fission track radiographic observations, is that at depth in the Stripa quartz monzonite, U is primarily associated with fracture-filling chlorite and not with accessory minerals. Andrews et al., (1982) suggest that at Stripa, U may be deposited with fracture calcite, though this occurrence has not been confirmed by radiography. The association of U with fracture minerals indicates that U has been, and may still be relatively mobile. It may be removed from near-surface rock where slightly acidic and oxidizing conditions prevail (as reported by Andrews et al. (1982)), and transported in fractures by groundwater to deeper zones where more reducing conditions favor its concentration in fracture-filling material. The gradational increase in U with depth in the rock below 410 m, shown in Figure 11, then might result from redistribution and concentration in fracture filling material by the groundwater system. The concomitant increase in Th with depth may also be explained by its association with U in fracture minerals. Thorium-rich accessory minerals are very rare in the Stripa quartz monzonite, compared with the other plutons in the region and with granitic rocks in general.

The mobility of uranium in the Stripa quartz monzonite is also demonstrated by results of examination of core from "drillback" holes (Figure 12), drilled through the walls of a hole that contained an electric heater to simulate the thermal effects of the introduction of radioactive waste (Flexser et al. 1982). The effects of in-situ heating of the monzonite were studied with respect to petrologic alterations and mechanical damage to the rock. The suite of core samples was examined in thin sections, by alpha radiography, gamma spectrometry, x-ray diffraction, and by electron microprobe. Mineralogic alterations in the rock adjacent to the heater were most pronounced in chlorite, which showed a marked change in colour associated with proximity to fractures as well as to the heater hole. Structural changes in chlorite included decrease in the dimensions of the unit cell, a change to heaxagonal or pseudo-hexagonal symmetry, and possibly disorder in layer stacking perpendicular to the c-axis. Intergrowth of fine hematite with chlorite also occurred.

Chlorite from within 5 cm of the heater hole contained slightly less SiO_2 and MgO and more FeO than chlorite in the unheated rock. Muscovite in the heated rock showed faint color changes associated with heating but was structurally unaltered. Muscovite near the heater hole was generally consistent in chemical composition, although it showed some variability at grain margins and in fracture fillings.

The distribution of uranium and thorium in the heated rock was studied by alpha radiography, which provided qualitative evidence for the addition of U or Th to sites of disseminated acculations of these elements in samples near the heater hole. These accumulations occurred in fractures, cleavage planes, and grain boundaries. Sources of the added U or Th were not positively identified, but gamma-spectral analyses suggested depletion of U in rock away from the heater and its migration toward the heater hole (Figure 13).

Therefore at Stripa, where U occurs predominantly in fracture-filling chlorite, there is evidence for present-day mobility of this element in the groundwater system and in response to a one-year heater test.

NEWBERRY, OREGON: A PRESENT-DAY HYDROTHERMAL SYSTEM

A set of samples of andestic basalt, from a hydrothermal regime where temperatures range from 150 to 265 ^{o}C, was obtained from core from a 950 m deep hole drilled by the U.S. Geological Survey in the Newberry Caldera, Oregon (Macleod and Sammel, 1982). Saturated rock at these temperatures may be analogous to conditions in the near-field of a repository, within a few hundred years following emplacement of radioactive waste.

Twenty-four samples from the U.S.G.S. core repository in Vancouver, Washington were selected from the lower 200 m of the hole, encompassing andesitic basalt that exhibits varying degrees of brecciation and alteration. The alteration mineral assemblage in the basalt was preliminary documented by Keith and Barger (1983) and is shown in Figure 14. The generally straight temperature gradient in the lower portion of the hole suggests conductive thermal conditions, so that the Newberry basalt flows are low-permeability layers that inhibit vertical fluid flow. Some horizontal fluid flow probably occurs along flow-top breccia zones, indicated by the strongly altered brecciated zones in the core.

Preliminary whole-rock gamma spectrometric analyses of U, Th and K in core from the lower 200 m of Newberry 2 are plotted in Figure 15. A general decrease of U and Th with increasing depth in the basalt is evident, and appears to be independent of the degree of alteration. This decrease may be attributed to more prevalent oxidizing conditions at depth, evidenced by the increasing scarcity of sulfide minerals and appearance of sulfates. However, a definitive explanation for this variation awaits detailed petrography to determine more accurately the alteration mineralogy; radiography to determine the mineral association of these elements; and, ultimately, analysis of fluid samples to determine Eh and pH conditions at depth.

CONCLUSIONS

In some contact zones between intrusives and gneissic, tuffaceous and basaltic country rock, migration of elements of interest in radioactive waste isolation has been confined to within a few meters of the contacts. The apparent lack of movement of radioelements and absence of appreciable redistribution of them, either in response to the conductive thermal regime at Eldora, Colorado or to the convective hydrothermal system at Platoro, Colorado is attributed primarily to the sites of the radioelements in accessory minerals. In contrast, the apparent mobility of uranium in the groundwater in the Stripa quartz monzonite and in response to a one-year heater experiment at Stripa, is based on the principal locus of U in chloritic fracture-filling material, more readily attackable by the moderately oxidizing groundwater.

The apparent depletion of U with depth in basalt at Newberry, Oregon is also probably attributable to oxidizing conditions.

Investigation of present-day active hydrothermal systems, where temperatures approximate those expected in the near-field of a repository, would disclose the distribution of elements in rocks and fluids and the associated mineral assemblages in conditions most analogous to repository environments. Calculation of aqueous chemical species using water-rock equilibration codes, substantiated by such observations, would help define the source terms for prediction of radionuclide transport from waste canisters into and through their encompassing hydrologic systems.

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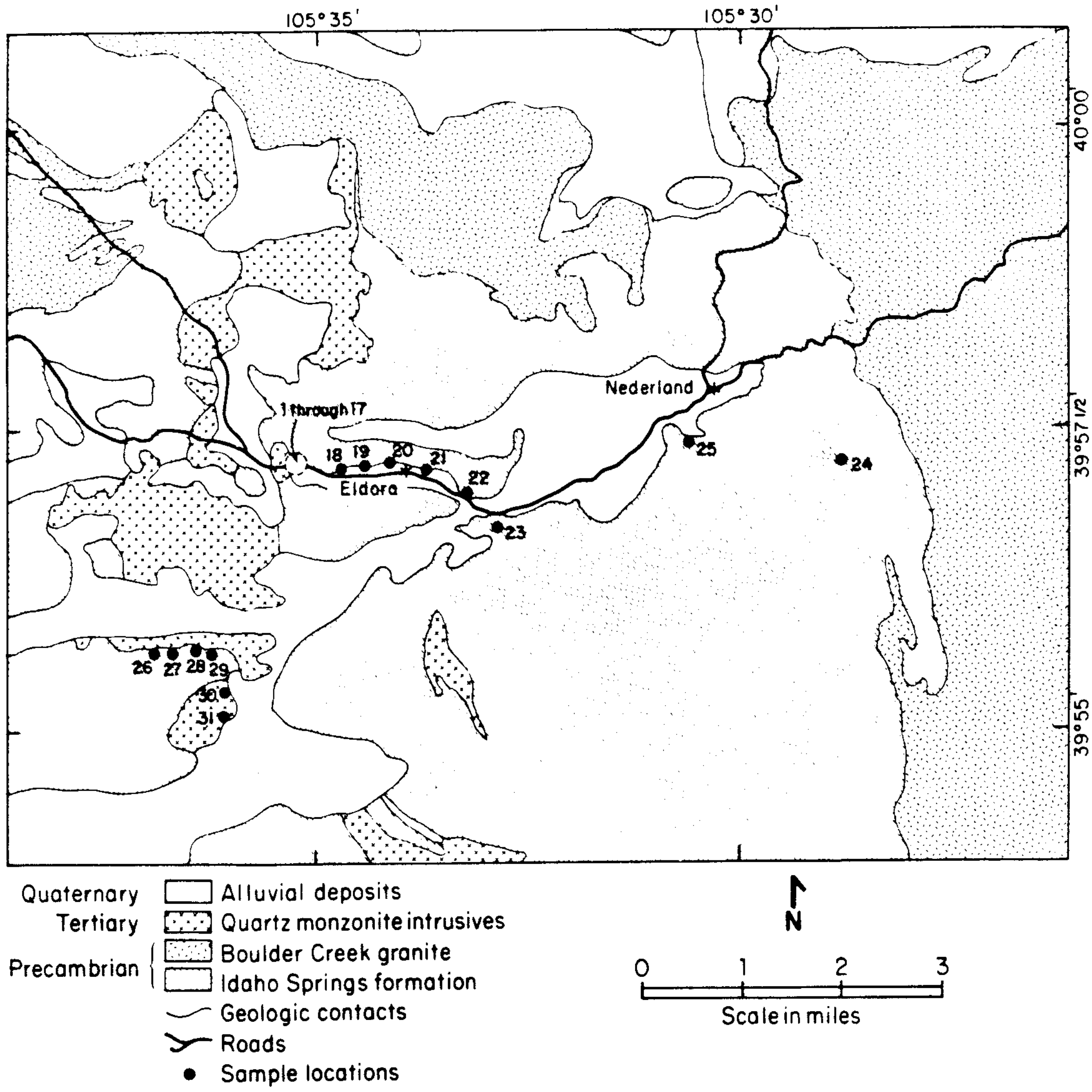
Table 1. Mean radioelement contents of rocks in the Stripa region.

Rock	U(ppm)	Th(ppm)	K(%)	Th/U
STRIPA QUARTZ MONZONITE				
Surface	27	33	4.6	1.1
Underground	37	29	3.9	0.8
LEPTITE				
Surface	3.3	12	3.1	3.6
Underground	5.4	18	2.8	3.9
REGIONAL GRANITIC ROCKS	18	27	5.2	2.4
REGIONAL METAMORPHIC ROCKS	6.1	15	2.5	2.6



XBL 817-3377

Figure 1. Simplified geologic map (after Hart, et al., 1968) showing sampling locations in the Eldora Stock-Idaho Springs Formation, Colorado.

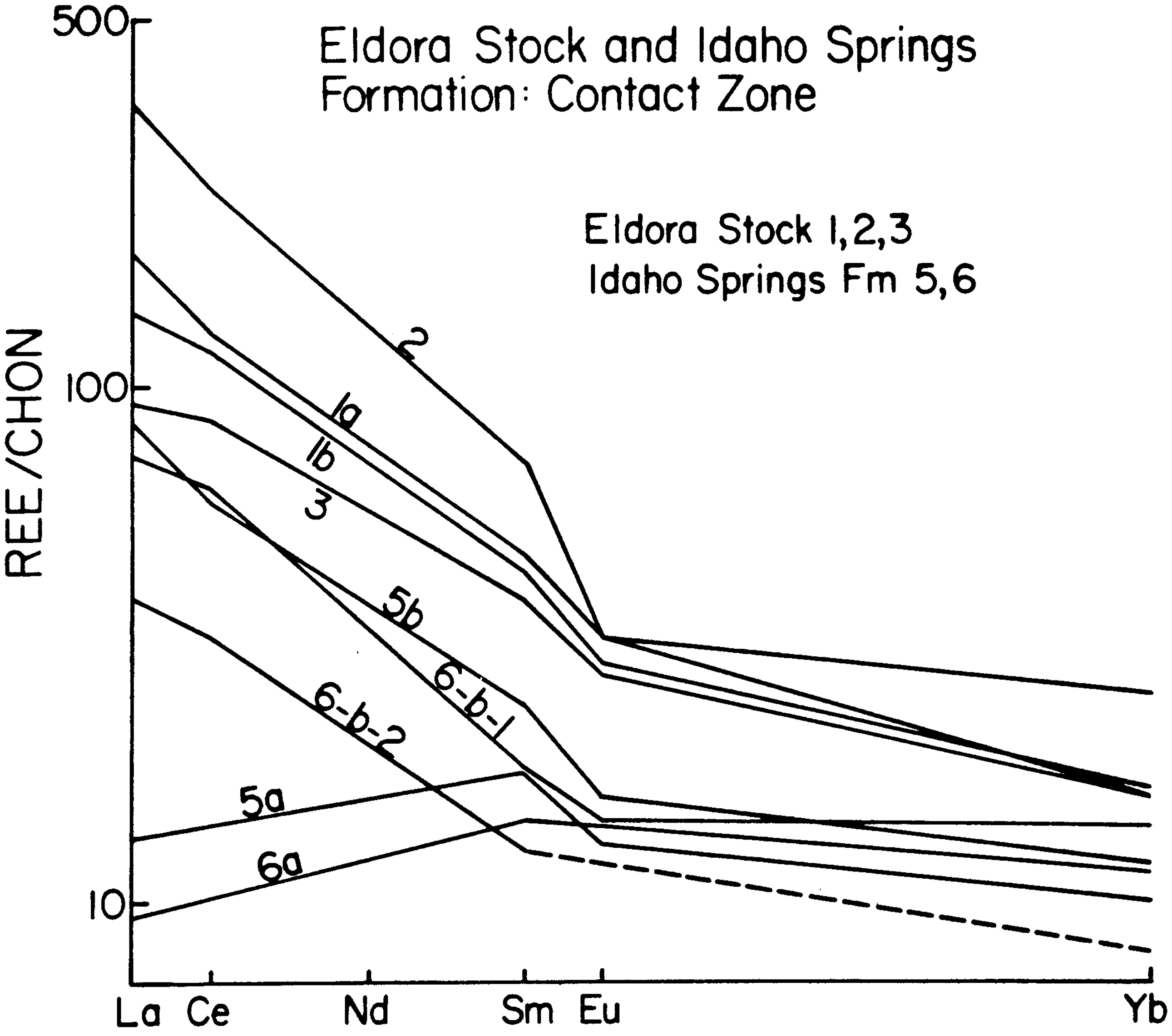


Figure 2. Rare earth element distribution plots for Eldora stock (Nos. 1a, 1b), Idaho Springs Formation (5a, 5b, 6a, 6b), and mixed samples (2, 3).

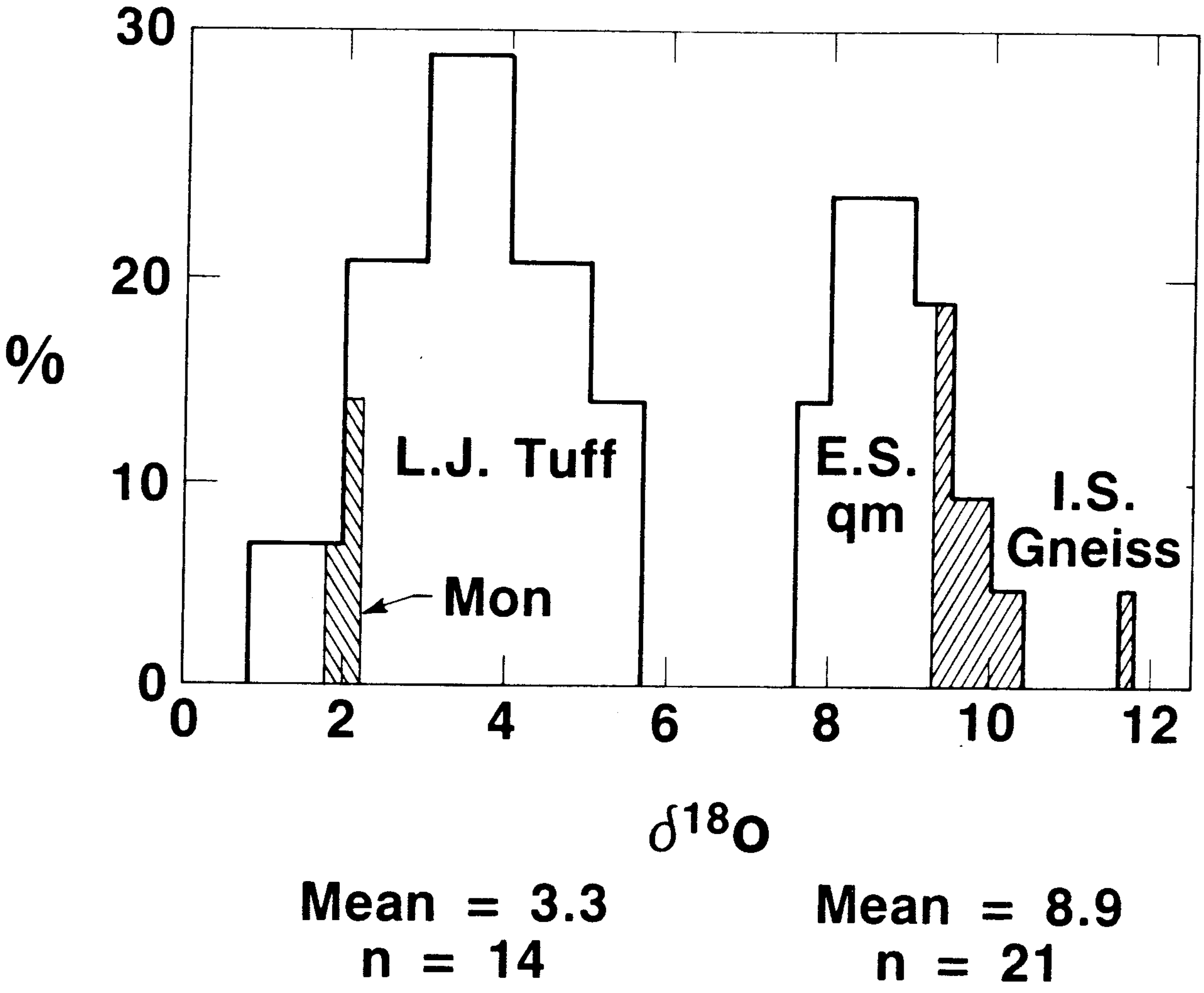


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Figure 3. Frequency distributions of $\delta^{18}O$ from the contact zones investigated at Eldora and Platoro, Colorado.

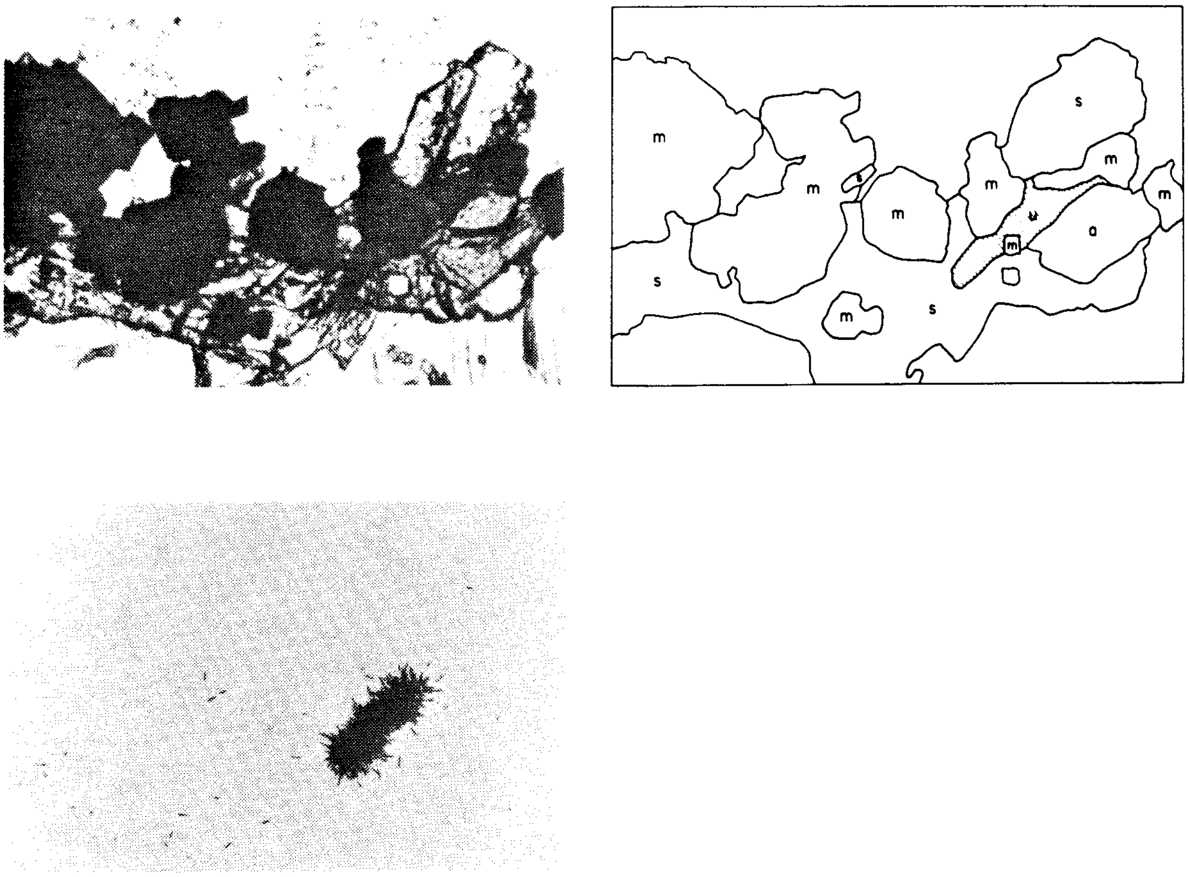


Figure 4. Uraniferous mineral, with dense association of fission tracks, from quartz monzonite of Eldora Stock adjacent to contact with country rock. Sparser fission tracks are associated with sphene. Plane-polarized light. (u-uraniferous mineral; s-sphene; m-magnetite: a-allanite; d-diopside; h-hematite. Lighter areas are feldspars and quartz).

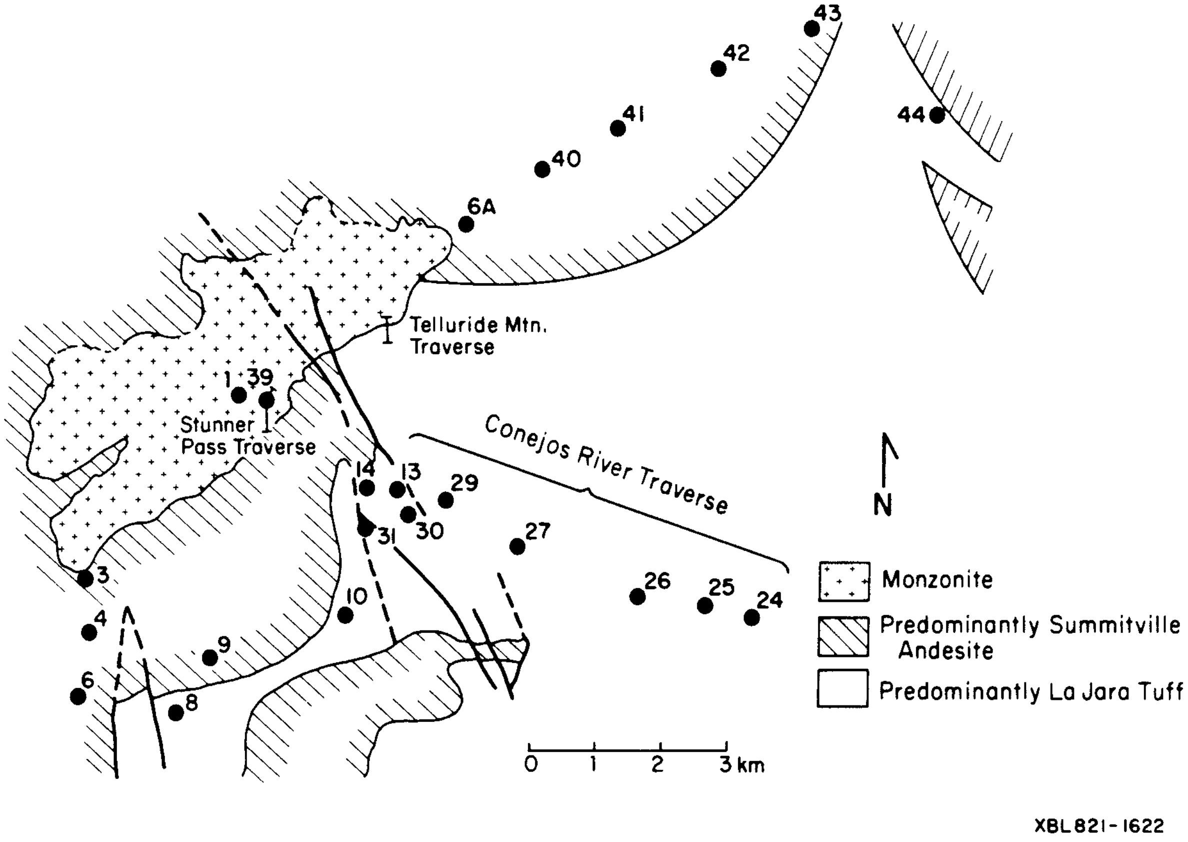
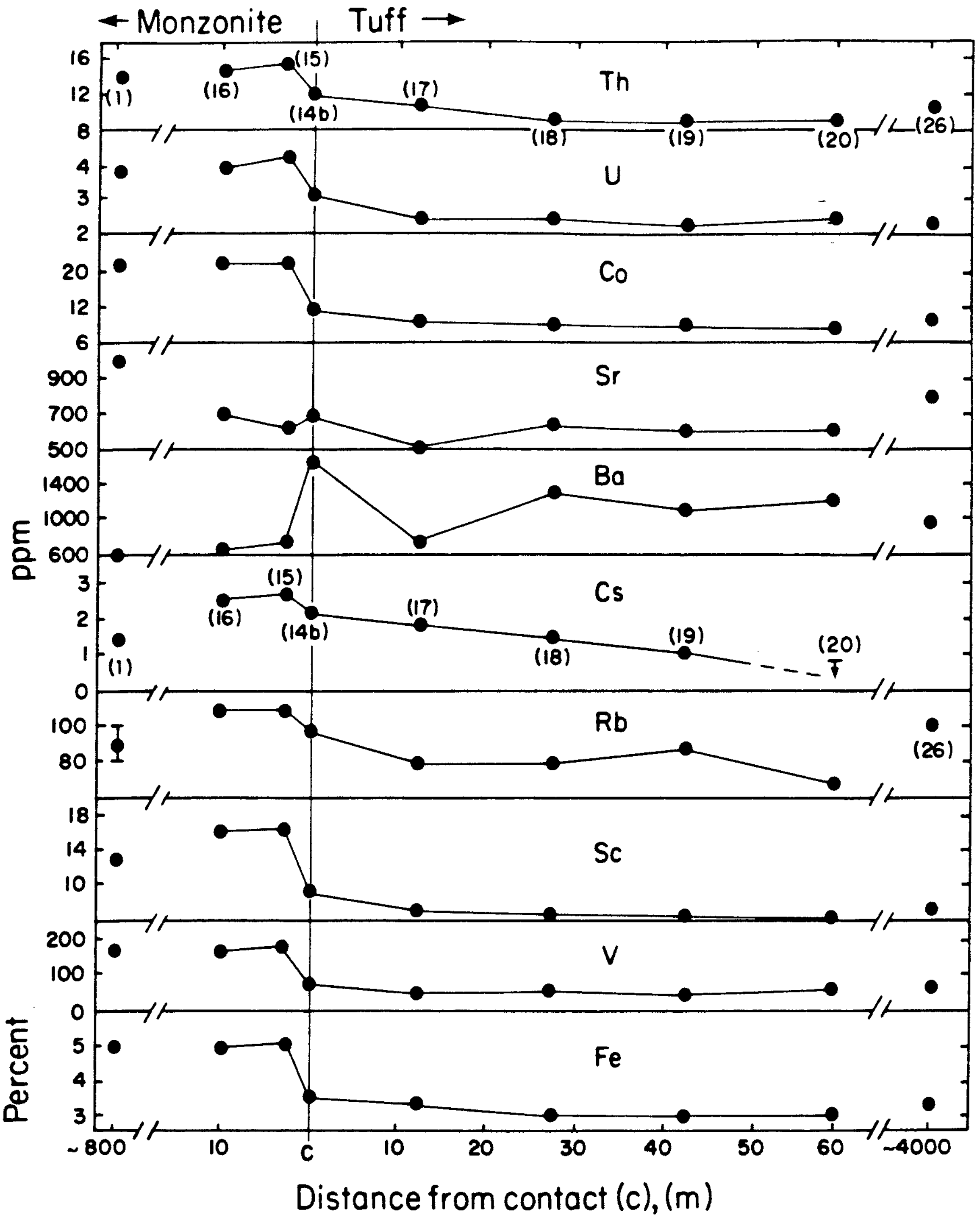
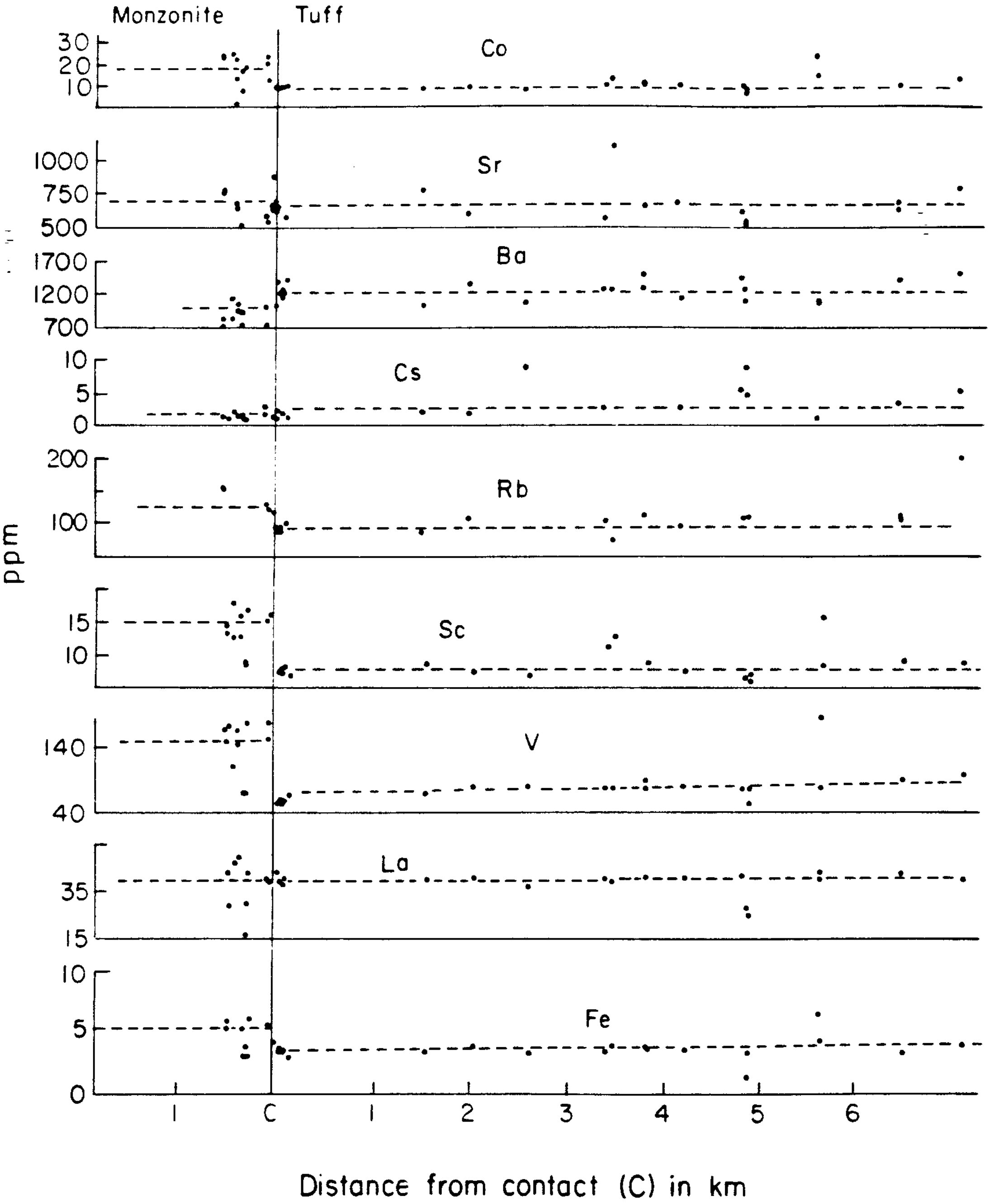


Figure 5. Simplified geologic map of the Platoro area, Colorado, showing sampling traverses in monzonite, tuff and andesite.



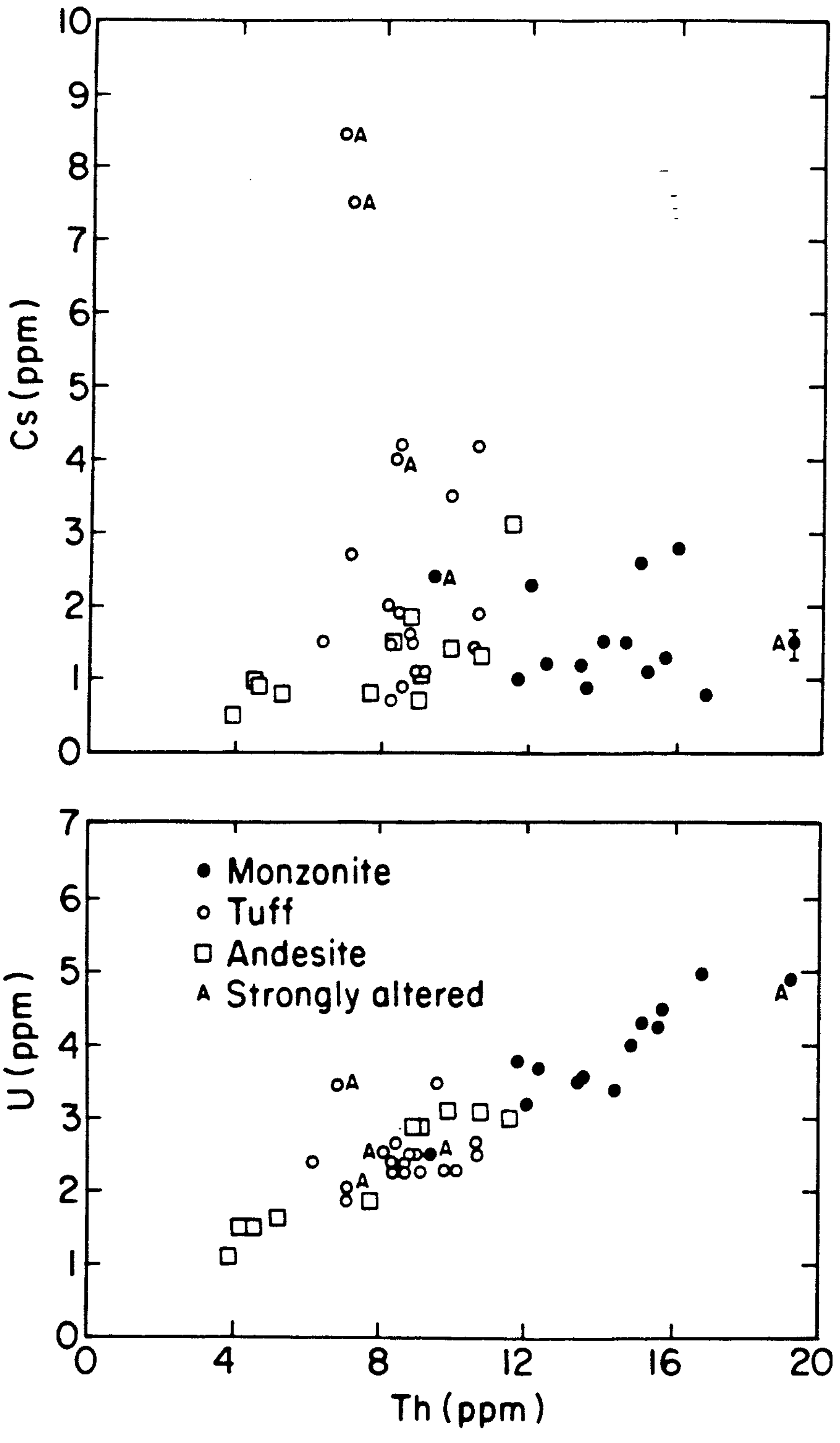
XBL 828-2325

Figure 6. Element variations across the contact between monzonite and tuff, Telluride Mountain traverse, Platoro area, Colorado.



XBL 8211 – 7339

Figure 7. Element variations with distance from the contact between monzonite and tuff, Platoro area Colorado.



XBL831-1663

Figure 8. Cesium and uranium versus thorium in strongly altered and less altered tuff, monzonite and andesite of the Platoro caldera.

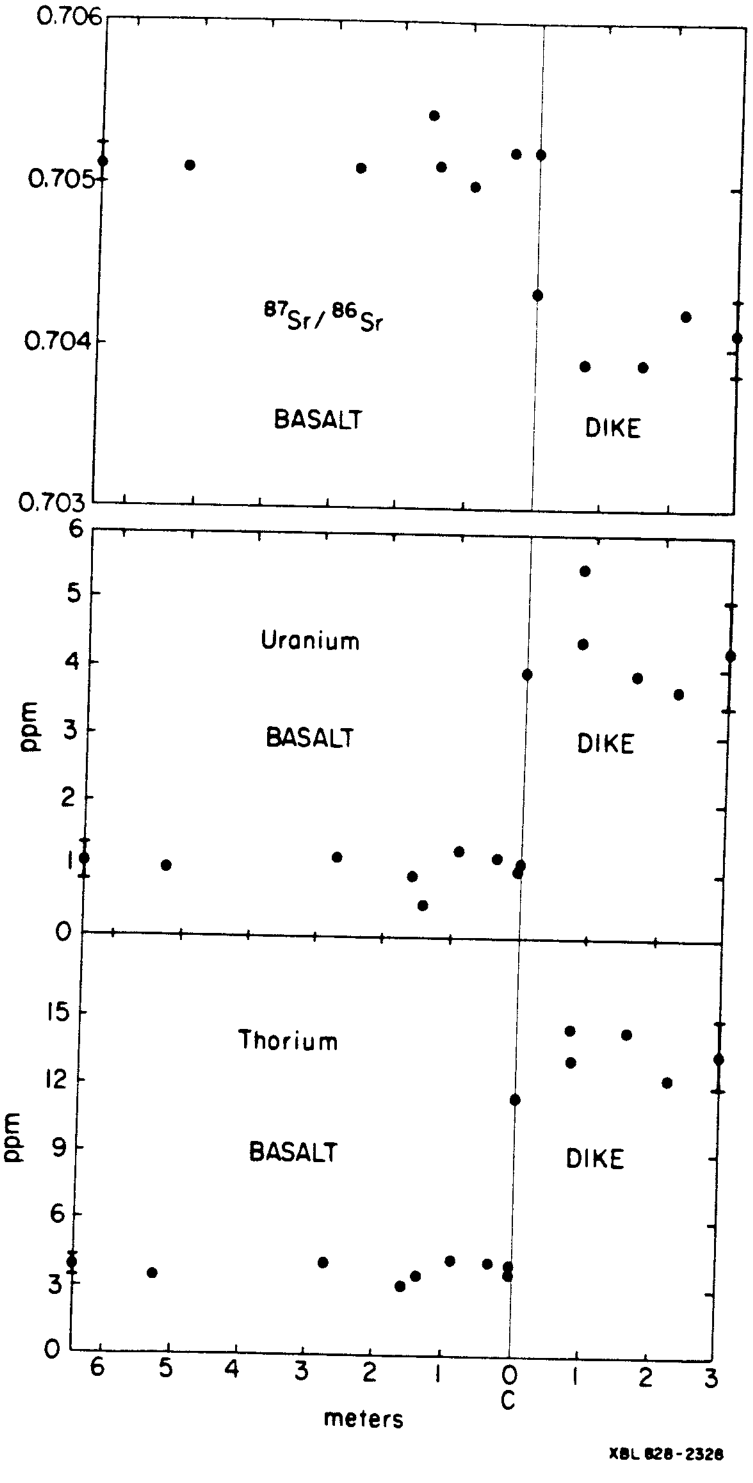
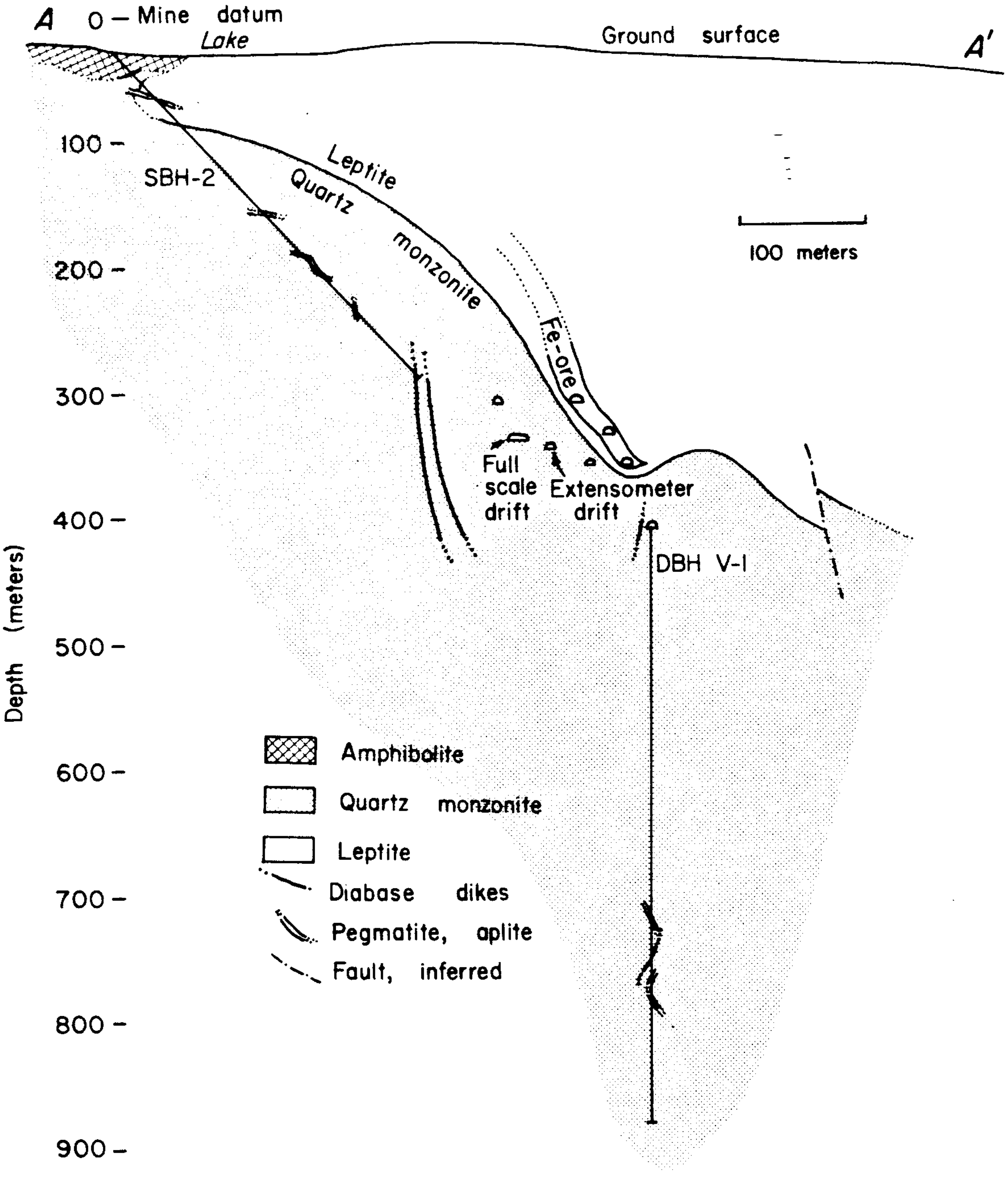
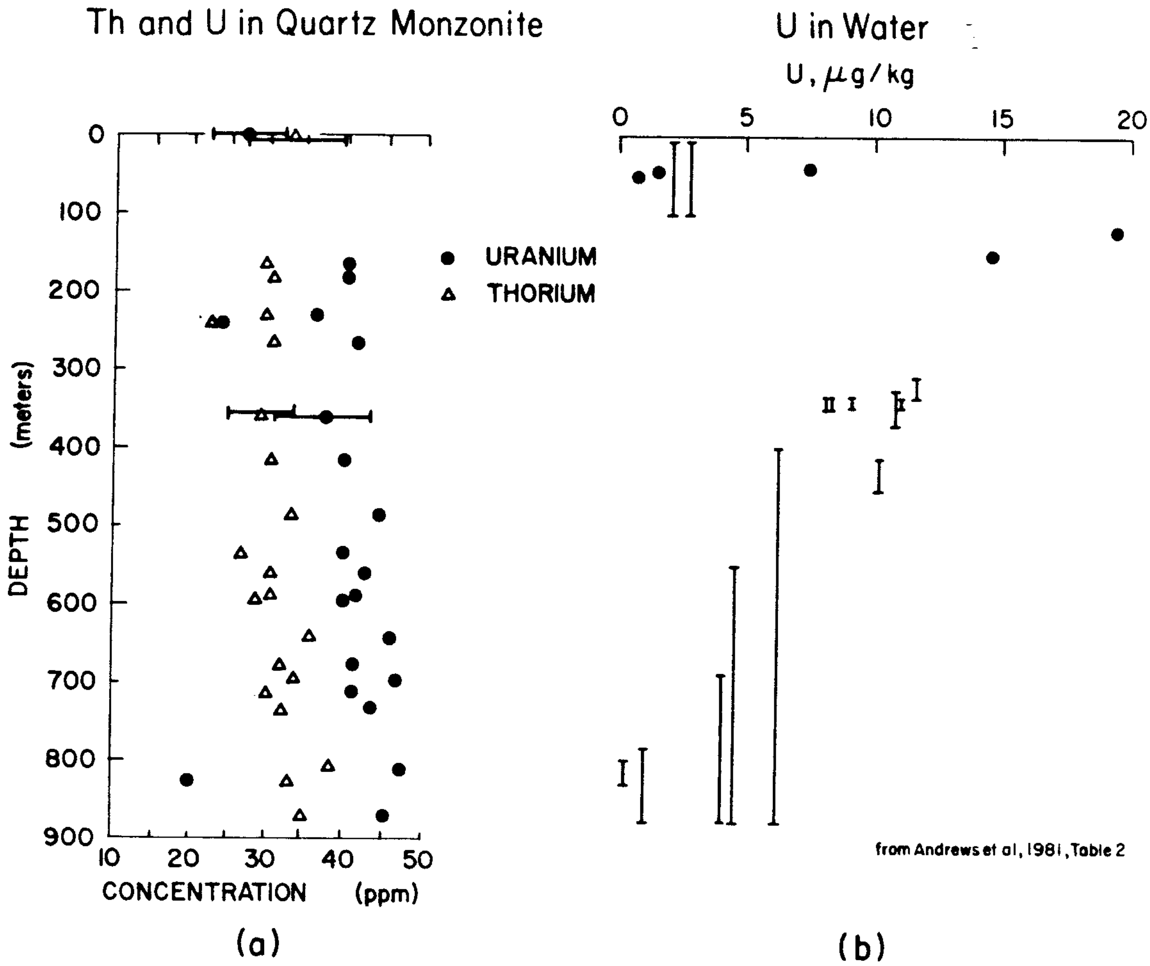


Figure 9. Strontium isotope ratios, uranium and thorium in rhyodacite dike and basalt, quarry on Hood River, Oregon.



XBL 812-8006

Figure 10. Vertical cross-section through the Stripa experimental area.



XBL 821-1607

Figure 11. Distribution of Th and U in rock and U in groundwater at Stripa, Sweden. Vertical bars represent water samples from varying depth intervals (from Andrews et al., 1982).

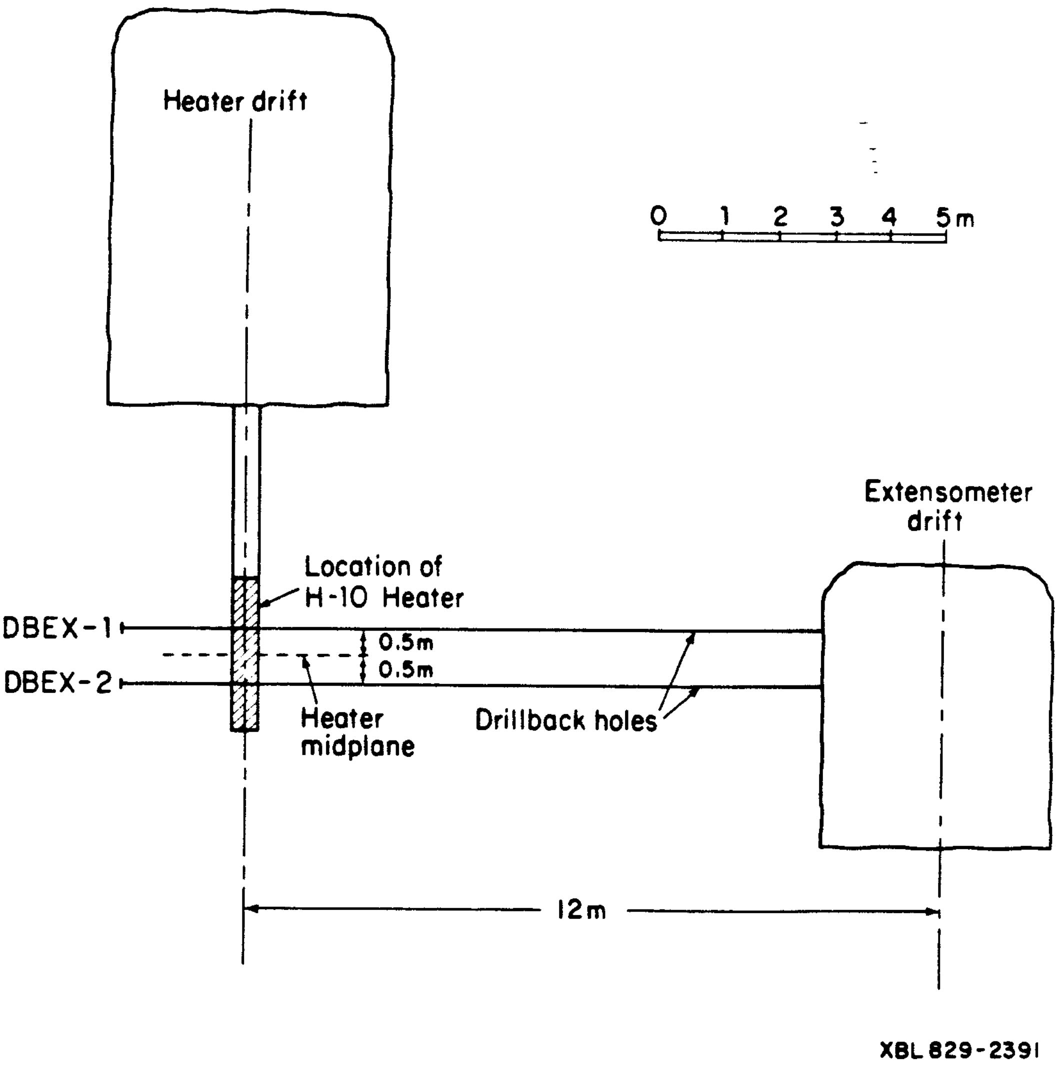


Figure 12. Vertical cross-section through the H-10 heater hole and the heater and extensometer drifts, Stripa experimental facility, showing the location of drill-back holes.

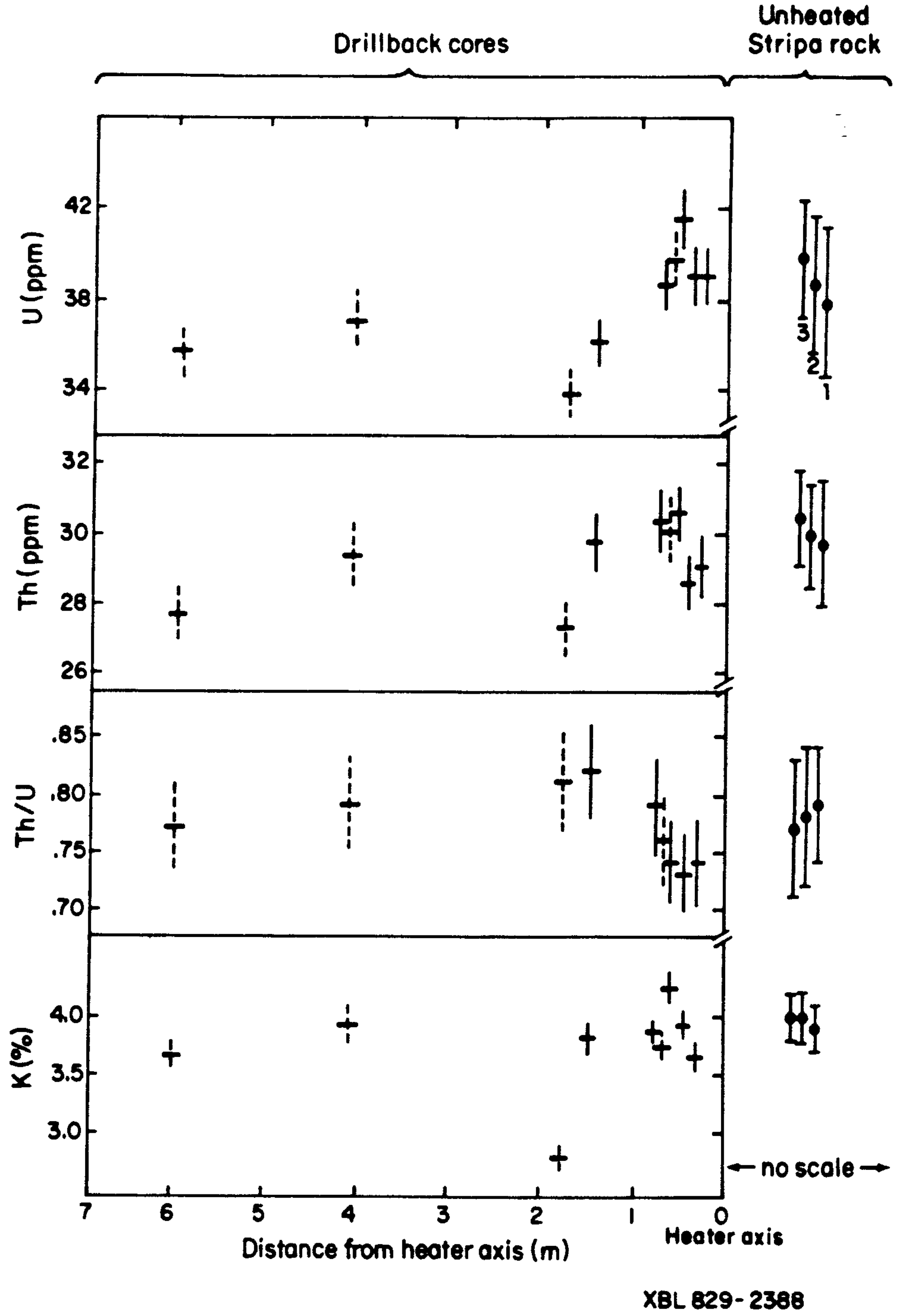


Figure 13. Variation of U, Th, and K with distance from the H-10 heater and comparison with analyses of unheated Stripa rock.

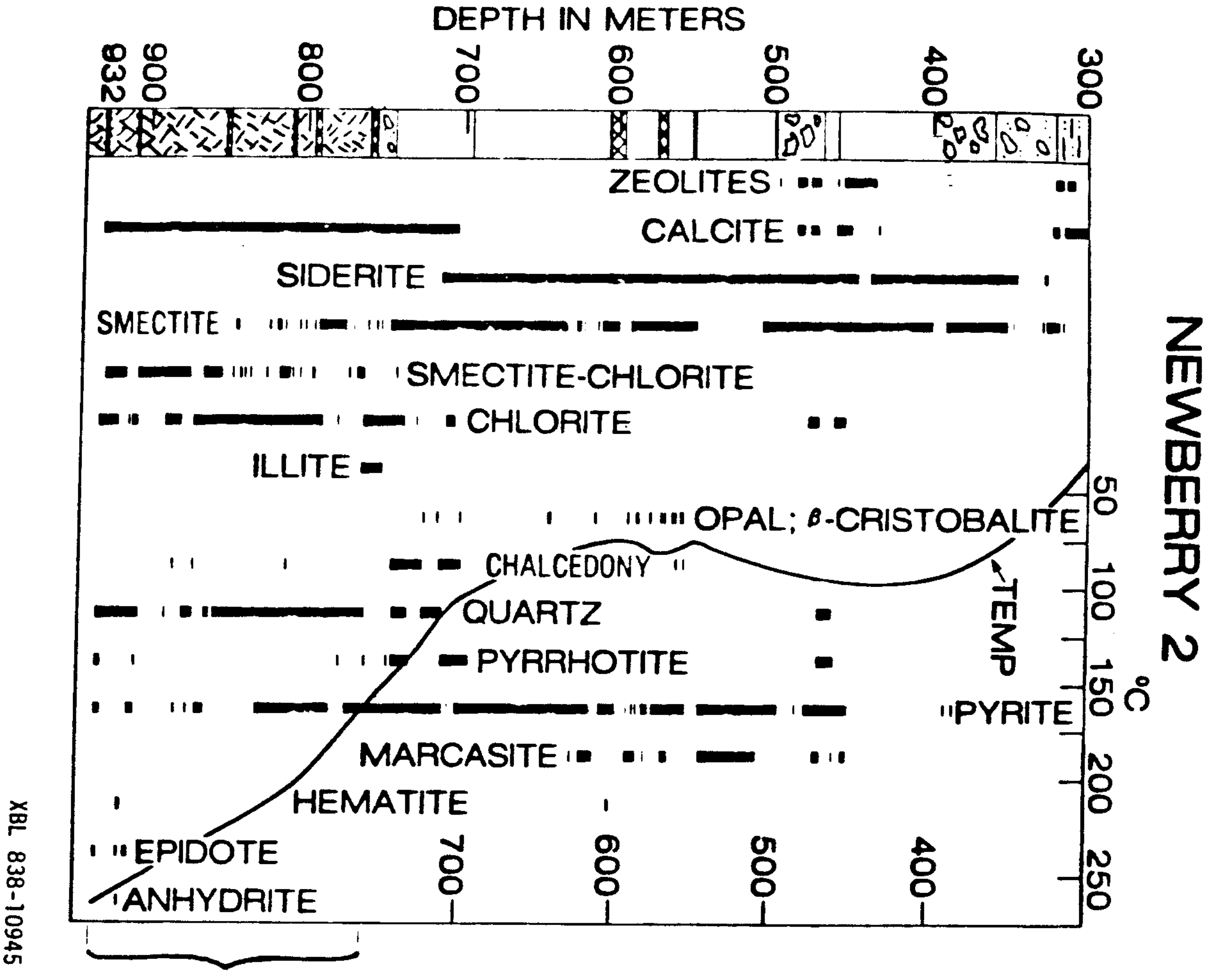


Figure 14. Preliminary observations of the mineralogy in the Newberry 2 hole, Oregon (Keith and Barger, 1982). The bracketed basaltic zone in the bottom portion of the hole indicates the extent of our samples.

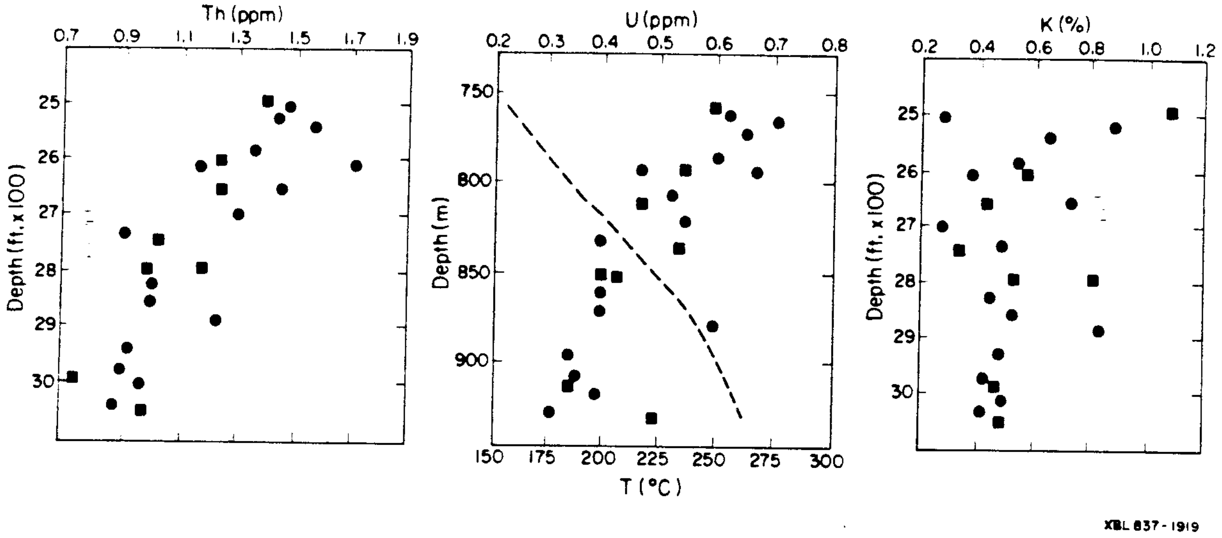


Figure 15. Variation with depth of radioelements in basalt of the Newberry 2 core. The most strongly altered samples are designated by squares. The dashed line is the temperature gradient determined by bottom-hole measurements during drilling (Macleod and Sammel, 1982).

NATURAL ANALOGS FOR RADWASTE DISPOSAL: ELEMENTAL MIGRATION IN IGNEOUS CONTACT ZONES

D.G. Brookins

Department of Geology, Univ. of New Mexico, Albuquerque, NM 87131

ABSTRACT

Chemical studies of various igneous rocks intrusive into many different rocks have been examined to see if elemental transfer has taken place. Systems examined include granite intrusive into shale and siltstone, basalt intrusive into granodiorite, diorite, rhyolite and dolomite, diabase intrusive into rhyolite and extrusive over arkose, rhyolite extrusive over basalt, lamprophyre intrusive into evaporites, monzonite intrusive into tuff and andesite, and quartz monzonite intrusive into metasedimentary rocks. The mechanism for elemental transport in these systems is due in part to diffusion and in part to chemical reaction between intrusive and host rocks. Evidence for transport of elements from intrusive into intruded rocks is noted for several elements. In some cases, the distribution of some elements is mineralogically controlled, and variations in Co, Cr, REE, Ni, Cu, Zr, Mn, Ti, Rb, Sr, U, Th can be attributed to more-or-less specific reactions. In a few contact zones, there has been limited migration of Cs, but usually only within 0.5 to 1.0 meters of the igneous rock contact. Thermal effects of the igneous intrusions are to reset some mineral isotopic systematics (loss of ^{40}Ar, redistribution of ^{*87}Sr, ^{18}O), but otherwise the whole rock chemistry usually remains unchanged. Collectively, the data for elemental behavior in the vicinity of the igneous contacts studied show that elemental migration of redistribution is often restricted to within 0.5 to 1.0 meters of the contact, thus suggesting that for hypothetically stored radioactive waste canisters, emplaced at much lower temperatures, little if any elemental transport would take place in the event of breaching of the waste package.

IGNEOUS CONTACTS AS ANALOGUES FOR BURIED RADWASTE

The disposal of HLW calls for emplacement at depth of the HLW package in geologic media such as tuff, basalt, evaporites, granites and possibly other rocks (See Brookins, 1984). The HLW package will be heat producing due to radioactive decay, and in the United States of America plans call for thermal loading such that the temperature is equal or less than about 250°C. This temperature is a few to several hundred degrees celsius below crystallization temperatures for igneous rocks, and the dimension of a typical waste canister is on the order of 0.3 m diameter and 3 m length, many orders of magnitude less than the dimension of an igneous pluton of moderate size. It is further presumed that the waste package can only be breached and radionuclides released by events requiring the presence of water. When first buried and sealed, the waste package will be encased in a low temperature, dry medium. This environment will possess low oxidation potential by design. Most media will be below the water table, hence such media are by definition saturated with respect to water, and the "dry" surroundings to the HLW package will be subjected to encroachment of some water, probably within one hundred years or so after emplacement.

Ideally one would like a laboratory study that would allow consideration of waste package - medium interaction at low temperature and over several tens to possibly a few thousands of years. Since this is impossible, then laboratory studies must, by definition, be conducted under possibly atypical conditions in order to carry our such experiments in the shortest time which will give reasonable results. Typical leaching experiments, for example, commonly run from days to months and sometimes longer. After a few days to months the fraction leached is asymptotic to the time axis, and extrapolations to much greater times are based on this fact. While this approach is certainly necessary in order to conduct the experimentation, it is also questionable in that such things as phase changes, new complexes in solution, etc., may form at a considerable time under a natural setting. This would be missed in the experiments due to the short time factor. Hence one must look at natural analogs to attempt to address this and other time-temperature-fluid parameters.

Igneous rocks as analogs for the waste package are obvious choices. The suite of fission product, actinide and actinide daughter elements is present in most igneous rocks, and this is especially true for rocks of granitic composition, in which elements such as Cs, Rb, REE, Ba, U Th, Zr, Mo, Pb may be significantly enriched. If the intruded rock is compositionally more basic in composition, then a favorable chemical gradient between intrusive and intruded rock exists, and potential for elemental migration thus exists.

The use of igneous rocks as analogs for buried HLW packages is, however, exceedingly complex. In addition to the problem of extreme differences in temperature and dimensions, many smaller igneous bodies (i.e. narrow dikes) will cool rapidly while the HLW package cools more slowly. Yet dikes may possess a great content closer to that of buried radwaste than plutons. Further, the naturally occurring igneous rock may be impermeable, or else permeable, with the intrusive rock either impermeable or more or less or equal in permeability to the intrusive. These differences will, of course, be of most importance if the cooling of the intrusive body is by convection rather than conduction, although both conditions must be examined. Even in the absence of large scale convective systems about an intrusive body, the anhydrous nature of the contact zone in the intruded rock attests to some transport of water. In some cases (see discussion later in this report) this results in migration of intruded rock water into the igneous rock, often with concomitant transfer of some elements as well. In the case of a radwaste container, this can be interpreted to mean that the HLW package may act as a heat sink which might promote transfer of water (and possibly other constituents) from the intruded rock to the package. This will be addressed later.

The point to be stressed in this paper is the transfer of elements from one place to another in the contact zones of igneous rocks. Where such transfer occurs, and where it does not, will provide information on elemental behavior in natural rock systems. Further, in some cases it may be possible to place time-temperature values on long-time elemental transfer, and then to compare such information with the extrapolations of laboratory results.

Most studies conducted in contact zone aureoles are aimed at a precise mineralogic and phase rule interpretation, with careful estimation of temperature, compositional changes in minerals, and related items. Only somewhat infrequently do investigators look into the problem of possible elemental transfer from intrusive to intruded rock of vice versa. Yet the authors has identified from the literature more than one hundred such examples (Brookins, ms. in preparation), a few of which will be summarized in the report to follow.

In most of these cases, traverses have been made across the intrusive contacts, but commonly only one or two traverses per occurrence was conducted. This is unfortunate for reasons to be outlined later. In the cases discussed herein, no attempt is made to explain the chemical trends in terms of rock permeability, fracture patterns, thermal characteristics, thermal diffusivities, and related parameters. Such studies must be conducted for specific sites with analogue question in mind.

COOLING OF INTRUSIVE BY CONDUCTION

In this and following discussion, it is assumed that the shape of the intrusive body is that of a nearly vertical sheet. This assumption is satisfactory for many dikes and sills, and may be adequate for elongated plutons as well. In the simplest case, it is further assumed that the conductivity of the intrusive body is about equal to that of the intruded rock. Jaeger (1957, 1959, 1961, 1964) has summarized his work on this subject in detail. and Winkler (1979) has presented a slightly abridged version of the problem as well. Winkler (1979) notes that the temperature contours about an intrusive body are symmetric, and mineral zonation about an intrusive contact will also be symmetric. When the geometry of the intrusive body is irregular, obviously the temperature profiles about the contact will also be complex. Length of cooling of bodies meeting the criteria of equal conductivities in both intrusive and intruded rocks can be estimated (Jaeger, op. cit.). For the maximum temperatures, the length which this temperature will be maintained is proportional to the square of the thickness of the intrusive body; and given by (Winkler, 1979) 0.01 D^2 where K is the thickness of the intrusive body. For D=1 m, the maximum temperature is maintained for about 3 days, for 10 m about one year, for 100 m about 100 years, and for 1,000 m about 10,000 years.

With respect to the analog applicability of intrusive bodies that cool by conduction only, it is obvious that elemental migration in response to the intrusive well, in essence, be diffusion controlled. Further, such migration must be quite limited. Early studies on K-Ar and Rb-Sr systematics of contact zones of conductively cooled igneous rock bodies (Hart, 1964; Westcott, 1966; Hanson and Gast, 1967) show that there is pronounced loss of radiogenic ^{*40}Ar and ^{*87}Sr from certain minerals as a function of distance from the intrusive contact. Yet subsequent studies show, at least for the Eldora stock in Colorado, that whole rock Rb-Sr systematics, and therefore ^{*87}Sr, were unaffected. Thus the ^{*87}Sr lost from Rb-rich minerals such as biotite was incorporated into other phases (plagioclase, etc.), and on a scale of microns to millimeters. Thus in the case of narrow dikes, despite an initially high temperature and a possible favorable chemical gradient between the molten rock and solid, in the absence of a fluid phase, the temperature is not maintained for a sufficiently long period to promote elemental migration. This probably explains the total lack of any elemental or isotopic migration between rhyolite dike and Wanampum basalt reported by Brookins et al. (1984). In an unusual case, that of a lamprophyre dike intrusive into evaporites in southeastern New Mexico (See Brookins, 1981), local partial melting of halite-mixed salts occurred along the contact, thus providing a fluid medium for possible elemental migration. This will be discussed later.

COOLING BY CONVECTION

Many igneous bodies cool by convective means. When the intruded rocks are permeable, they will contain appreciable amounts of water, and this water is heated in response to the crystallizing magmatic body, with convection of the meteoric water occurring at the same time. The intruded rock may be less or more permeable than the intrusive rock. In the case of a more permeable intrusive rock than intruded rock, favorable chemical gradients may exist for potential transfer of remobilized elements into the intrusive rock and the favorable gradient is from the intrusive into the intruded rock. The thermal regime of convectively cooled igneous rock systems is complex. Parmentier and Schedl (1981) have examined the problem in detail. They argue that the distribution of isotherms about various hypothetical intrusions with different conditions for permeability and open versus closed circulation. What is most important about their work is that the isotherms are irregularly distributed (although entirely predictable from the cooling models invoked). Yet if elemental migration is taking place in response to both heat and availability of an aqueous medium, then the direction of the migration can be determined. In natural rock systems, such as the Alamosa River stock, Colorado (See Brookins et al., 1983), the opportunity to test for convective-induced elemental migration is possible. This will be discussed below.

In the case of a buried radwaste package (waste-form plus container ± overpack), it is difficult to fully assess the role of convective cooling. Certainly the ratio of available water to waste package container is great compared to a groundwater-igneous stock system, yet the thermal effects about the waste package will be many orders of magnitude lower than that for the natural system. Hence no large scale convective system for the generation of typical hydrothermal fluids (or geothermal fluids) exists. Rather the effect is for minimum heat transfer to the surrounding geologic medium, with only local sources for reaction, and no large scale transfer of matter will probably occur.

REPRESENTATIVE EXAMPLES

Case 1: Eldora Stock Intrusive into Idaho Springs Formation, Colorado

The 60 Ma. Eldora stock, a quartz monzonite, intrudes the Precambrian schists and gneisses and pegmatites of the Idaho Springs Formation near Nederland, Colorado. This area is the subject of the classic work of Hart (1964) for mobility of ^{*40}Ar and ^{*87}Sr from mineral systems due to heat of intrusion, and was chosen for analog work because of the preliminary control. The studies of elemental migration are summarized by Brookins et al. (1981, 1982). Cooling of the stock was by conduction, and no elemental transfer from stock into intruded rock was suggested past the immediate 0-2 meter contact zone where there is evident some apophyses of stock into the metamorphic rocks. Even in the cases where ^{*40}Ar and ^{*87}Sr were lost from minerals, the ^{*87}Sr was retained in the whole rock samples, indicating movement of $*^{87}Sr$ only on a scale of microns to millimeters. Since the cooling time is estimated (Hart, 1964) to be between 10^5 and possibly 10^6 y., this attests to the fact that elemental transport in the absence of a convective fluid medium is minimal. This is important because at the time of intrusion (approximately 60 Ma.) it is safe to assume that the Idaho Springs rocks were saturated with water, but, due to its low permeability och porosity, even such a drastic event as the intrusion of the Eldora stock was insufficient to set up flow of this water.

Case 2: Alamosa River Stock Intrusive into Tuffs and Andesites

The Alamosa River stock, a monzonite, intrudes tuffaceous and andesitic volcanic rocks of the Platoro Caldera complex, Colorado. This site was chosen for analog study because the work of Williams (1981) had shown the presence of a large convective system around the stock, based on oxygen isotopic studies, and some preliminary K-Ar data which indicated that a 0.5 to 1.5 Ma. time of hydrothermal constraint could be placed on the rocks as well (See Brookins et al., 1983). Detailed study of two traverses from well within the stock into the tuffaceous rocks were conducted, and part of the data are shown as Figure 1. Significantly, elemental migration is again indicated only in the few centimeters to meters closest to the contact. Hence even the presence of the very long hydrothermal event was possibly insufficient to cause widespread elemental migration.

More important, though, is the potential of this site to yield more interesting information. From the preliminary work, and the defining of areas of well time-documented hydrothermal activity, it should be possible to obtain more fine detail information for elements showing the limited migration. Hence it may be possible to quantify the amount of elemental migration over a time-temperature framework of 10^5 - 10^6 y. and 500° - 800°C and then extrapolate to t=0 and compare with laboratory measured leach rate information. Despite many apparent pitfalls, this site has the potential for obtaining long time, high temperature data which are badly needed in assessing radwaste analogs and long-term radwaste behavior in rocks.

Case 3: Lamprophyre Dike Intrusive into Bedded Evaporite

Brookins (1981) has reported on trace element studies of a lamprophyre dike intrusive into the Salado formation halite of the WIPP site area. This dike was emplaced at a temperature of about 850°C some 34 Ma. ago (Brookins, 1981). Loehr (1979) made a study of recrystallization of clay minerals in the halite as a function of distance from the contact. She found that within ten feet of the contact, the normal clay sequence was observed, and isochemical recrystallization occurred inward toward the dike. Only in the immediate contact zone of a few centimeters were there any pronounced effects; i.e. partial melting of halite with new salts formed. A new generation of polyhalite formed in the contact zone, which is of interest as this mineral contains two structurally bonded water molecules. The source of this water is unknown, but must have originated from within that zone as fluid inclusions less than two meters away give normal crystallization temperatures (Loehr, 1979). No large scale migration of fluids toward the dike is evident, and no apparent transfer of elements from the dike into the evaporite is observed (Brookins, 1981), including U, Th, REE, Rb, Sr, Cr, Ni. Finally, while time-temperature parameters are not clear, the dike does thick and thin considerably such that an estimated cooling time of one year or so may be estimated (Brookins, unpub.). The polyhalite from the contact zone yields a date of 21.4 Ma., which at first might suggest post-dike waters using the dike - evaporite interface as a conduit. Brookins (1982) has shown, however, that this apparently young age is due to normal loss of radiogenic ^{40}Ar, and corrected age of 30 Ma. is argued. Some of the detail is shown in Figure 2.

OTHER STUDIES

The writer is in process of compiling all available information on intrusive contact zone studies relevant to radwaste natural analogs. To date, relatively few analog studies of this type have been specificially conducted. Joint UNM-LBL study has been conducted in the analog area (See Cases 1, 2; and Brookins et al., 1984) and new projects proposed. In addition, Laul and Papike (1981) have reported on the intrusive effects of granite on silt-carbonate rocks, and Laul et al. (1984) on pegmatite intrusive into amphibolites and other country rock. While some chemical mobility is argued from these studies, the authors have not unequivocally demonstrated their case and follow up work is needed. Numerous intrusive contact zones were examined by Dennen (1949) for major element chemical variations, and these same samples analyzed for their trace element contacts by Brookins and Dennen (1964). For cases including basalt dikes intrusive into arkose, granite, diabase, rhyolite; for granite intrusive into arkose and diabase, and for diabase intrusive into dolomite and rhyolite into basalt, the apparent chemical migration of elements has been limited to within a few fractions of microns to centimeters. Very little information was obtained on the cooling history of the intrusives, their permeabilities, and other important information, yet the data from these studies, as well as from over one hundred additional sources, suggest a lack of widespread elemental transfer due to igneous intrusions.

CHARACTERIZATION OF INTRUSIVE CONTACT ZONES FOR ANALOG STUDIES

In order to be useful for radwaste analog purposes, intrusive and intruded rocks must be characterized fully. It is important to clearly distinguish between conductive versus convective cooling histories, as well as to fully evaluate the relative permebilities of both intrusive and intruded rocks. Especially important is evaluating the paleopermeability of each rock, as the present day permeability, especially for slightly weathered rock, may be quite different from the original rock.

Preliminary oxygen isotopic studies allows reconnaissance evaluation of conductive versus convective cooling, as well as valuable information on possible directions favored for fluid flow in intruded rocks.

The mineralogy and complete chemistry of the rock should be characterized fully. Too often the failure to do this detracts from some studies. It is also of importance to conduct geochronologic studies in the rocks. This allows semiquantitative to quantitative assessment of the magnitude of some elemental transfer (i.e. Sr, Rb, Cs). For example, when it is proposed that Rb has migrated from intrusive into intruded rocks (See Laul et al., 1984), this can be easily tested by dating the rock in question by the Rb-Sr method. If the age of the rock is much younger than the age determined from samples far removed from the contact, then a case for Rb addition (or perhaps *Sr loss) can be made. If the first rock yields an age identical to the latter, however, then the proposed Rb migration has not occurred. The point here is that this is an easy matter to test by rock dating, and it is unfortunate that many workers ignore such isotopic studies.

Still further, the chemical-mineralogical characterization of the rocks should include microprobe data, primarily to determine where the elements of interest are located in the rocks. Should elemental migration have occurred, then in all probability there will be a concentration of the mobile elements along the peripheries of grains, etc. as opposed to the grain interiors. Subsequent leaching studies will also be much easier to understand with the availability of such data. For U-Th systematics, microradiography has also been shown to be an important tool for rock characterization.

Special focus must be placed on elemental-mineralogic abundances and distribution in fractures, alteration rinds on rock forming minerals, and in grain defects, as it is likely that these (and similar) zones in the rocks will house mobile elements regardless of source. Analytical techniques are now sufficient to allow the detailed analyses necessary to characterize such materials.

Where possible, fluid inclusion work should be carried out to unravel the complex temperature profiles in igneous contact zones. Initial attempts at analogue work, including many of the data reported in this note, are necessarily of a survey nature. Now, however, it is equally as necessary to more fully characterize the rocks to attempt to allow better comparison of laboratory versus field data, in turn to better our knowledge of predictions of HLW in geomedia.

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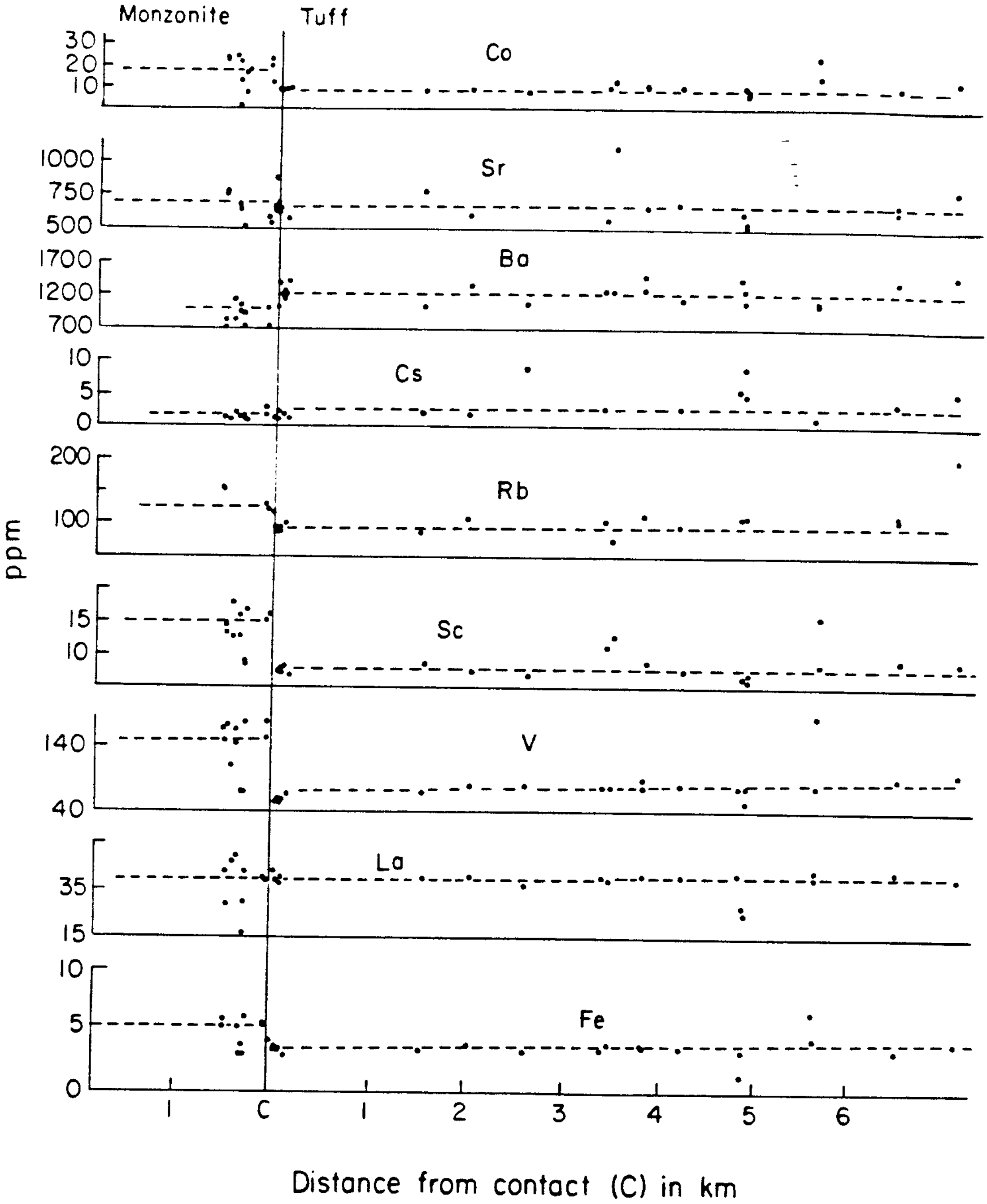

Figure 1. Element variations with distance from the contact between monzonite and tuff, Platoro region, Colorado.

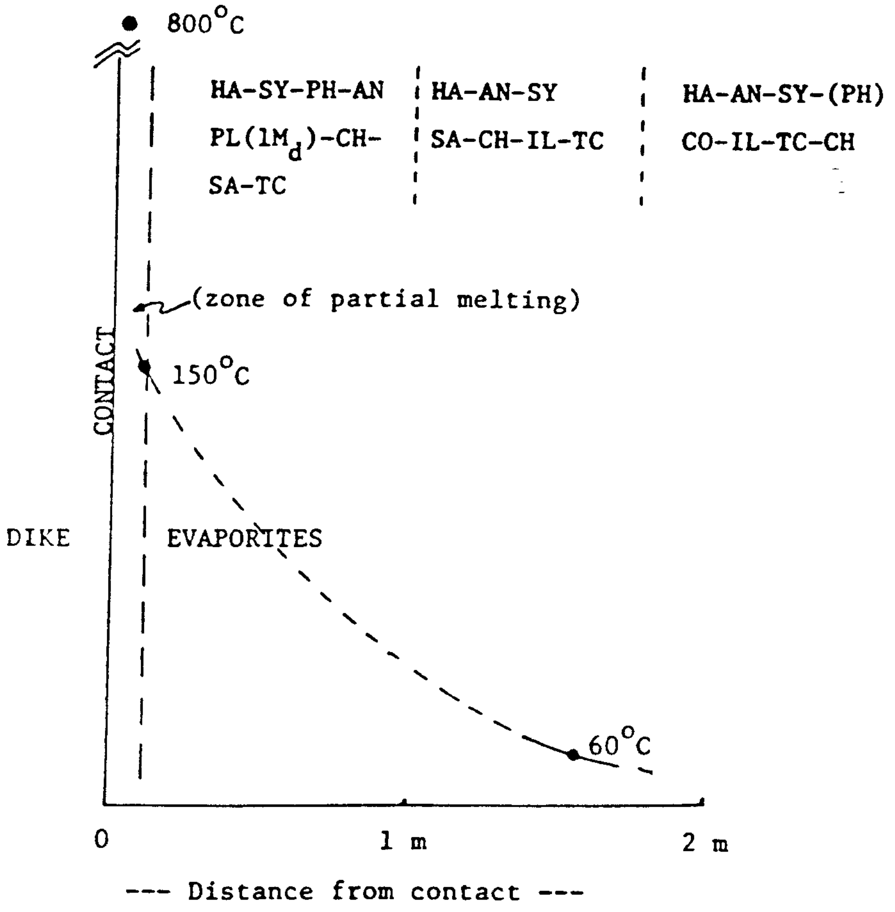

Figure 2. Temperature profile and mineral assemblages for lamprophyre dike intrusive into bedded evaporites (HA=halite, SY=sylvite, PH=polyhalite, AN=anhydrite, PL=phlogopite, CH=chlorite, SA=saponite, IL=illite, CO=corrensite, TC=talc).

INVESTIGATIONS OF THE EMPIRE CREEK STOCK, MONTANA, AS A POSSIBLE ANALOGUE TO A NUCLEAR WASTE REPOSITORY

H.Y. Tammemagi and B. Haverslew

RE/SPEC LTD., 005-4616 Valiant Drive, N.W., Calgary, Alberta T3A 0X9, Canada

ABSTRACT

A case history of a mild geothermal area in western Montana, USA, has been compiled to learn about the effects that long-term heat generated by a repository containing spent nuclear fuel might have on the surrounding rock mass. The results of previous geological, geophysical and hydrogeological studies are summarized. In addition, extensive petrological studies have been undertaken on core samples obtained from a 2 km deep borehole drilled into the Empire Creek Stock. These include a detailed petrographic study, x-ray diffraction analyses, scanning electron microscope and electron microprobe analyses, porosity and permeability measurements, oxygen isotope analyses, uranium disequilibrium analyses and K-Ar age determinations. The implications to deep burial of nuclear wastes are discussed.

INTRODUCTION

An accurate prediction of the long-term performance and safety of a nuclear waste repository is seriously complicated by the long time periods which will be involved (tens of thousands of years) as well as the inherent complexity of the repository/geology/groundwater system. Therefore, the study of natural phenomena which imitate anticipated repository behaviour, the so-called natural analogues, is increasingly being recognized as an important complement to mathematical models.

A specific concern for disposal of spent fuel in granite is the effect that the heat will have on the rock mass and hydrogeologic system. Current repository concepts being developed by Atomic Energy of Canada Ltd. (AECL) predict that temperatures of approximately 80 to 100°C will be sustained in the region of a spent fuel repository for approximately 20,000 years (Acres et al., 1980; Mayman et al., 1980). In contrast, temperatures near a reprocessed waste repository will dissipate in a few hundred years. It is not clear how the rock mass will react to elevated temperatures over a period of time which approaches the geologic time scale. To develop a better understanding, this study has investigated a mild geothermal area in Montana as a possible natural analogue to a repository system.

The geothermal anomaly near Marysville, Montana was discovered in 1965 (Blackwell, 1969) and was unusual in that it was "blind", showing no surface manifestations such as fumaroles, hotsprings, etc. The anomaly was extensively explored from 1972-1974 in order to assess its potential as an economic geothermal energy resource (McSpadden et al., 1974; Blackwell et al., 1974; McSpadden et al., 1975).

The exploration activities included geological mapping, geophysical surveys, and the drilling of a 2.1 km deep borehole. The studies revealed that the anomaly was related to a Cenozoic granite pluton, the Empire Creek stock, which intrudes metamorphosed Precambrian sediments. The deep borehole penetrated an extensive hydrothermal zone; however, the temperatures encountered never exceeded 100°C and, thus, were too low to support commercial energy extraction and the project was terminated.

Although unsuitable for energy exploitation, the Marysville anomaly was thought to be well suited to be an analogue for a nuclear waste repository the following reasons: (a) temperatures in the ground are approximately the same as those anticipated in a repository (95°C maximum) and (b) the anomaly is associated with a granitic pluton.

In addition, a considerable amount of information is available from the geothermal exploration. For example, the deep borehole extends considerable deeper in a pluton than any boreholes drilled in nuclear waste disposal programs.

The present study consisted of two phases. The first was a literature review of the Marysville geothermal anomaly from a nuclear waste disposal perspective (Tammemagi et al., 1983). That review hypothesized that the active groundwater circulation, the alteration of the rock mass, and the relatively permeable fracture zones in the Empire Creek stock may have been, at least in part, caused by the thermal anomaly. It is well known that igneous rocks, both intrusive and extrusive, in geothermal regions may develop significant fracture permeability and, thus, increase their capability to transmit heat by groundwater convection. Many questions require resolution, however, before the Marysville anomaly may be used as an analogue. For example, is the present groundwater circulation/permeability associated with thermal conditions similar to a spent fuel repository or were they caused by considerably higher temperatures in the past acting over much longer periods? Is the ECS highly fractured and permeable as a result of the original emplacement or has it been caused subsequently? Etc.

Eleven core samples and numerous cuttings of the Empire Creek stock had been procured at approximately regular intervals through the 2.1 km deep geothermal borehole. The second phase of this study entailed a detailed petrological and geochemical analysis of these cores and cuttings. The purpose was to establish the petrologic character and genesis of the stock and to determine the history of the hydrothermal mineralization and related alteration.

This paper will summarized both phases of the study but will emphasize the second, that is, the petrological and geochemical analyses of the core samples from the deep boreholes.

GEOLOGICAL SETTING

The Marysville "blind" geothermal anomaly is located about 30 km northwest of Helena, Montana, and 4.5 km west of the old gold mining town of Marysville, (Figure 1). The area is located within the North American Cordilleran Orogen and has been affected variously by periods of volcanism, plutonism, folding, thrusting, normal faulting and/or seismicity since Late Cretaceous time.

The regional geology is dominated by the Boulder batholith, a large composite plutonic mass which has an outcrop of over 6,000 km^2 (2200 mi^2). The batholith and its satellitic stocks intruded and metamorphosed sedimentary rocks of Precambrian to Mesozoic age, and intrude the genetically related contemporaneous Elkhorn Mountains volcanics (Robinson et al., 1968). Radiometric age dating indicates that the main body of the Boulder batholith was emplaced from 78 to 72 million years ago. Intrusion of the batholith was accompanied and followed by folding and thrusting on a regional scale.

Renewed volcanic activity occurred regionally at about 50 million years and 40 - 37 million years ago. Normal faulting is responsible for much of the present physiography of the region, and the Helena area has experienced episodes of strong seismic activity in recent times (Friedline et al., 1976).

The main features of surficial bedrock geology in the area of the Marysville Geothermal anomaly are the contact metamorphosed sedimentary rocks of the Precambrian Belt series and the Marysville granodiorite stock, a satellitic intrusion of the Boulder batholith.

The oldest igneous rocks of the Marysville region are microdiorite sills of probable Precambrian age. The Marysville granodiorite is the next dated igneous event at 78 my (Baadsgaard et al., 1961). The Empire Creek Stock, which has been dated at 40 my, does not have surface outcrop. Farther to the southwest, remnants of a previously more extensive suite of rhyolitic volcanics, the Hope Creek volcanics, are dated at 37 my and probably represent the extrusive equivalent of the Empire Creek porphyry.

The main structural feature of the area is a dome in the sedimentary rocks, the core of which is expressed by the outcrop area of the Empire shale. The dome in the Empire shale corresponds closely with both the geothermal anomaly and other contact-metamorphic zones which are interpreted as being related to the intrusion of the Empire Creek stock.

Some faulting in this area is demonstrably later than the intrusion of the granodiorite, and microearthquake activity has been recorded southeast of the geothermal anomaly (Friedline et al., 1976).

REVIEW OF GEOTHERMAL INVESTIGATIONS

The geothermal investigations carried out in 1972-74 provide an interesting case history with much useful information for nuclear waste disposal. Only a brief description is provided here since a comprehensive summary is available (Tammemagi et al., 1983).

A number of hydrogeological studies were done as part of the geothermal project (McSpadden et al., 1975; McSpadden, 1977). Significant fracture zones with groundwater flow were encountered at approximately 460 m, 550 m, 1000 m, 1400 m, 1800 - 1900 m and 2040 - 2070 m in the deep borehole. There was a flow of about 16 l/s from the 1000 m zone to the 2040 - 2070 zone until the bottom of the drill hole was plugged with cement. There appeared to be good vertical hydraulic connectivity between major subhorizontal permeable zones which permits convective groundwater motion to occur. Water samples were collected from the deep borehole. Samples from near surface (<171 m) are similar to the shallow groundwater in the area which is predominantly a calcium bicarbonate water with a median chloride concentration about 8 mg/l. Samples are distinctly different generally demonstrating a dilute sodium-bicarbonate-sulfate water with a relatively high fluoride content and are similar to thermal springs in the region.

^{18}O analyses indicated little or no shift from the meteoric water line relating ^{18}O to ^{2}H in western Montana (McSpadden et al., 1975), suggesting that the temperatures of the geothermal source are below 150°C and the circulating waters are of relatively recent meteoric origin. The temperatures calculated by the SiO_2 and Na-K-Ca geothermometer methods are 110-130° and 165-180°C respectively.

A comprehensive suite of geophysical exploration surveys was used in the geothermal project (McSpadden et al., 1974; Blackwell et al., 1974; McSpadden et al., 1975). The methods employed included heat flow, gravity, electrical resistivity, magnetotellurics, magnetics, seismic ground noise and borehole logging. Important information arising from these surveys was that:

1) Heat flow measurements in shallow boreholes yielded geothermal gradients up to 240°C/km and heat transfer of up to 800 mW/m^2, values which are approximately 10 times the world average.

2) Temperature logs recorded in the deep borehole (Figure 2) indicated that conductive heat transfer was occurring in the upper region whereas convective heat transfer was occurring in the middle and lower regions.

3) The surface geophysical surveys did not predict the vigorous groundwater flow system occurring in the Empire Creek Stock.

4) An intriguing contrast exists between the adjacent Empire Creek stock and Marysville stock. The latter showed a normal heat flow and a normal gravity field, had a large magnetic anomaly and a high electrical resistivity. The Empire Creek stock in contrast had a high heat flow anomaly, a negative gravity anomaly, normal magnetic field and high electrical resistivity.

PETROGRAPHIC AND GEOCHEMICAL ANALYSES OF CORE

Eleven granite cores were originally taken from the deep geothermal well. These were obtained from archives and studied as part of the present project. Over 60 thin sections were optically studied and a brief summary of the borehole petrography is presented below.

Petrography

The essential primary mineralogy of the Empire Creek stock cores is relatively consistent in composition with essential minerals consisting dominantly of subequal amounts of quartz and alkali feldspar (orthoclase microperthite), with lesser amounts of plagioclase (approximately An_5) and around 5 percent biotite. Accessory primary minerals consist of fluorite, zircon, trace amounts of apatite in all cores, and topaz, muscovite, and opaques [{αλ′ νετιτε′ ιω{ενιτε [ʃμö in some of the cores. Primary rock textures are generally porphyritic, with an aphanitic groundmass in Cores 5 and 6, and more coarsely crystalline groundmass present in the intermediate cores. The deepest cores, although still containing K-feldspar megacrysts, are coarsely crystalline and more equigranular. Groundmass textures and phenocryst abundance are variable throughout the well.

Complex grain boundary textures are present, particularly in the feldspars, but locally also in quartz grains, throughout the core. Inclusions of quartz and plagioclase are common in K-feldspar phenocrysts and megacrysts throughout the length of the well.

Alteration and vein morphology and mineralogy varies throughout the well. Core 5 is characterized by the most variable and complex alteration, veining and mineralization. Alteration and vein minerals include quartz, K-feldspar (adularia), sericite, biotite, chlorite, montmorillonite, kaolinite, fluorite, calcite, pyrite, topaz and molybdenite. Veining consists of a complex stockwork of crosscutting veins from discontinuous or horsetailing quartz veins to intensely altered zones of biotite-sericite-quartz-pyrite. Zoned veins indicating multistage alteration and mineralization episodes are also present. Alteration envelopes may or may not be present around veins.

Feldspars are variably altered to sericite and/or kaolinite ± montmorillonite in the middle cores, with the strongest kaolinite alteration in Core 12. Minor amounts of K-feldspar, biotite, chlorite, sericite and fluorite are present in veins in some of the other cores, but the most prominent type of veining is quartz veining which occurs as cryptocrystalline to microcrystalline fracture filling of intensely fractured and/or sheared and brecciated wall rock. Veining ranges from passive fracture filling of shattered but unmoved mineral and rock to brecciation and obvious displacement of rock and mineral fragments. Veining and/or brecciation were not observed in Cores 13 and 15, but are present in all other cores.

Partial alteration of plagioclase and biotite to calcite ± chlorite is common in Core 13, and biotite in Core 15 is partially altered to bright green chlorite.

Miarolitic cavities are common in Cores 13, 14 and 15 and are partially to completely filled with fluorite, calcite, muscovite or quartz. Miarolitic cavities are locally present in some of the upper cores but are generally filled with quartz or kaolinite.

Oxygen Isotope Analyses

Oxygen isotope ratios were measured in quartz and feldspar separates from samples of the upper (300 m), middle (1300 m), and lower (2000 m) parts of the granite core, in kaolinite from the middle part of the granite core (albite alteration product), and in narrow (1-2 cm) sericite-biotite alteration zones around a molybdenite-bearing vein in the upper part of the granite core. Data are given in Table 1.

Primary $\delta^{18}O$ values in unaltered granites are typically 9.5 for quartz and 8 for feldspar (Taylor, 1968). It should be noted that quartz is generally very resistant to oxygen exchange at temperatures below 250°C, as concluded from studies of quartz in active geothermal systems (Truesdell and Hulston, 1980). The measured $\delta^{18}O$ value of quartz (7.0) in core 5 (upper part of granite core) indicates some exchange of oxygen with a relatively low ^{18}O fluid at a temperature probably in excess of 250°C. The ^{18}O value of quartz in the middle (core 12) and lower (core 15) parts of the granite core are 9.4 and 9.1 respectively, indicating negligible deviation from primary values, and thus negligible evidence for high-temperature (250°C) water-rock interaction in this portion of the granite.

Assuming an initial $\delta^{18}O$ value of 8 for the feldspars, the measured $\delta^{18}O$ values in feldspar indicate that significant volumes of water have reacted with the rock, even in the middle and lower parts of the granite core. In lower portions of the granite core, where 95°C water is now convectively circulating, the observed oxygen shift in the rock is reasonably attributable to present conditions. This case implies continuous recharge of surface water into the system to account for the minimal $\delta^{18}O$ shift observed in the drill hole water. Alternatively, the rock shift could have been effected by early high-temperature exchange to a smaller extent than observed in core 5, and subsequent low-temperature exchange under present conditions may be limited by very low diffusion rates at 95°C. These hypotheses will be evaluated quantitatively in future work, and temporal constraints on thermal history derived from ongoing fission-track studies will prove useful in this regard.

The magnitudes of kaolinite-water and chalcedony-water fractionations are consistent with these minerals forming under the present temperature conditions, near equilibrium with -19 o/oo water.

Porosity, Permeability and Density Data

Porosity, permeability and grain density measurements were performed and results for four core samples and one standard sample are summarized in Table 2.

The high porosity values in Cores 5, 11 and 12, in part reflect the abundance of clay alteration. The fabric of aggregates of clay minerals is highly microporous. The very high porosity values for Cores 11 and 12 also reflect the abundance of fractures and the microscopic voids along quartz veins. In addition, a certain amount of microporosity is present within altered feldspars, either due to direct leaching of feldspar or due to leaching or physical removal by water of alteration products. Microporosity within the fabric of aggregates of kaolinite booklets and platelets, and microporosity within leached (?) feldspars was observed during SEM examination of Core 12 samples. Pore spaces in leached feldspars generally are controlled by cleavage direction and generally are less than 3 μm in diameter.

Pore space in Core 14 is mainly made up of miarolitic cavities and microporosity within clay alteration. Some fracturing and veining was observed in thin section of Core 14, and some porosity may be associated with this fracturing and veining, if it was present in the particular portion of the sample cut for analysis.

The permeability values for Cores 5, 11 and 14 were below detection limits of the analysis technique, but a permeability of 1.01 was measured for Core 12. This value probably represents permeability along a fracture present in this sample rather than only through the micropores of feldspars and clays.

A sample of the Lac du Bonnet granite from eastern Manitoba was submitted with the Empire Creek Stock cores for use as a check. The physical properties of the Lac du Bonnet granite have been thoroughly studied as part of the nuclear waste disposal program in Canada and yield 0.24% porosity and a density of 2640 kg/m^3, which are in good agreement with the values in Table 2.

The Empire Creek stock core samples have a very high porosity and are considerably greater than values generally reported for granites.

X-Ray Diffractometry and X-Ray Energy Spectrometry

Fracture coatings from several cores, porous altered samples of Core 12, and cuttings samples from near or within apparent significant fracture zones throughout the well were analysed by x-ray diffractometry and/or x-ray energy spectrometry.

Qualitative analysis of alteration from Cores 8, 11, 12 and 15 by x-ray diffractometry indicates the presence of a significant amount of kaolinite, with lesser but variable amounts of quartz, fluorite and albite, + illite. Illite peaks are coincident with sericite, muscovite and biotite peaks, so a mineral identified as illite is probably sericite and/or biotite. A "chalcedonic" vein from one of the cores is made up primarily of alpha quartz with a minor amount of kaolinite.

A thin brown coating on fracture surfaces and kaolinite alteration in plagioclase grains in Core 12 was hand picked for XRD analysis, but only kaolinite (35 percent), illite (sericite - 24 percent, quartz - 26 percent and feldspar - 14 percent) were detected in significant amounts along with 1 percent calcite.

Cuttings samples were selected for x-ray diffractometry from within or as close as possible to significant fracture zones within the well as determined by geophysical log analysis, drilling reports, or high water flow. Some of the samples were hand-picked under a binocular microscope to separate possible alteration, vein or fracture-fill material. No minerals were detected which were not observed optically as well, although the wide range of secondary feldspar peaks could have masked peaks of minor minerals.

Fracture surfaces and porous zones from Core 12 samples were examined on a scanning electron microscope equipped with a Kevex x-ray energy spectrometer. In addition to kaolinite, other secondary minerals identified included submicroscopic quartz crystals, calcite and anhydrite. Calcite and anhydrite were detected in only trace amounts, but minute quartz crystals have formed on fracture surfaces and within porosity in leached feldspars. No other fracture coating minerals are identified either visually or by elemental analysis during scanning electron microscopy.

Electron Microprobe Analysis

The minerals biotite, muscovite and alkali feldspar from core samples were quantitatively analyzed. Of particular interest was the optically spectacular color zonation (from dark red-brown cores through light blue-green rims) in biotite from Core 10. This zonation was investigated to determine its relations, if any, to hydrothermal processes. A sharp outward decrease in Ti content was observed and probably accounts for the color zonation (Deer et al., 1966), and is interpreted to be a primary igneous effect rather than a hydrothermal effect.

In Core 5, unzoned brown biotite has composition similar to that of biotite cores in Core 10. Secondary muscovite is Fe-rich.

Alkali feldspars in Cores 10 and 12 are similar. Albite is near pure $NaAlSi_3O_8$. Exsolution lamellae of albite in perthite grains are slightly more calcic. Microline lamellae in perthite are near pure $KAlSi_3O_8$. The near end-member compositions of perthite exsolution lamellae indicate equilibration temperatures on the order of 300 - 400°C (Whitney and Stormer, 1977).

Inclusions in biotite were identified by energy-dispersive X-ray analysis. Found were: niobian rutile (TiO_2 phase), monazite (rare earth phosphate), and zircon ($ZrSiO_4$). These inclusions are generally surrounded by a small dark "pleochroic halo" of radiation damage due to alpha-emitting trace constituents.

Potassium - Argon Age Dating

Two samples of the Empire Creek stock core were submitted for conventional potassium-argon age determination. One sample each from Core 5 and Core 15 was submitted. The Core 5 sample was from the most highly altered portion of the core, and a sericite mineral concentrate was separated and analysed rather than the whole rock, in an attempt to date the time of hydrothermal quartz-sericite alteration characteristic of Core 5.

The Core 15 sample was fresh, pink, coarse-grained granite, and a potassium feldspar separate (orthoclase micropertbite) was analysed from the sample to determine the age of emplacement and cooling of the deep portions of the Empire Creek stock.

An age of 38.5 +/- 1.5 my was determined for the sericite concentrate from Core 5, and an age of 37.8 +/- 1.5 my was determined for the fresh orthoclase microperthite from Core 15. The age data indicates that there is a very close relationship between intrusion and hydrothermal alteration in the Empire Creek stock and suggests multiple pulses of intrusion and alteration over a short period of time. Although the Core 15 sample was dated as slightly younger than the sericitic alteration of Core 5, the analytical errors of +/- 1.5 my for each date overlap, indicating the presence of a complex episode of intrusion with closely associated hydrothermal alteration.

Further Work

Work is presently under way to obtain fission track age dates for apatite separated from core samples. Uranium disequilibrium studies are also being attempted in order to provide age limits on the present phase of hydrothermal activity.

DISCUSSION

Any interpretation of the petrographic and specialized analysis data obtained from the Empire Creek stock (ECS) core samples must take into account that only a total of 14.7 m of core from 11 cored intervals has been used to represent the 1776 m drilled through the Empire Creek stock.

Analyses of the ECS samples indicate that the stock is a composite intrusive body made up of a series of genetically related and compositionally similar granite porphyry stocks and dikes, probably successive intrusive pulses from a common deep magma source.

The presence of biotite, muscovite, fluorite and locally topaz and calcite in reltively unaltered rock, as well as the miarolitic cavities, particularly in the lower cores, indicate a relatively high volatile content in the magmas.

Complex grain boundary and grain contact relationships all indicate that the various intrusions have undergone a complex crystallization and cooling history characterized by changing pressure, temperature and chemical conditions. Some of these conditions may have been related to venting at the surface during the eruption of the apparently contemporaneous Hope Creek rhyolitic volcanics.

Alteration, fracturing and veining have affected most of the samples examined in some way. In the deepest core there is evidence of deuteric alteration by residual solutions and volatiles during late magmatic and post-magmatic stages of consolidation. Intense fracturing of rock and shattering of grains in the middle cores took place at least in part after complete consolidation, but healing of fractured grains by magmatic minerals, and discontinuity of fractures as they pass into less competent minerals suggests that some fracturing took place very early. The alteration observed in the upper cores is characteristic of a post magmatic hydrothermal system, probably with a significant meteoric component.

The alteration, mineralization, veining and host rock of the Empire Creek porphyries are typical in texture, composition and distribution of the porphyry copper/molybdenum deposits throughout western North and South America which are characterized by fracturing, vein stockworks, hydrothermal alteration, strong silicification and the presence of topaz and fluorite.

Petrographic examinations, K-Ar dating and fluid inclusion geothermometry indicate that the hydrothermal alteration of the upper cores, at least, occurred during the post-magmatic phase of the cooling of the porphyry intrusions. In the deeper cores, some open fractures are apparent, and altered feldspars (Core 12) appear leached. Plagioclase feldspars are strongly kaolinized. Microcrystals of quartz have formed on fracture surfaces, across leached and altered feldspars. These quartz crystals appear to have precipitated from circulating waters, and may have formed from waters of the present convective geothermal system.

Oxygen isotope data for kaolinite from Core 12 and cryptocrystalline quartz, vein material from Core 9 are consistent with formation under present geothermal conditions. Unfortunately, it has not been possible to date this material. The Empire Creek stock could have undergone more than one period of geothermal convection during the past 38 my. A fracture system has been present since the emplacement and cooling of the intrusive complex, and the region has been tectonically active. None of the alteration, veining or fracturing throughout the core is inconsistent with processes which would occur during initial consolidation and cooling of a volatile-rich magma at shallow depths where interaction with meteoric water would be a natural occurrence. Fission-track analysis of apatites from the deep part of the stock and uranium disequilibrium studying could potentially provide important information on the timing of the last heating of the intrusions.

It is not clear whether the recent mild hydrothermal activity has been responsible for opening the deeper fractures or not. Certainly, evidence from elsewhere suggests that open fractures are an unstable condition and that they will reseal eventually. Thus, it seems that the present mild, hydrothermal system has, at least in part, contributed to the unsealing of the preexisting vein-filled fractures and for the creation of the unusually high matrix porosity in the rock mass.

SUMMARY

This study of the Empire Creek stock has clearly shown that vigorous, convective groundwater motion is possible in granite plutons when heat is involved. Significant fracture permeability is developed which extends to considerable depths (2 km). There does not appear to be a decrease in permeability with depth as is generally thought to occur in such rocks. The porosity of the Empire Creek stock core samples is far larger than values usually quoted for granitic rocks and indicates that hydrothermal activity can have a significant effect on this parameter. It is noteworthy that surface geophysical techniques such as electrical resistivity and magnetotellurics were not able to detect this rather anomolous situation.

Performance assessment studies of conceptual repositories in crystalline rocks have generally assumed hydrogeological conditions considerably different than those encountered in this study. It is important to determine whether the thermal conditions anticipated for spent fuel repositories can cause similar effects, that is, whether the Empire Creek stock is a valid natural analog for a spent fuel repository. Unfortunately, this study has not been able to categorically answer this question. If anything, the available evidence suggests that the present conditions at ECS are largely due to the original emplacement of the stock and is characteristic of Cu/Mo porphyry intrusives. Nevertheless, considerable more research is necessary. This analog study has highlighted the very dramatic effects that long-term heat can have on igneous intrusive rocks and indicates that repository design and performance criteria for spent fuel repositories need to be defined carefully (and separately from those for a reprocessed fuel repository).

ACKNOWLEDGEMENTS

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Table 1. Oxygen Isotope Data for Mineral Separates from the Empire Creek Stock.

Core		$\delta^{18}O$ SMOW
5	Dark Green Alteration Zone	5.2
5	Pale Green Alteration Zone	3.1
5	Quartz	7.0
5	Feldspar (?)	-0.6
9	Chalcedony Vein	7.8
12	Quartz	9.5
12	Mostly K Feldspar	6.4
12	Kaolinite	2.4
15	Quartz	9.1
15	K Feldspar	6.8

Table 2. Porosity, Permebility and Density Data.

	Porosity (%)	Permeability (milliDarcies)	Grain Density (Kg/m^3)
Core 5	6.7	0.01	2729
Core 11	11.6	0.01	2682
Core 12	8.8	1.01	2678
Core 14	4.5	0.01	2636
Lac du Bonnet Granite	0.1	-	2630

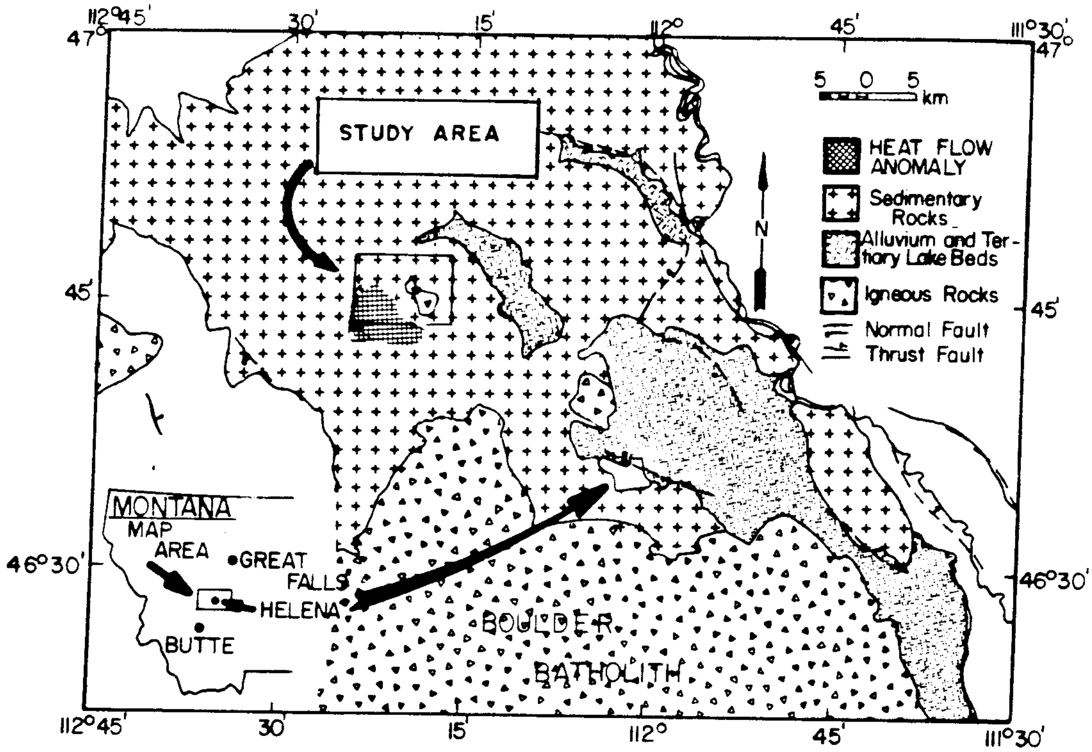

Figure 1. Generalized Geologic Map of the Helena, Montana Region, (After Friedline et al., 1976).

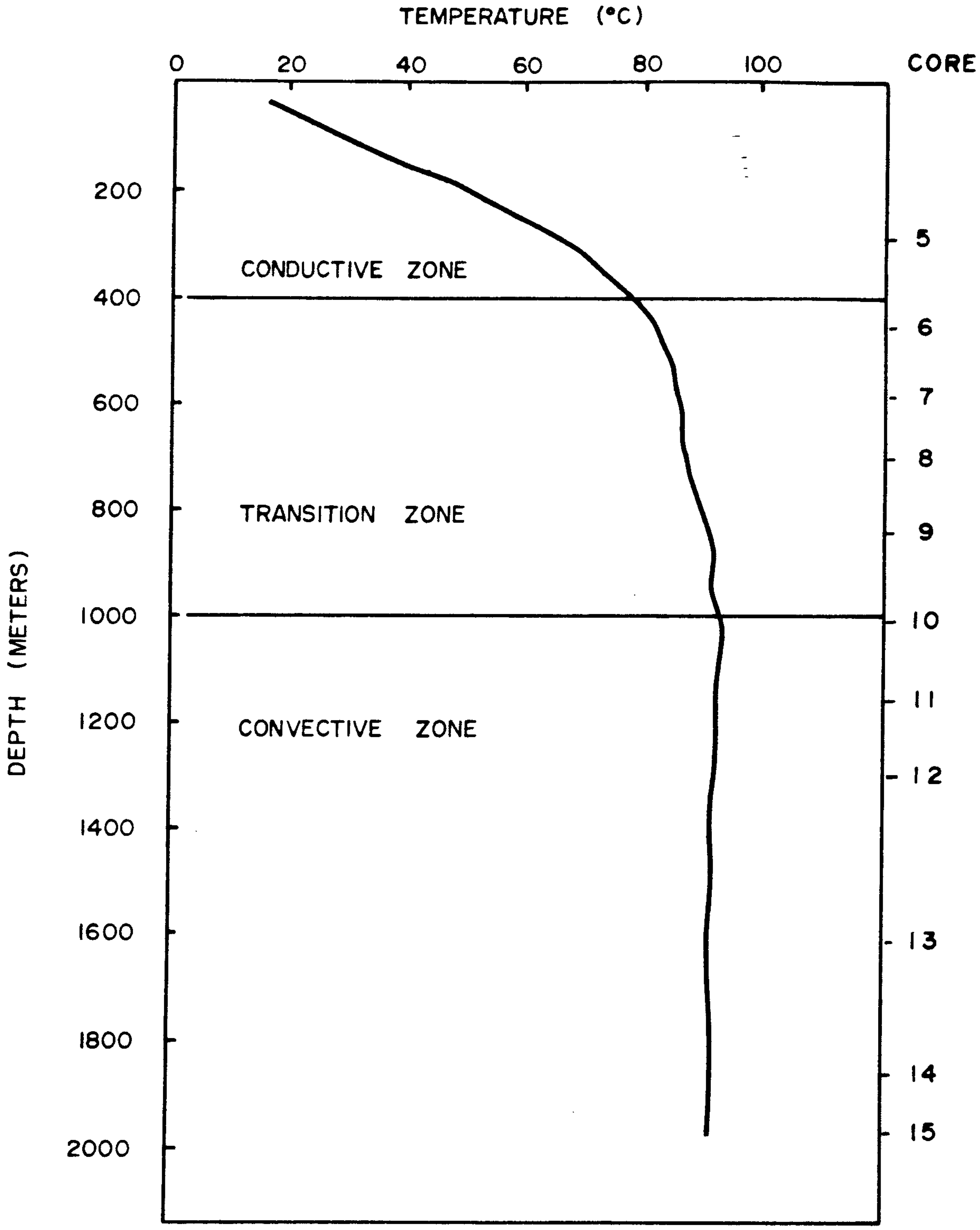

Figure 2. Temperatures Measured in the Deep Borehole, (Blackwell et al., 1975), showing the Location of the Core Samples.

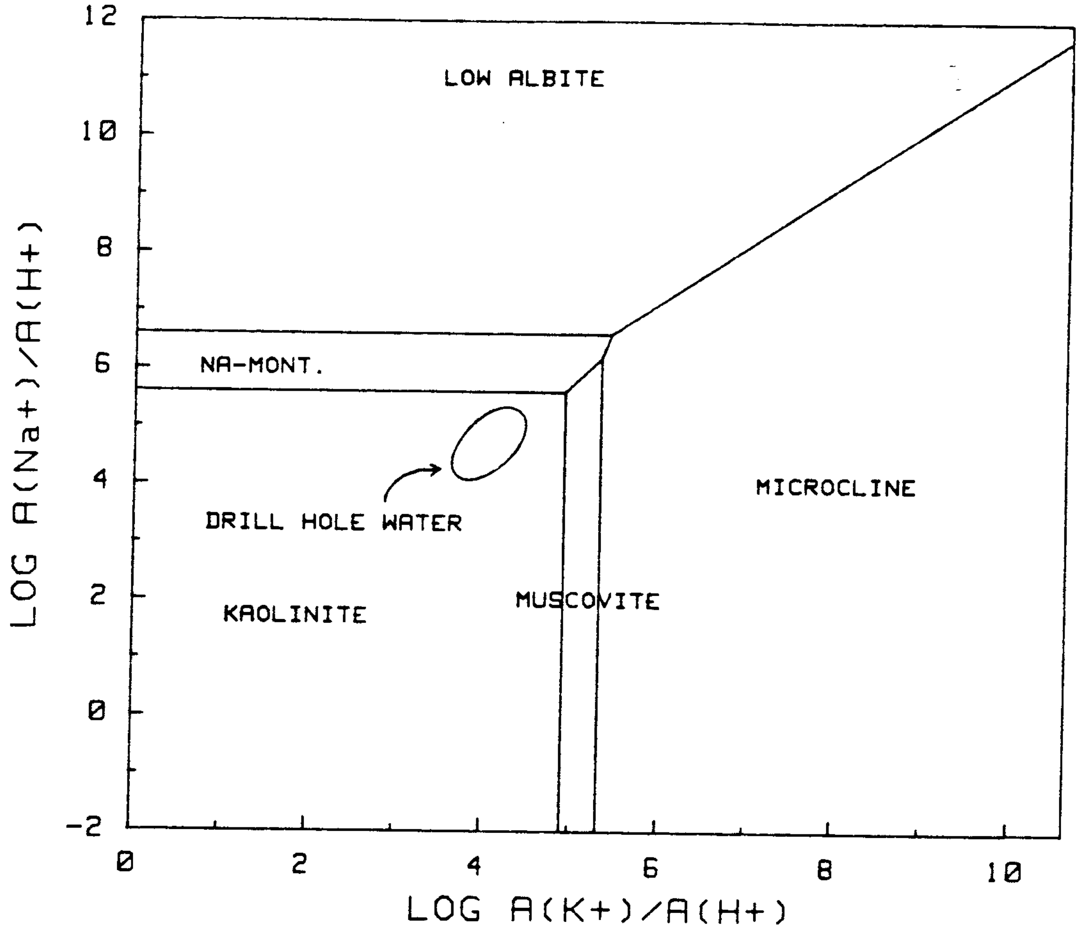

Figure 3. The System $HCl-H_2O-Al_2O_3-K_2O-Na_2O-SiO_2$ at 100°C Showing Field of Deep Drill Hole Water Composition. (After Helgeson et al., 1969).

SESSION F

ANALOGUES OF LOW TEMPERATURE RADIONUCLIDE MIGRATION AND SORPTION

Chairman: John S. Stuckless

THE DISTRIBUTION OF URANIUM, THORIUM AND RARE EARTH ELEMENTS IN GRANITIC ROCKS - A STUDY OF SOME ANALOGUE ELEMENTS

D.C. Kamineni

Atomic Energy of Canada Limited/on Attachment to Geological Survey of Canada, 601 Booth Street, Ottawa, Canada, K1A 0E8

ABSTRACT

The distribution of uranium, thorium and rare earth elements in the Eye-Dashwa lakes pluton near Atikokan, Ontario is examined. Materials analyzed include (1) unaltered granite, (2) altered granite, (3) highly altered granite adjacent to open fractures, and (4) fracture-filling minerals. Distinct distribution patterns are noted for uranium and some rare earth elements among the four types of samples; thorium shows higher concentrations in materials (3) and (4). Compared with unaltered and altered granite, the highly altered granite and some fracture fillings have greater concentrations of uranium, thorium and rare earth elements. The large concentrations of uranium, thorium and rare earth elements in these materials are due to both sorption on selective materials and precipitation as mineral phases containing these elements. The occurrence of uraninite, bastnaesite and thorogummite coatings on fracture fillings are examples of this precipitation.

INTRODUCTION

As a part of the assessment of the concept of disposal of nuclear fuel waste in plutonic rocks, Atomic Energy of Canada Limited is studying a number of granitic plutons in the Canadian Shield. One facet of the geotechnical research involves the study of rock alteration and fracture-filling minerals. It is expected that this will contribute to an understanding of the mobility in the geosphere of some radionuclides in nuclear fuel waste.

Uranium, thorium and rare earth elements in granitic rocks are normally concentrated in various accessory minerals such as zircon, monazite, allanite, sphene and apatite. These elements represent two important groups in nuclear fuel waste: (1) actinides and (2) fission products. Accessory minerals in granitic rocks when subjected to post-consolidation alteration processes may release various chemical constituents that are generally concentrated in secondary minerals occurring in the altered rock matrix and fractures.

In this report, the distributions in the Eye-Dashwa lakes pluton, of uranium, thorium and rare earth elements, considered to be analogues of neptunium, putonium, americium and curium, are discussed.

GEOLOGY OF THE EYE-DASHWA LAKES PLUTON

The Eye-Dashwa lakes pluton occurs within the Superior Structural Province of the Canadian Shield, and is located about 30 km northwest of Atikokan, NW Ontario (Figure 1). Peterman et al. (in press) reported an age of 2 674 Ma for this pluton, based on U-Pb concordia of zircons. Detailed mapping by Brown et al. (1980) revealed that the pluton has an elliptical shape. A subsequent petrochemical study demonstrated that the pluton is zoned and that it evolved through a sequence of fractional crystallization, with an early phase consisting of quartz monzonite and tonalite followed by granodiorite and granitic phases (Kamineni and Brown, 1981).

The Eye-Dashwa lakes pluton is intersected by a series of fractures that are invariably filled, or coated, with mineral matter (Kamineni et al., 1980). Based on the type of filling materials, the fractures were divided into four groups (Stone and Kamineni, 1983): (1) granite-filled fractures (pegmatite and aplite), (2) epidote-filled fractures, (3) chlorite-filled fractures, and (4) low-temperature, mineral-filled fractures. From cross-cutting relations and temperatures of crystallization of the filling minerals, these four groups constitute a chronological sequence. Among the four groups of fractures, the epidote-filled ones are most abundant, and invariably the low-temperature group is associated with them. From this it is interpreted that the low-temperature mineral-filled fractures were formed by reactivation of older epidote-filled fractures (Kamineni, 1983; Kamineni and Stone, 1983; Stone and Kamineni, 1982). A close genetic relationship has been established between the fractures, fracture infillings and rock alteration (Kamineni and Dugal, 1982).

SAMPLES AND METHODS OF INVESTIGATION

A variety of samples, comprising various degrees and types of alteration and fracture-filling minerals, was investigated, using the following techniques: (1) petrographic analysis, (2) electron microprobe analysis, (3) scanning electron microscopy, (4) X-ray diffraction, (5) bulk chemical analysis, (6) mineral separation, (7) X-ray fluorescent analysis, and (8) neutron activation.

The samples analyzed for uranium and thorium can be grouped into five categories: (1) unaltered granite, (2) altered granite, (3) highly altered granitic rock-matrix near open fractures, (4) goethite, and (5) kaolinite. The last two groups occur as fillings in open fractures.

The samples analyzed for rare earth elements (REE) fall into three categories: (1) unaltered granite, (2) altered granite, and (3) mineral separates (from the rock matrix and fracture fillings). The last group, specifically, includes sphene, epidote, chlorite, calcite, goethite, kaolinite and gypsum. In addition, six samples of highly altered rock matrix near open fractures were selected for REE analysis. These latter analyses are not yet complete.

The samples were analyzed for thorium using X-ray fluorescence, and for uranium using delayed neutron activation. The precision of the analysis is estimated to be ± 5% (2 σ) for uranium and ± 10% (2 σ) for thorium. The precision is generally considered to be less for rocks containing < 2 μg/g uranium and < 10 μg/g thorium.

The rare earth elements were analyzed by instrumental neutron activation analysis. The samples were activated for 4 h in a flux of 1×10^{12} neutrons $cm^{-2}s^{-1}$. Counting was performed using a Ge(Li) detector with a resolution of 1.6 keV at 122 keV. The precision is approximately ± 5% (2 σ) for all elements except cerium and neodymium, for which the precision is ± 10% (2 σ).

DISTRIBUTION OF URANIUM AND THORIUM

The uranium and thorium contents of the various types of materials analyzed from the Eye-Dashwa lakes pluton are given in Table 1.

Examination of Table 1 and Figure 2 shows that the uranium concentrations in the unaltered, altered and highly altered grnitic samples differ, whereas the thorium concentrations are indistinguishable in the first three groups.

The unaltered granite in Table 1 represents the pristine part of the Eye-Dashwa lakes pluton, as the $\delta^{18}O$ values (8.1 to 8.6 o/oo) for these samples are within the range of isotopically "normal" granitic rocks, defined by Taylor (1978) to be + 6 o/oo $< \delta^{18}O < + 9$ o/oo. On the other hand, the altered granite has been affected by hydrothermal alteration and contains fractures that are filled with epidote, sphene and chlorite, etc. Samples of this group show higher $\delta^{18}O$ values (= 12 o/oo), indicating isotopic exchange with alteration fluids (Kerrich and Kamineni, in Press). This alteration process is associated with oxidation, as indicated by the higher ferric iron concentration (0.9 vs 1.1%) in these samples (Kamineni and Dugal, 1982).

The depletion of uranium in the altered rocks, compared with the unaltered rocks, can be attributed to mobilization of this element during hydrothermal alteration. The occurrence of oxidizing conditions during rock alteration brings uranium to the hexavalent state, and in this state it can be mobilized from its original sites. A process similar to this has been suggested by many investigators (e.g., Ragland et al., 1967; Rosholt et al., 1973). The mobilized uranium appears to be scavenged by fracture fillings formed during this alteration stage. For example, fracture-filling sphene, epidote and chlorite contain high concentrations of uranium (600 $\mu g \cdot g^{-1}$, 30 $\mu g \cdot g^{-1}$ and 9 $\mu g \cdot g^{-1}$, respectively). Hematite, which is another fracture-filling mineral associated with epidote, also shows high concentrations of uranium in energy dispersive spectra during scanning electron microscopic analysis. Pyrite with high uranium content is also found in some epidote-filled fractures. Powder X-ray diffraction patterns suggest this material is uraninite. The occurrence of uraninite in these iron oxide-sulfide fracture fillings is believed to be governed by redox reactions (Kamineni et al., 1982).

The third group of granitic samples from the Eye-Dashwa lakes pluton comprises highly altered rock matrix adjacent to fractures transmitting groundwater. These fractures are interpreted to be reactivated epidote-filled fractures, in which the epidote has altered to goethite and kaolinite (Kamineni and Stone, 1983; Kamineni et al., 1982). They are well exposed in the road cuts on Highway 622 (see Figure 1). Kaolinites separated from these zones have a $\delta^{18}O$ value of about 23 o/oo, implying large Δ^{18} (mineral-water), which is common under weathering conditions (O´Neil, 1979).

The higher concentrations of uranium in the third group are due to its association with goethite and clay, which are abundant in this group. Iron oxides and iron-titanium hydroxides are recognized as good scavengers of trace metals in geological systems (Means et al., 1978; Kooms et al., 1980). Similarly, clay minerals are well known for their large exchange capacity (Grim, 1962). This is further supported by the analyses of goethite and kaolinite separates from these disintegrated zones. High concentrations of uranium in these co-genetic low-temperature alteration products evidently are simply a redistribution of this element from disintegrated epidote. This suggests limited migration of uranium in these zones.

Coexisting goethite and kaolinite from one of the open fracture zones were analyzed by J. Rosholt (United States Geological Survey) for uranium disequilibrium (Rosholt, 1983). The clay sample has isotopic ratios of $^{234}U/^{238}U$ (0.98), $^{230}Th/^{238}U$ (0.98),

$^{230}Th/^{234}U$ (1.00), whereas the goethite yields $^{234}U/^{238}U$ (0.88), $^{230}Th/^{238}U$ (0.89), and $^{230}Th/^{234}U$ (1.01). The isotopic compositions can be represented on a triangular diagram (see Figure 3). From Figure 3, it can be ascertained that the clay sample is near radioactive equilibrium, whereas the goethite has undergone significant ^{234}U depletion in the past 1/4 Ma. This contrasting behaviour between two coexisting and co-genetic minerals can be attributed to the nature of the crystal structure and the degree of hydration in these minerals. In other words, compared with goethite, the crystal structure of kaolinite is more likely to retain some of the daughter products of uranium.

There is no difference in thorium concentration between unaltered and altered granite samples, suggesting that it is immobile during hydrothermal alteration. There is a slight increase in thorium content in samples subjected to low-temperature alteration, i.e., in the highly altered group (see Table 1 and Figure 4). The high concentrations of thorium in group (3) can be related to abundances of goethite and kaolinite. The former appears to have been preferentially enriched with this element, which is evident from the analysis of mineral separates (Table 3). Goethites analyzed in this study may contain some hydrous iron-titanium oxides, formed by the degradation of sphene crystals that existed in fractures and the adjacent rock matrix. Pseudomorphs of hydrous iron-titanium oxide (Figure 5) are commonly noted in the rock matrix adjacent to open fractures. Energy dispersive analysis of some sphene crystals, especially the ones that are partially replaced, showed spectra of calcium, silicon and thorium. Material producing such spectra is noted to occur essentially as a thin rim around sphene grains. This material is identified as thorogummite, using powder X-ray diffraction work. These observations suggest that low-temperature alteration of sphene, and perhaps epidote, conserved thorium, and it was slightly enriched in low-temperature alteration products.

DISTRIBUTION OF RARE EARTH ELEMENTS

The REE abundances and their means in the unaltered and altered samples are presented in Table 2. The mean REE values show that there is a definite decrease in these elements (except for Tm, Yb and Lu) in the altered samples. This is displayed in a Box and Whisker plot for La, Ce and Nd (Figure 6).

The chondrite-normalized patterns of REE abundances in the unaltered and altered samples, obtained using the data of Haskin et al. (1968), Masuda et al. (1973), and Nakamura (1974), are shown in Figure 7, which shows a clear depletion of La, Ce, Nd and Sm in the altered samples. Sufficient theoretical and experimental data for REE behaviour during hydrothermal alteration of granitic rocks are not yet available. However, the mobility and redistribution of these elements has been demonstrated convincingly for sea-floor alteration and low-grade metamorphism (Frey, 1969; Frey et al., 1974; Floyd, 1977). The REE mobility and depletion during rock alteration results in either sub-parallel downshifting of the chondrite-normalized patterns (e.g. Hellman and Henderson, 1977; Hellman et al., 1977), or significant negative fractionation for La, Ce, Nd and Sm due to more pronounced mobilization of these elements (Wood et al., 1976). Chondrite-normalized data from the Eye-Dashwa lakes pluton show a definite depletion for these same elements in the altered group of samples, suggesting they all were mobilized in a coherent fashion.

The REE leached from the rock matrix are concentrated in the fracture-filling minerals. Filling minerals formed at this stage of alteration include sphene, epidote and chlorite (Kamineni and Dugal, 1982; Stone and Kamineni, 1982). Analysis shows that these minerals indeed contain large concentrations of REE (see Table 3). Mobilization of REE by hydrothermal alteration processes and their redistribution in alteration products such as fracture fillings suggest that there may be limited migration for these elements. A mass-balance calculation is needed to substantiate this. The necessary data for such a calculation are now being collected.

In addition to mobilization during hydrothermal alteration, yet another cause of REE mobility can be found in the Eye-Dashwa lakes pluton, i.e. that due to groundwater interaction. Some epidote-filled fractures, especially the ones located in the top 400 m of the pluton, were reactivated and contain evidence of low-temperature alteration (Kamineni and Stone, 1983). Generally, in fractures that are not reactivated, the epidote and sphene occurring in the rock matrix and fractures show little difference in their REE contents (Figures 8 and 9). However, in reactivated fractures, epidotes show a significant drop in REE concentrations (Figure 9). Chlorites separated from fractures show significant, but variable, amounts of REE (Figure 10). The variability is perhaps due to the type of chlorite present in fractures.

The REE mobilized from reactivated epidote fractures are redistributed in the low-temperature alteration products, such as goethite and clay (see Table 3). Some partially reactivated epidote fractures also contain calcite, and one of the calcites separated from this zone contains significant amounts of REE. The chondrite-normalized patterns for these minerals suggest enrichment in REE (Figure 11).

In the reactivated fracture zones, the REE are also concentrated by precipitation. For example, bastnaesite, a fluor cerium-lanthanum carbonate, is commonly noted as a thin coating on epidote fillings (Kamineni and Bonardi, 1983). In the Eye-Dashwa lakes pluton bastnaesite is found in fractures occurring as deep as 300 m in the boreholes.

Gypsum is another low-temperature fracture-filling mineral analyzed for REE. This mineral is invariably associated with epidote and has restricted occurrence, as it is concentrated at depths below 500 m (Kamineni, 1983). Saline waters enriched in Ca are common in these zones (Dickin et al., 1984) The REE analyses (except La, for which analysis is not available at present) of gypsum are given in Table 4, and show high concentrations of these elements. The chondrite-normalized REE patterns for gypsum are plotted in Figure 12. The anhydrite analyses reported by Morgan and Wandless (1980) are also plotted in Figure 12, which shows that gypsum from the Eye-Dashwa pluton is enriched in REE.

SUMMARY AND DISCUSSION

The results and interpretation presented in the preceding section contain various aspects that are relevant to nuclear fuel waste disposal. By studying alteration and fracture fillings of Archean granitic plutons (which are some of the oldest in the earth´s crust) from the time of crystallization through hydrothermal alteration to present-day rock-water interaction, one may be able to infer the mobility and redistribution of certain elements that can chemically represent radionuclides of interest in nuclear fuel waste disposal. The geochemical behvaiour of uranium is quite similar to plutonium and neptunium (Bagnal, 1972); the geochemical behaviour of thorium, under certain conditions, is similar to that of plutonium (Krauskopf, 1984); and the geochemical behaviour of lanthanum and neodymium are similar to americium and curium, respectively (Cotton and Wilkinson, 1962; Krauskopf, 1984). There are three processes involved in the concentration of these elements:

1) Occurrence in the structural sites of minerals. For example, uranium and REE, mobilized during hydrothermal alteration, are redistributed in suitable sinks located in fractures. The most common sinks are epidote, sphene, calcite and gypsum. This obviously operates during both high-temperature and low-temperature alteration.

2) Absorption on clay minerals. Kaolinite, chlorite and goethite are the examples. The process appears to be predominantly a low-temperature one, but chlorite is an exception.

3) Precipitation of minerals. Formation of REE minerals, such as bastnaesite and thorogummite, are examples of this process. This is essentially a low-temperature process.

The results presented in this study suggest that mobilization of some elements in granitic rocks is possible due to rock alteration along fractures, but some proportion of these mobilized elements is conserved by the three processes described above. If all the mass mobilized were conserved, then, on a macroscale, the alteration reactions in granitic rocks could be considered as occurring in a closed system. Mass-balance studies involving analogue elements are required to investigate this possibility and have been initiated.

Another important aspect that emerged from the study of the Eye-Dashwa lakes pluton is the occurrence of highly saline waters and the behaviour of analogue elements in these waters. These highly saline waters are predominant at depths below 650 m along fracture zones, and widespread across the Canadian Shield (Frape et al., 1984). Hence, it appears that these waters may play an important role at disposal-vault depths (>1 km). Consequently, it is highly desirable to study the behaviour of analogue elements in samples recovered from these depths. In the present study, the gypsum samples analyzed for REE belong to this category. The preliminary analysis presented here, suggests that the analogue elements (REE) are indeed immobilized by low-temperature minerals.

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Table 1. Means, standard deviations and order statistics for uranium and thorium from various samples (expressed in μg.g^{-1}).

	Uranium					Thorium				
	Unaltered granite	Altered granite	Highly altered granite	Goethite	Clay	Unaltered granite	Altered granite	Highly altered granite	Clay	Goethite
No. of samples	20	18	15	10	10	20	18	15	10	10
Minimum	1.60	0.60	2.90	15.90	7.80	7.60	8.30	9.00	7.70	29.00
5%	2.39	1.48	4.17	16.78	8.85	9.83	9.74	10.47	9.02	31.95
Median	2.65	1.85	4.82	17.65	10.12	10.85	10.20	13.33	10.60	33.45
95%	3.07	2.54	5.62	19.63	12.64	11.49	11.29	14.84	11.94	36.50
Maximum	3.80	4.60	7.00	21.20	15.20	14.20	13.30	18.00	14.00	38.00
Mean	2.73	2.01	4.90	18.21	10.74	10.66	10.52	13.80	11.00	34.23
Standard deviation	0.72	1.07	1.31	1.99	2.64	1.77	1.65	1.88	1.34	3.17

Table 2. Means and Standard deviation of REE in unaltered and altered granitic samples (expressed in μg.g^{-1}).

Type of Material		La	Ce	Nd	Sm	Eu	Tb	Ho	Tm	Yb	Lu
Unaltered (N=20)	Mean	57.21	102.03	42.03	6.03	1.41	0.48	0.66	0.12	1.05	0.16
	Standard Deviation	7.57	12.67	5.37	1.21	0.45	0.16	0.47	0.09	0.24	0.04
Altered (N=28)	Mean	42.00	77.25	32.85	4.78	1.11	0.39	0.48	0.13	0.99	0.15
	Standard Deviation	11.66	19.95	9.00	1.18	0.26	0.12	0.24	0.05	0.20	0.05

Table 3: REE, uranium and thorium analyses of mineral separates (expressed in µ g.g^{-1}).

REE	1		1			2	1	2	3	4	5	5
	Sphene (Wall-rock)	Sphene (Fracture filling)	Epidote (Wall-rock)	Epidote (Fracture filling)	Epidote (Wall-rock)	Epidote (Fracture filling Reactivated)	Chlorite (fracture filling)	Chlorite (fracture filling)	Calcite (fracture filling)	Kaolinite (fracture filling)	Kaolinite (fracture filling)	Goethite (fracture filling)
La	2280	1820	2470	1890	1190	408	172	26.3	1550	404	643	1170
Ce	7520	6980	3460	3430	2053	836	299	41.4	2159	691	1170	1490
Nd	4501	4051	1054	1146	650	387	122	10.6	907	230	372	583
Sm	821	743	115.2	89.2	52.5	68.6	20.6	1.24	92.3	23.6	53.8	57.2
Eu	128	108	29.4	31.7	18.3	13.7	3.83	0.32	21.3	5.2	9.2	11.5
Tb	60	52	11.2	12.1	6.9	4.97	1.38	0.19	7.0	1.8	2.7	3.3
Ho	51	47	–	21.2	11.6	4.81	1.84	0.12	4.9	1.4	1.9	4.7
Tm	16	14	1.86	2.71	1.37	0.96	0.35	0.10	1.4	0.3	0.5	0.7
Yb	98	100	18.50	20.6	11.0	7.53	3.43	0.42	7.3	2.4	3.3	4.8
Lu	12	13	2.49	2.92	1.44	1.13	0.50	0.08	1.0	0.3	0.3	0.8
U	83	125	26	41	30.1	8.2	8.8	7.3	31.8	11.2	8.1	11.1
Th	318	612	275	264	230	59	60	2	24	15	13	27

Table 4: REE analyses of gypsum from ATK-1 borehole (expressed in µ g.g^{-1}).

Depth in metres	Ce	Nd	Sm	Eu	Gd	Tb	Yb	Lu
563.3	49.8	12.6	0.90	0.20	–	0.04	0.10	–
752.7	7.77	2.22	0.19	0.06	–	0.05	0.04	–
837.1	0.77	0.29	–	0.01	–	0.0042	0.0066	–
927.7	573.3	168.9	11.06	1.19	–	0.21	0.17	–
1093.2	84.4	35.2	3.39	0.72	1.57	0.15	0.10	–
1129.8	12.5	3.93	0.42	0.12	–	0.02	0.04	–

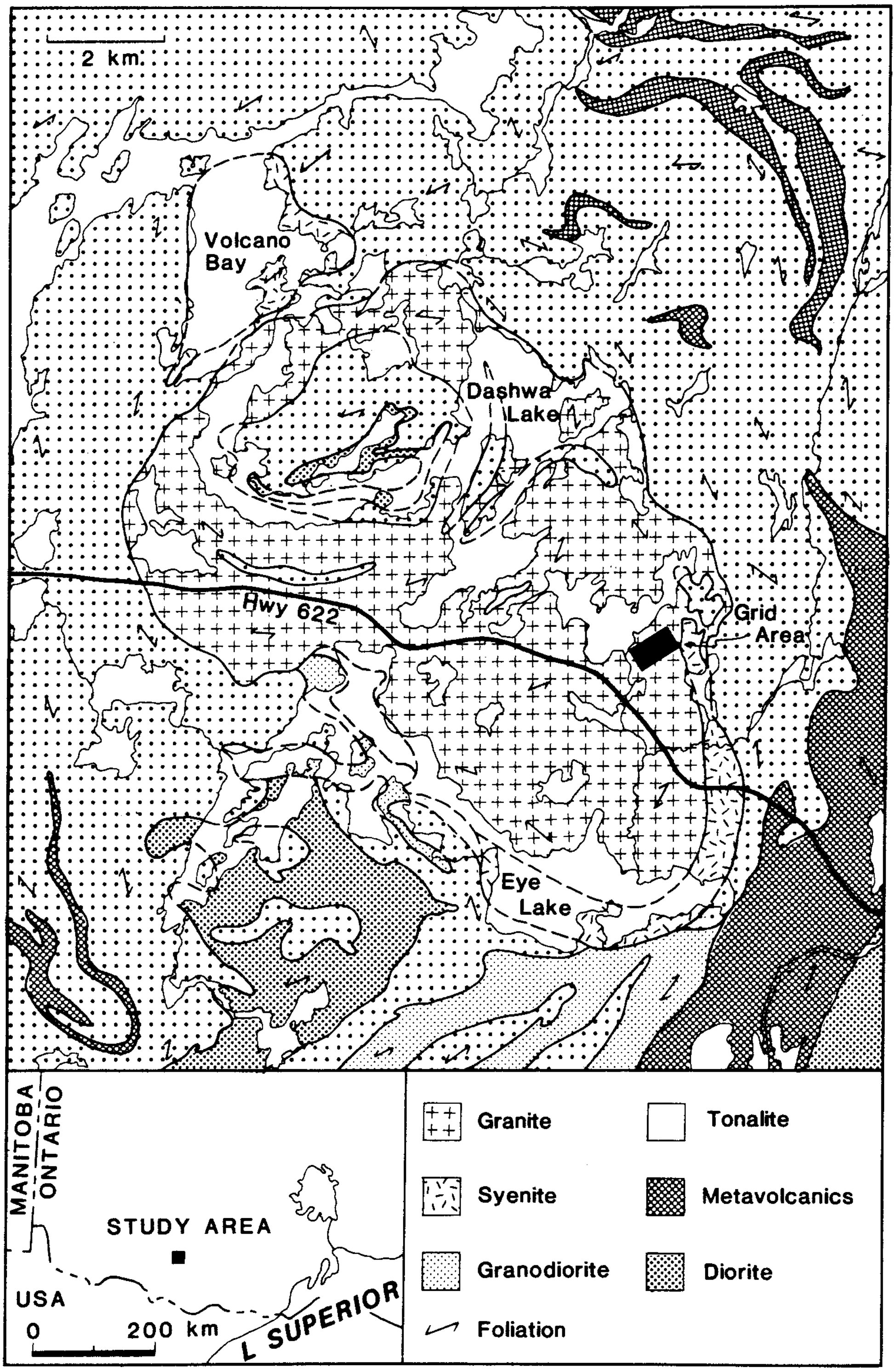

Figure 1. Geological map of the Eye-Dashwa lakes pluton and the surrounding area.

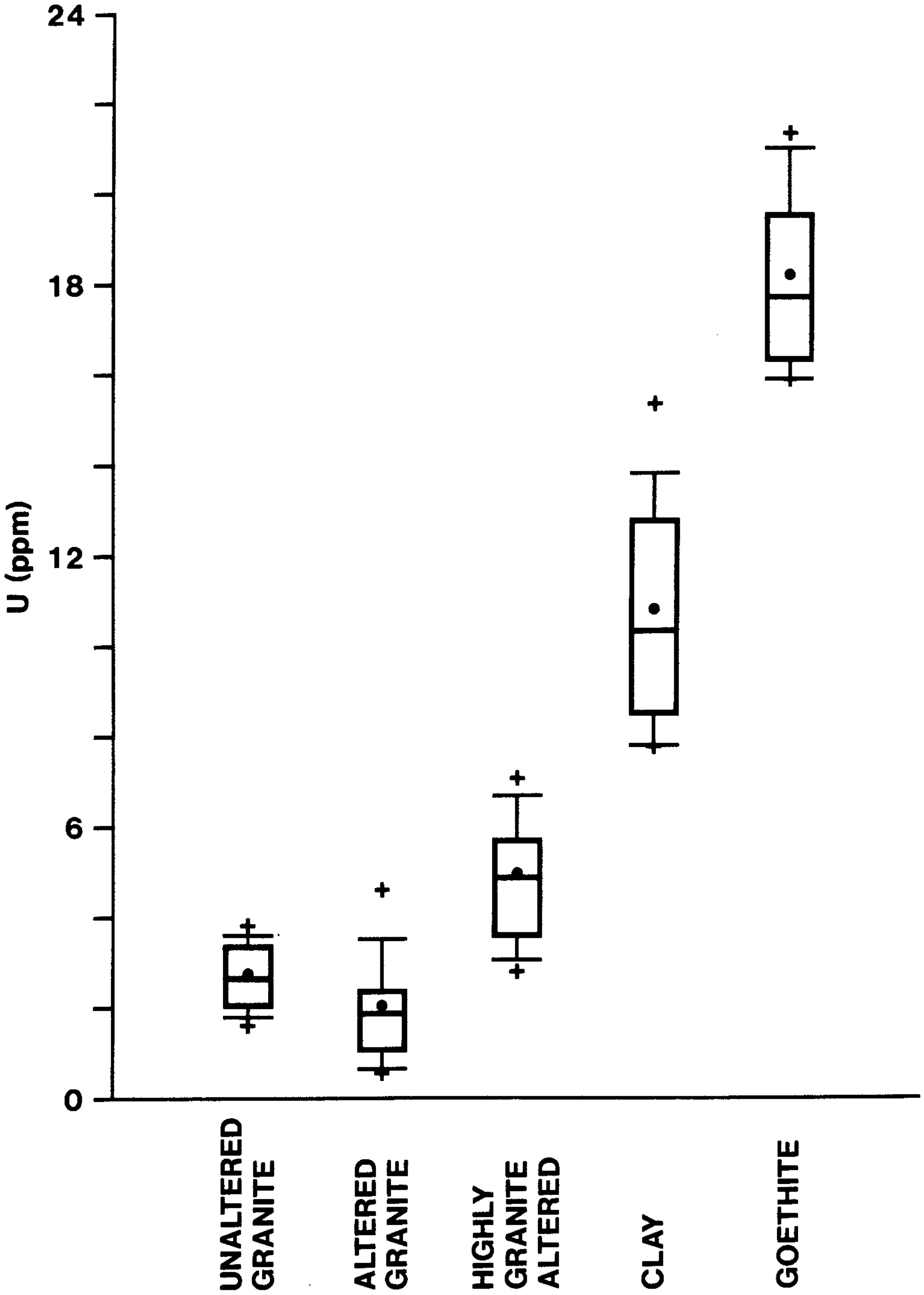

Figure 2. "Box and Whisker" plot (Tukey, 1977) for uranium in the various materials analyzed. Plus signs represent maximum and minimum values. The horizontal line within the box represents the median. The dots within the box represents the mean.

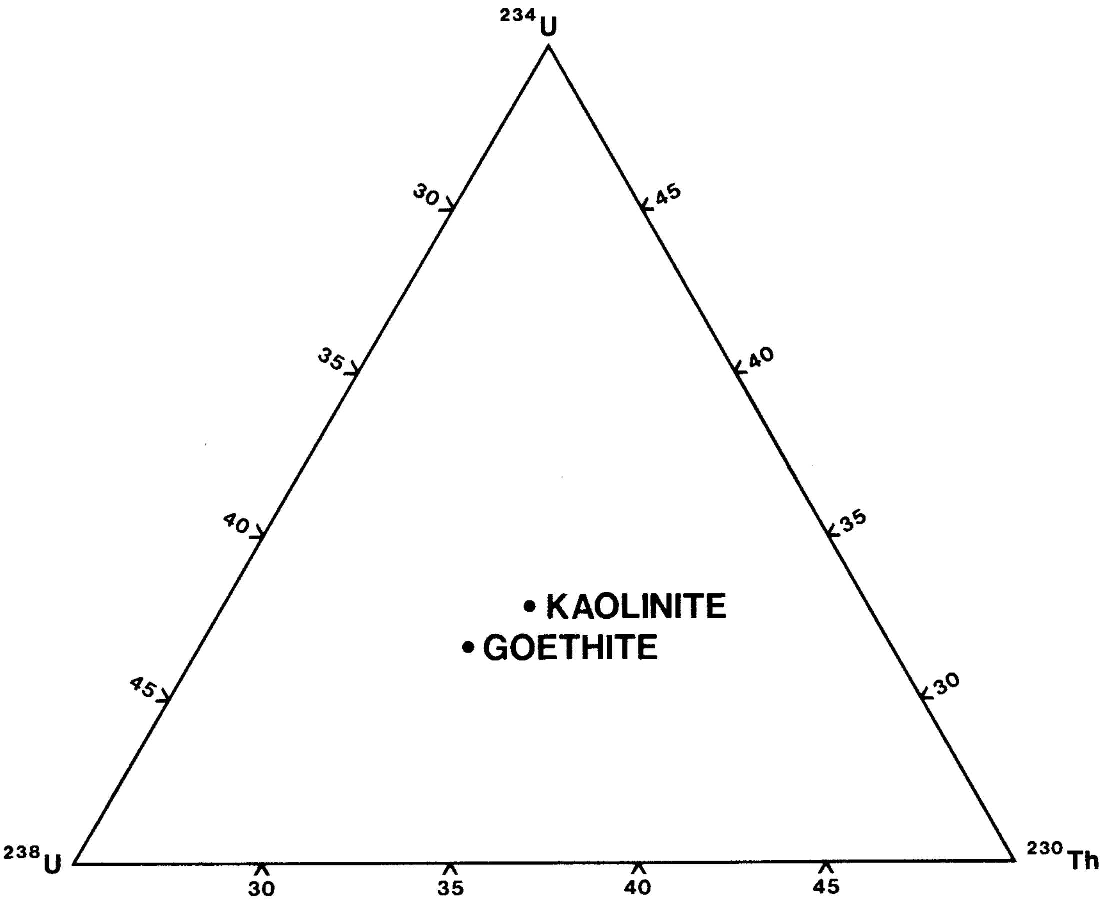

Figure 3. Ternary diagram showing isotopic data (Rosholt, 1983) for goethite and kaolinite obtained from an open fracture (located on Highway 622).

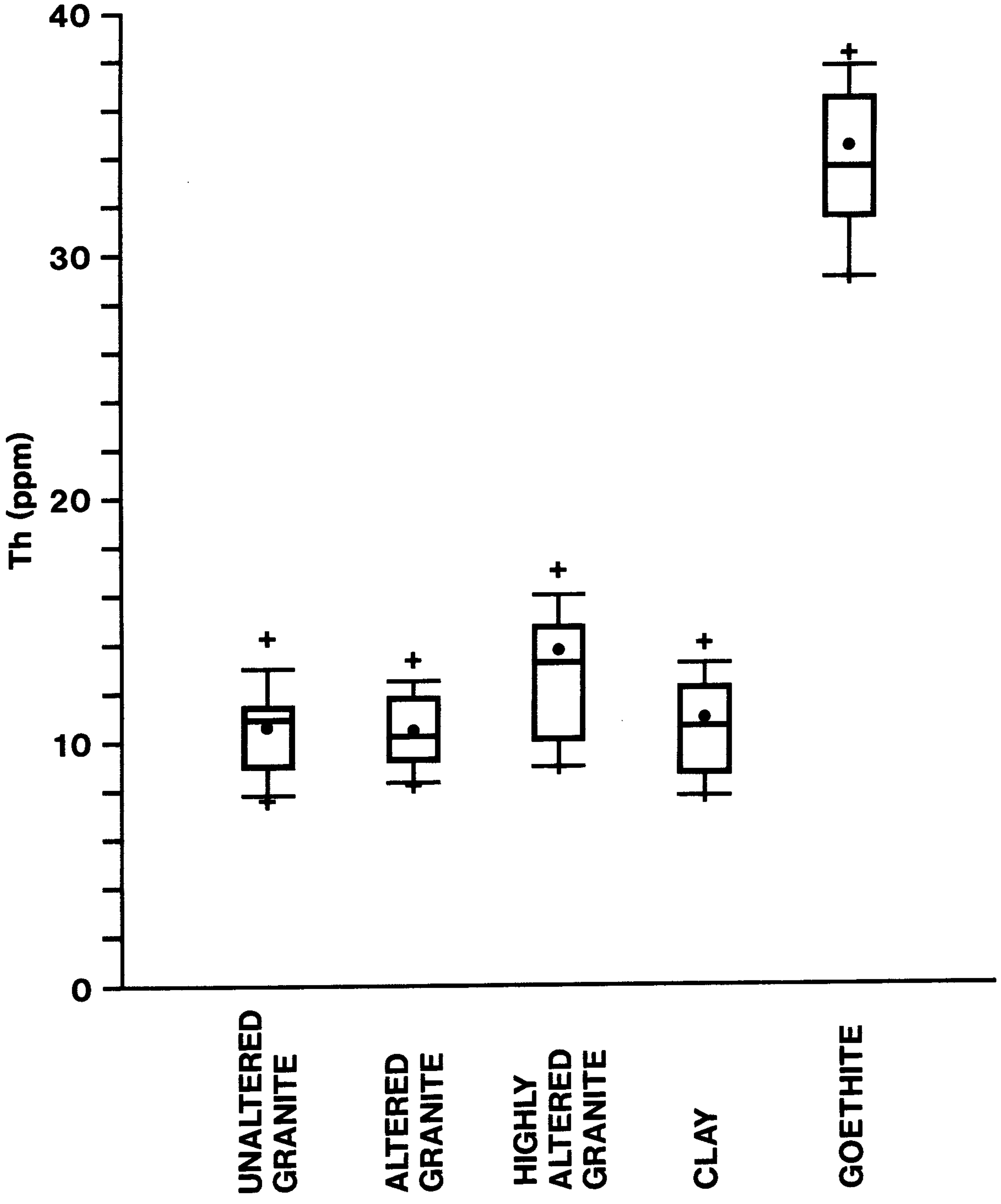

Figure 4. "Box and Whisker" plot for thorium in the various materials analyzed. (Symbols and explanation are the same as in Figure 2.)

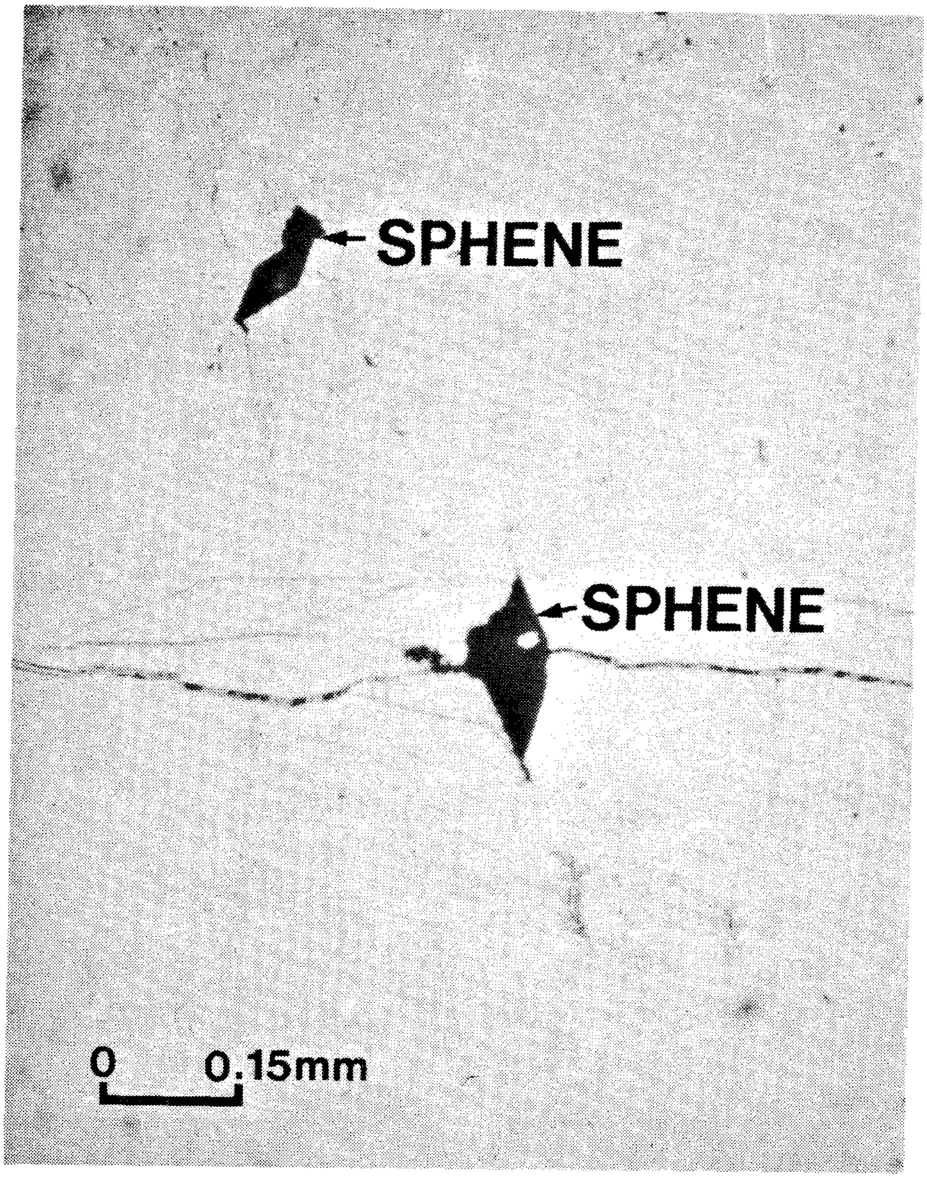

Figure 5. Photomicrograph showing pseudomorph of sphene containing hydrous iron-titanium oxides.

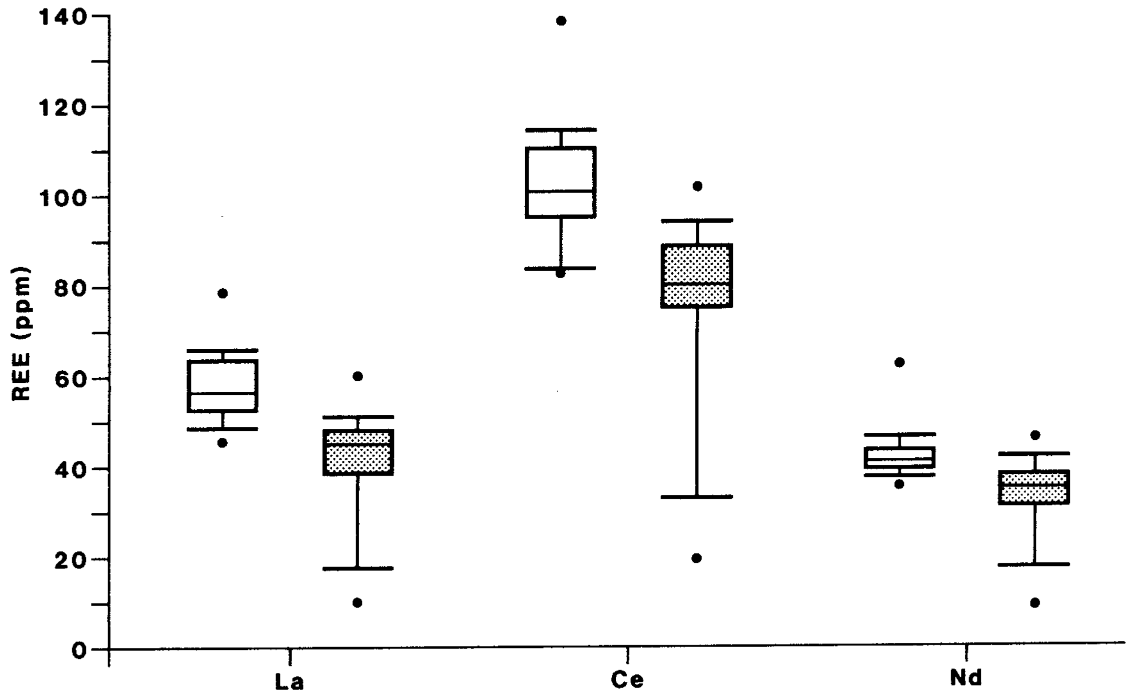

Figure 6. "Box and Whisker" plot for lanthanum, cerium and neodymium in unaltered and altered granitic samples. Clear boxes represent unaltered samples whilst shaded boxes correspond to altered samples. The horizontal line within the box is the median. The dots on either side of the "Box and Whisker" are the maximum and minimum values.

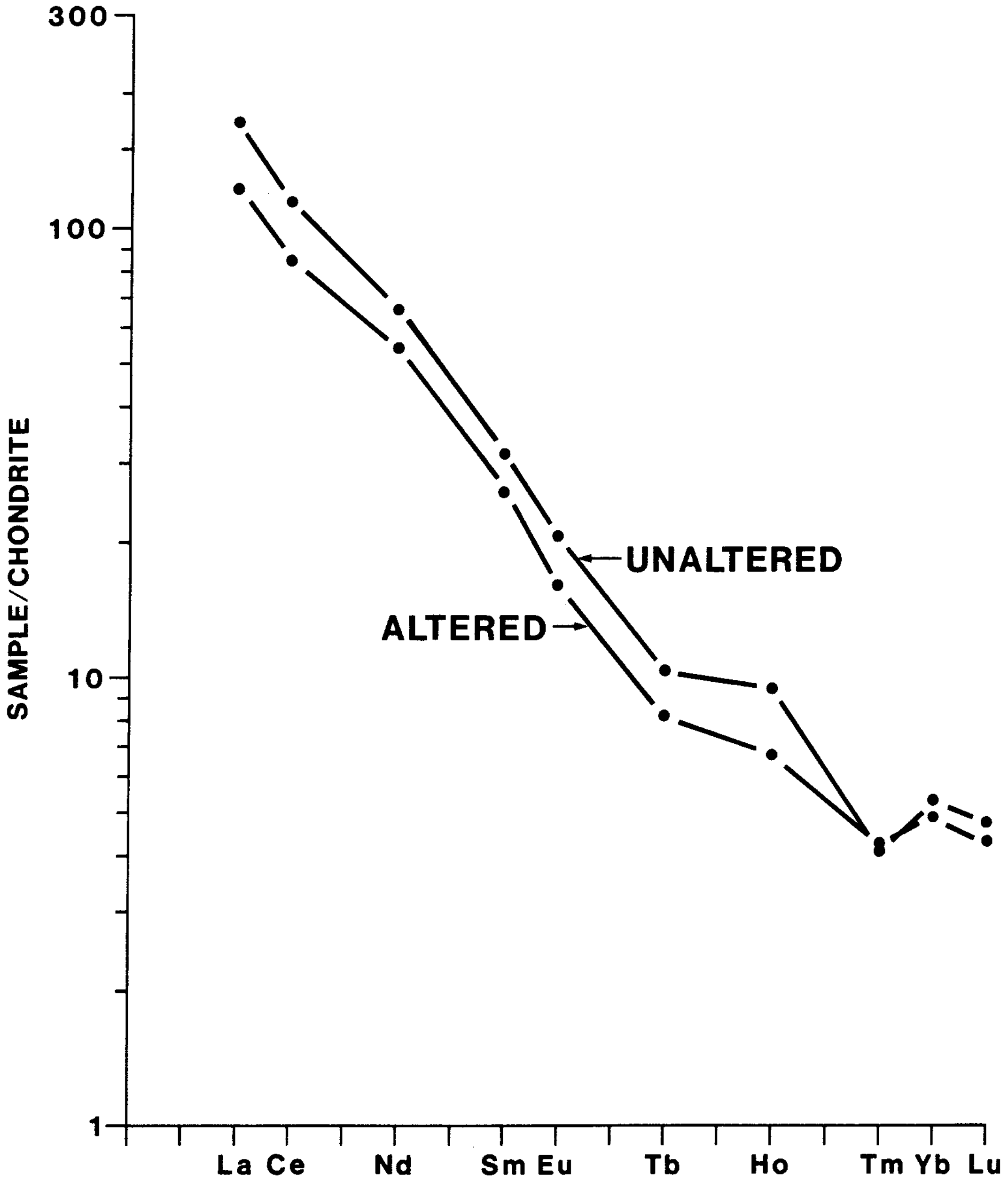

Figure 7. Chondrite-normalized patterns for REE in unaltered and altered samples.

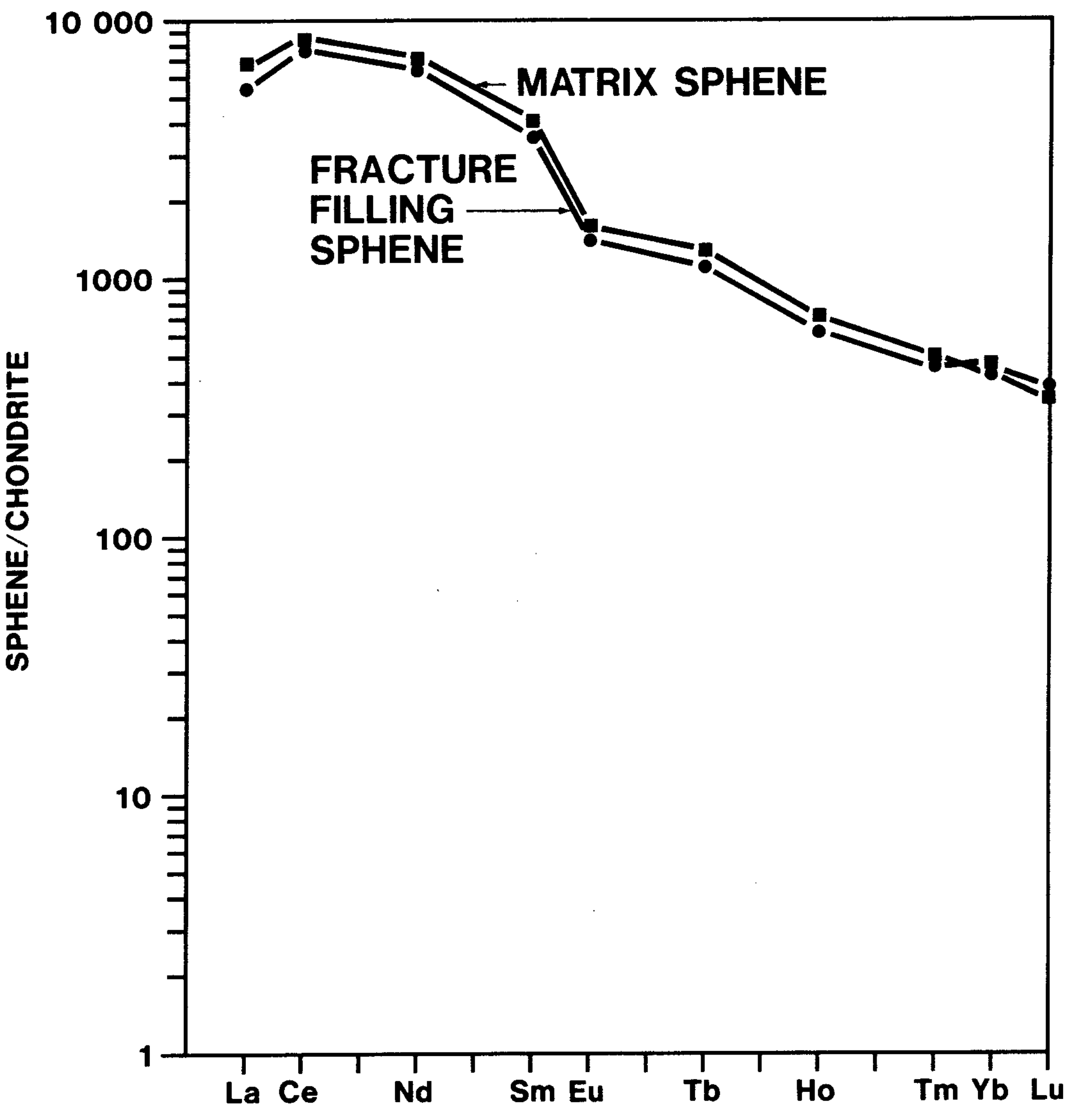

Figure 8. Chondrite-normalized patterns for REE in sphene separated from rock matrix and fractures. Note the little compositional difference between the two.

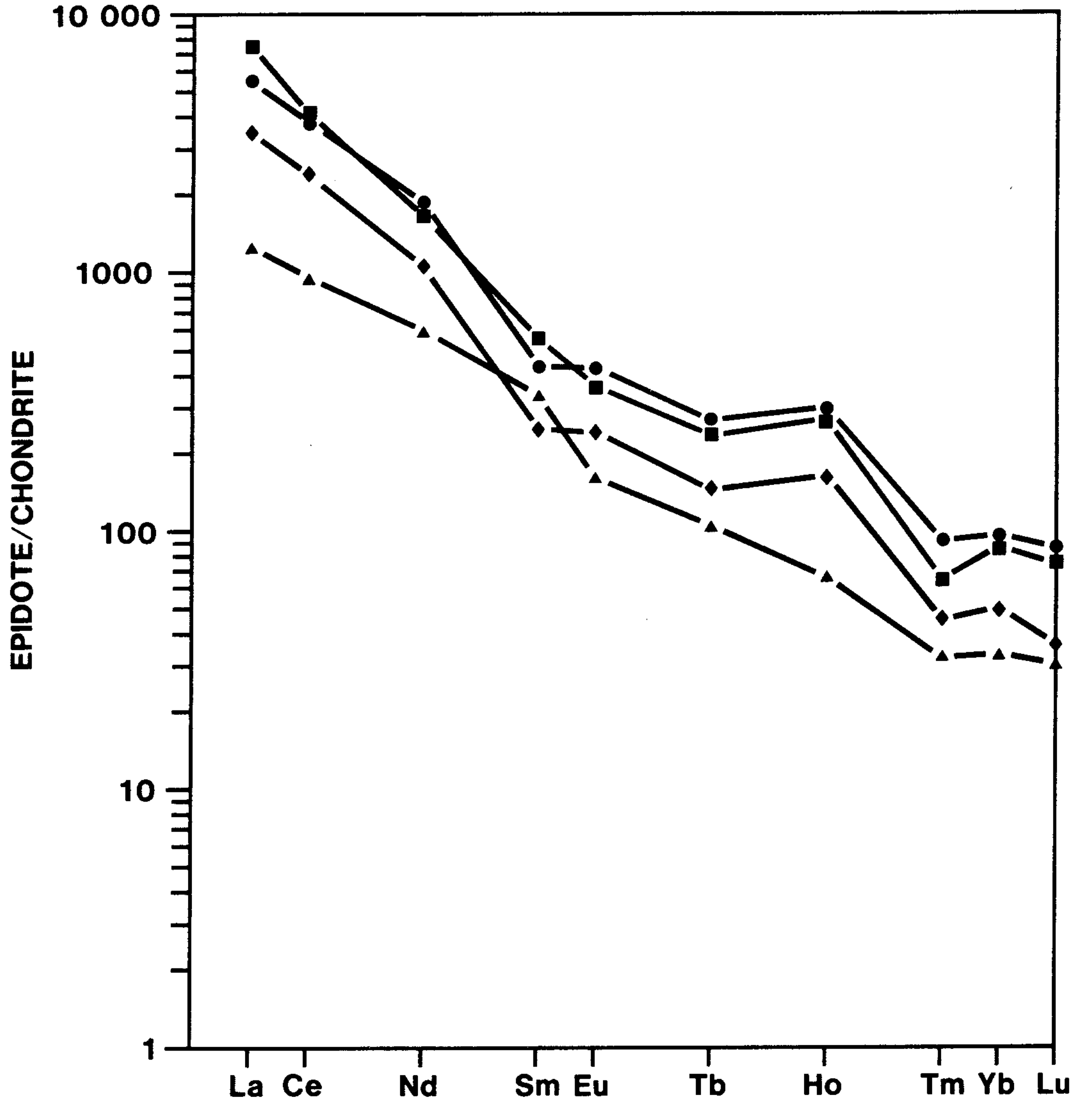

Figure 9. Chondrite-normalized patterns of two epidote pairs separated from the rock matrix and from fractures. Squares and diamonds represent analyses of epidotes from the rock matrix. Circles and triangles represent analyses of epidotes from fractures. Note the REE depletion indicated by the triangles; these data are for an epidote from a reactivated fracture.

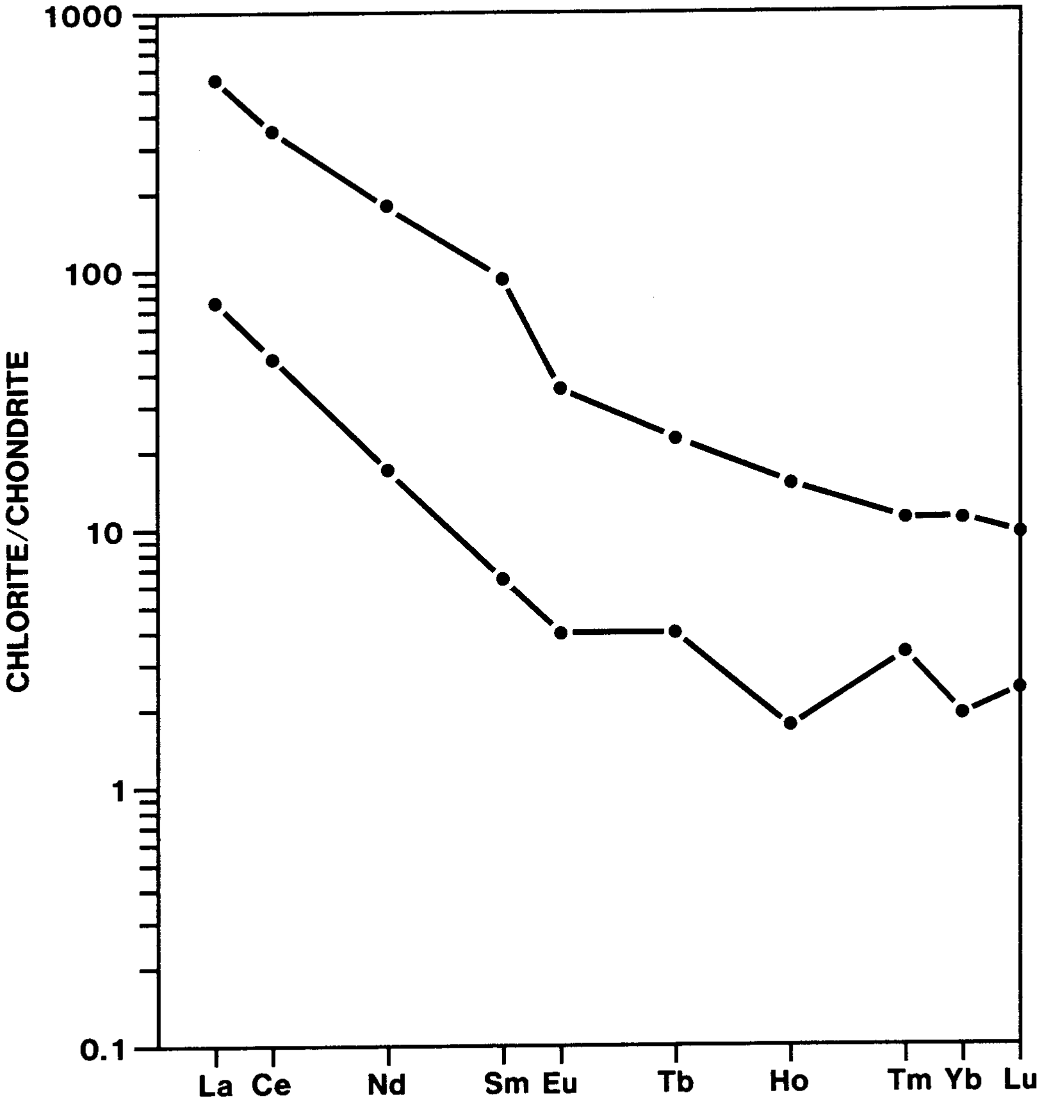

Figure 10. Chondrite-normalized patterns for two chlorites separated from fractures. The chlorite showing greater REE is iron-rich.

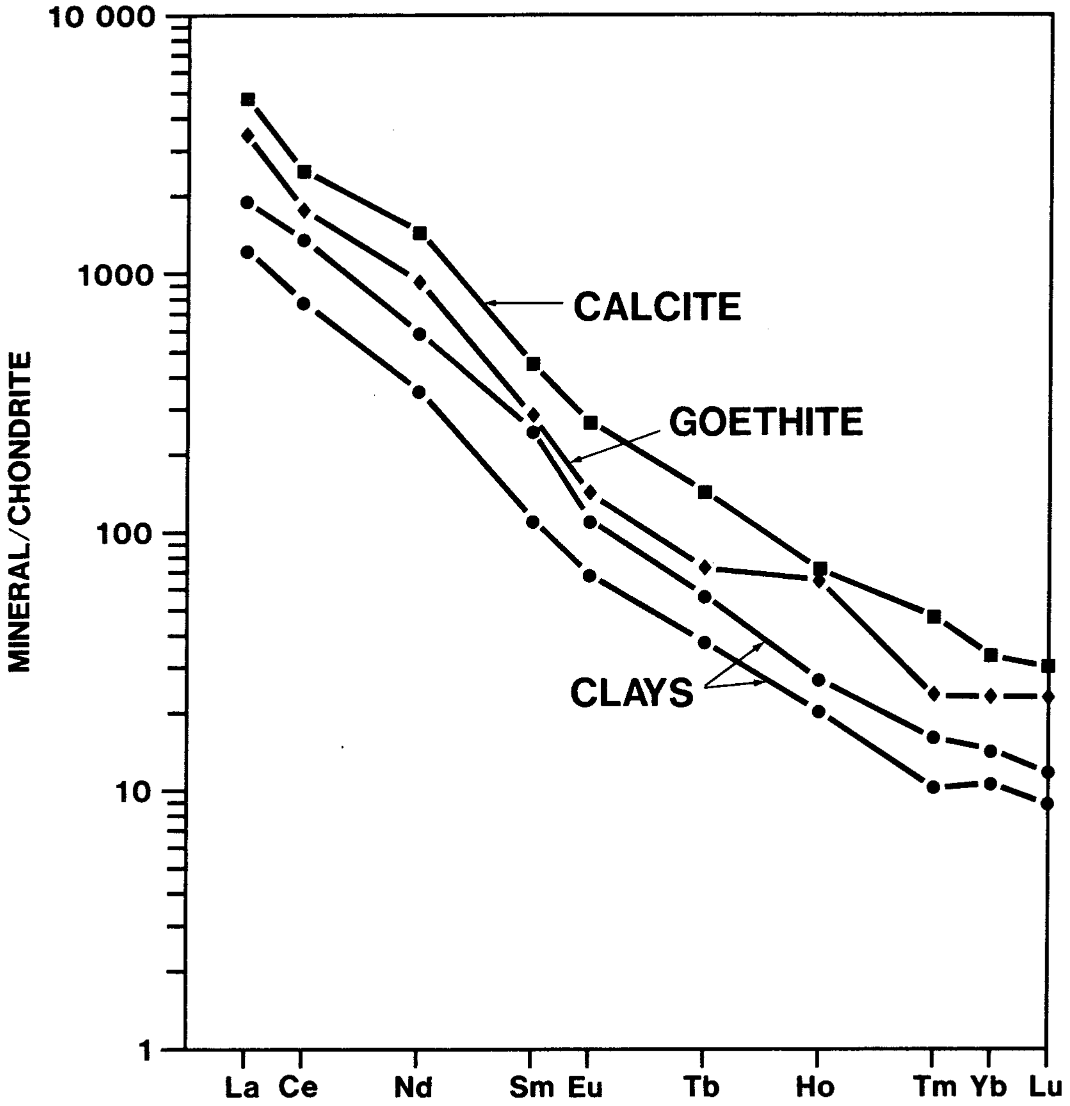

Figure 11. Chondrite-normalized patterns for calcite, goethite and clay. Note that all minerals are enriched in REE; the relative enrichments are calcite > goethite > clay.

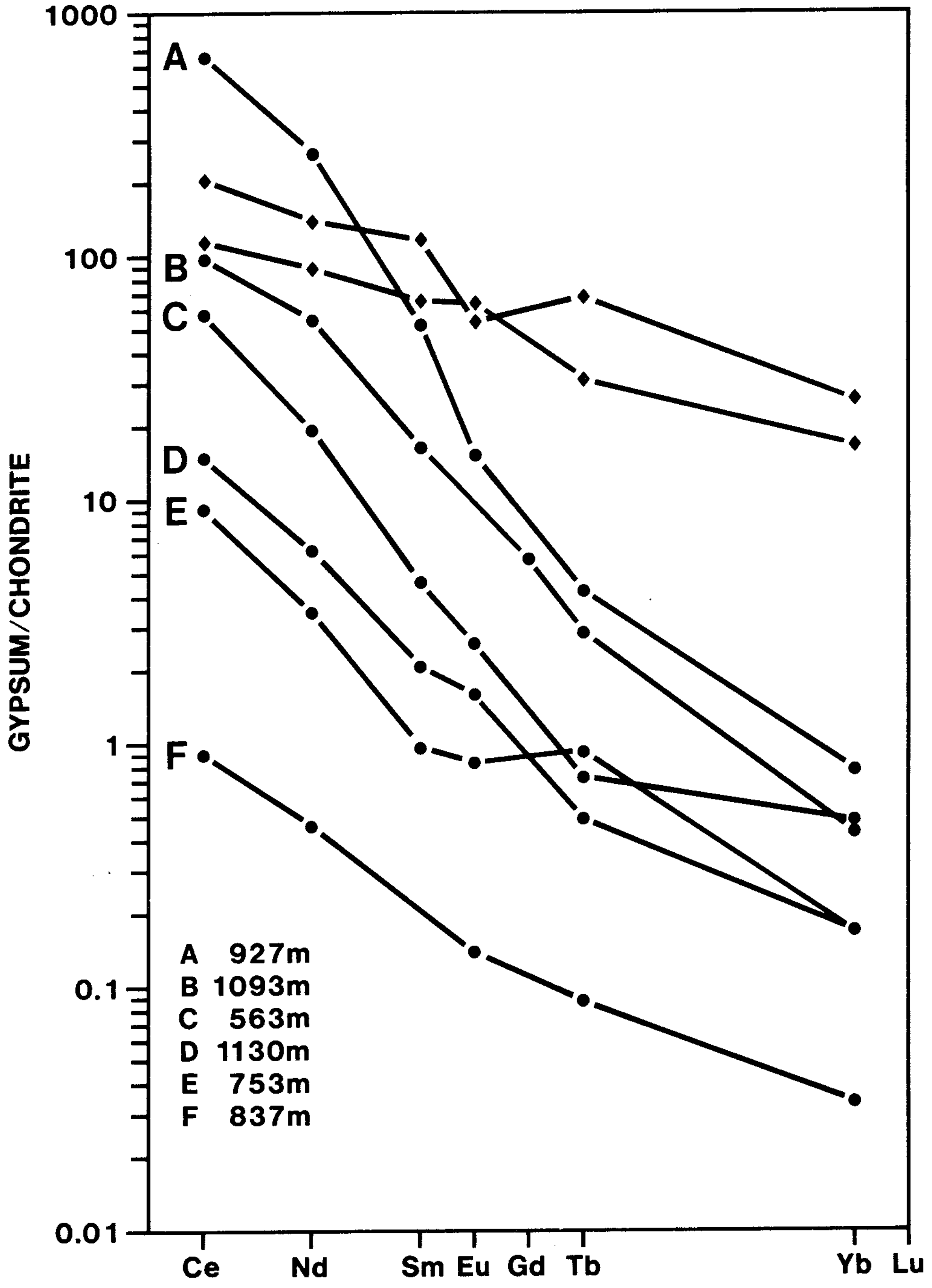

Figure 12. Chondrite normalized patterns of gypsum. Note gypsum is relatively enriched in cerium and neodymium compared to anhydrite (represented by diamonds).

A NATURAL ANALOGUE STUDY OF LONG-TERM (10^3 - 10^4 a) RADIONUCLIDE MIGRATION IN SATURATED SEDIMENTS FROM LOCH LOMOND, SCOTLAND

A.B. MacKenzie[1], I.M. Ridgway[1], R.D. Scott[1], P.J. Hooker[2], J.M. West[2] and I.G. McKinley[3].

[1] Scottish Universities Research & Reactor Centre, East Kilbride, Glasgow G75 0QU, U.K.
[2] British Geological Survey, Keyworth, Nottingham, NG12 5GG, U.K.
[3] Swiss Federal Institute for Reactor Research, CH-5303, Würenlingen, Switzerland.

ABSTRACT

Long-term migration of radionuclides through argillaceous material is difficult to quantify by extrapolation of laboratory sorption data, and is of concern in the safety assessment of a repository in the far-field. This study reports the findings from batch equilibrium sorption/desorption experiments carried out on sediments taken from a core collected in Loch Lomond, Scotland. A major feature of this essentially freshwater sequence of sediments is a marine layer which was deposited between ~6900 and 5400 years ago, and now lies between ~4 and 3 metres below the lake-bed surface. Sorption characteristics of the radioisotopes of Sr, Cs, Co, Ce, I, Tc and Np onto the lacustrine and marine material show some marked differences, and furthermore the desorption behaviour provides evidence for varying degrees of irreversibility of sorption. In addition the down-core bulk concentrations of a number of elements of relevance to radionuclide migration were determined by a combination of INAA and alpha-spectrometry. In general, comparison of observed with predicted profiles yields a poor match with little evidence of post depositional transport of iodine, bromine, uranium and radium-226 out of the marine band into the overlying freshwater deposits. Positive correlations exist between the distribution patterns for these elements and the profiles observed for total organic carbon and nitrogen indicating that organic host phases may govern their fixation, though their direct involvement is not proven.

INTRODUCTION

The notion that a marine band of sediments deposited in Loch Lomond 6900 - 5400 years ago can be regarded as a diffusion source term for the transport of natural elements into overlying freshwater deposits forms the basis of this analogue study of radionuclide migration through saturated clay-rich sediments. If redistribution of elements with radwaste interest from this discrete chemical discontinuity can be demonstrated then we have the advantage of a natural analogue of long-term radionuclide migration through cold saturated argillaceous sediments, for which process there is a paucity of data. Furthermore, such evidence would be invaluable in the validation of laboratory derived transport models. Predictive modelling over long time-scales is a precarious process when the data have been measured in relatively short-term experiments, and when the underlying assumption of reversible equilibrium interaction of the solute between the liquid and solid phases has to be made.

This paper describes the radwaste relevant results from an extensive analytical programme measuring the depth-concentration profiles of 27 different elements in a sediment core code-named LLRD1. Data are also presented from batch equilibrium sorption/ desorption experiments carried out on representative samples of the marine layer and the overlying lacustrine material.

SAMPLE DETAILS

The sedimentary material investigated and reported on here belonged to core LLRD1 recovered from the centre of the southern basin of Loch Lomond (Figure 1) by means of a Mackereth compressed air corer. The advantage of studying this 5 m length core is that it has been well characterised in the context of the Loch´s catchment area, geology and geography and has been calibrated by C-14 dating, paleomagnetic profiling and palynology (Dickson et al. 1978, Turner and Thompson, 1979). The marine sediment band interbedded between lacustrine material occupies the 4 to 3 m depth interval. This layer was a consequence of the Flandrian marine transgression which corresponds to a time-span of about 1500 years from 6900 to 5400 BP. Mineralogically approx. 80% of the deposits throughout the sequence are comprised of clays with varying proportions of kaolinite, mica, chlorite and minor smectite (MacKenzie et al., 1983). The non-clays constitute about 20% of the core with quartz and feldspars dominating except within the marine band where gypsum and jarosite are abundantly evident; these are most likely the result of the core drying out in the atmosphere which oxidises the iron pyrites originally present in the fresh sediments. The main disadvantage of core LLRD1 is its desiccation which precludes an analysis of its porewaters and causes some spurious sorption results with regard to strontium (see below).

Possible source materials for the sediment include glacial debris, weathered material from the surrounding catchment, biological material, authigenic minerals and, during the marine phase, inwashed marine particulates. The detrital and weathered material deposited might be expected to reflect the catchment bedrock which, for the southern basin, consists of Old Red Sandstone, Carboniferous Sandstone, marls and basalts and for the northern basin is mainly mica schist and shistose grit. The nature of the weathered particulates deposited will probably have varied during the sedimentary history of the Loch as a consequence of changes in the nature of the surrounding soil, climatic and vegetation variations and increasing human activity, particularly between 1700-1800 and 250-150 years ago (Dickson et al., 1978 and Baxter et al., 1981). On the basis of carbon-14 dating the average sedimentation rate was ~0.31 mm/year.

SORPTION/DESORPTION MEASUREMENTS

Results

Two bulk samples from core LLRD1 were examined, one of marine (LLM) and one of overlying lacustrine (LLL) sediment. Equilibration was carried out in distilled water solutions of the radionuclide spikes at 18 ± 3° C under both air and nitrogen atmospheres. Eh and pH were recorded but no attempt was made to constrain these parameters. Changes in γ-activity of the aqueous phase after 7 days of equilibration were used to calculate empirical rock/water partition coefficients for sorption (K sorp) and desorption (K desorp) from the elemental concentrations in the aqueous (C_W g/ml) and rock (C_R g/g) phases. A fuller description of the experimental method appears in MacKenzie et al. (1983). For I, Ce, Co, Tc and Np duplicate samples at a single spike concentration were run (Table 1a). For Cs and Sr the variation of sorption with elemental concentration was evaluated and the results (given in Figures 2 and 3) are presented as bestfit Freundlich isotherms in Table 1b, as previously reported in McKinley et al. (1984).

Discussion

Some general observations on these data can be made. The sorption/desorption isotherms for Sr and Cs are generally similar and show a marked dependence on concentration ($\beta<1$ of Table 1b). The anomalous behaviour of Sr on the LLM marine material with $\beta>1$ is attributed to precipitation of $SrSO_4$ resulting from the presence of gypsum. I and Np show similar sorption in terms of both absolute values (which are small but measurable) and also variations between samples, despite the large difference in their input concentrations (~6 orders of magnitude). Tc sorption on LLM is similar to that of I but is effectively zero onto LLL material. Ce and Co show a pattern of high sorption on the LLL sediments with much lower uptake on the marine deposits.

Most of the important points from the data in Table 1a can be seen in Figure 4 where the K_{sorp} and K_{desorp} values (ml/g) are shown as filled and open circles respectively plotted against the type of experiment conducted.

In making a comparison between the sorption and desorption data it should be noted that if the sorption reaction is reversible and linear K_{sorp} = K_{desorp} e.g. Co on the marine sediments (expts 3 & 4) when $K_{sorp} = K_{desorp} \approx 7$ ml/g. If the process is completely irreversible as with I and Np on the marine material (expts 3 & 4) $K_{desorp} = 2 \times K_{sorp}$, as a consequence of the dilution used to induce desorption. In some cases $K_{desorp} > 2K_{sorp}$ which is indicative of increased sorption after dilution e.g. I-131 on the lacustrine sediments in experiments 1 and 2, and to a lesser extent Co-60 and Ce-139. There are a number of ways of explaining this phenomenon e.g., slow kinetics may have prevented the attainment of equilibrium during the 7 day period for sorption; very slow kinetics of desorption combined with a change in sorption mechanism from physical to chemical; non linear sorption whereby dilution encourages sorption onto the solid substrate (witness the Cs isotherms). Of these the second cause is perhaps the most likely for I, involving a slow irreversible chemical reaction between the solute and substrate following fast initial physical adsorption.

Figure 5 summarises the behaviour of the sorption reactions for the different nuclides onto the marine and freshwater sediments. Of the seven elements studied only Cs and Sr are relatively well behaved with reversible characteristics. The main feature that emerges is that chemical rections with the solid substrate give rise to non-equilibrium or non-reversible sorption. Whether this is an artifact of the experimental procedure employing distilled water instead of interstitial water composition and a dried out core instead of fresh wet samples is difficult to judge. But these non-ideal characteristics do suggest that the usual sorption with diffusion models incorporating the assumptions of instantaneous equilibrium and reversible behaviour are not entirely suitable to describe the migration of most of the elements of radwaste interest through these sediments.

Notwithstanding, let us consider the idealistic case and examine the factors which affect an element's profile. If it is assumed that the fluid phase concentration of a particular element in the sediment deposited during the marine phase is greater than that in the lacustrine period but effectively constant over the time period when each of these environments existed, the diffusion with sorption model of Duursma and Hoede (1967) and Duursma and Bosch (1970) can be applied. This is based on the assumption that sorption is reversible, linear and involves rapid equilibration between liquid and solid phase and no advective flow. From the K_{sorp} value of about 3 ml/g measured for I which corresponds to an effective diffusion coefficient of 2.5×10^{-6} cm^2/s, the depth of penetration of the 10% concentration front would be expected to move at the rate of ~3 $m/10^3a$. An unretarded species would travel 10 m in 10^3 years. Cerium showed strong sorption (~10^3 ml/g equivalent to an effective diffusion coefficient of 5 x 10^{-9} cm^2/s) and should only travel 0.1 $m/10^3a$. Poorly sorbed species diffuse faster than the rate of deposition (0.31 $m/10^3a$) and are assisted by the effect of advection due to sediment compaction; consequently these solutes would not be expected to reveal a concentration profile.

A number of profiles can be imagined as illustrated in Figure 6 where diagram 1 corresponds to fixed irreversible sorption within the marine layer; diagram 2a and b depict slow and fast diffusions; diagram 3a shows the effect of advection without diffusion while 3b illustrates an asymmetrical peak, the result of advection with diffusion at different relative rates; diagrams 4a and b depict advection/diffusion together with low and high linear sorptions respectively, and 4c illustrates the added complication of non-linear sorption giving rise to a sharp penetration front as a result of increased sorption at lower fluid concentrations.

ELEMENTAL PROFILES

How far are these ideas supported by the elemental profiles measured in the core? Samples from 10 cm intervals within core LLRD1 were analysed for 23 elements (Na, K, Rb, Cs, Ba, Al, As, Sb, Br, I, Sc, Cr, Fe, Co, La, Hf, Ta, Ce, Sm, Eu, Tb, Lu, Th) by instrumental neutron activation analysis and isotope induced X-ray fluorescence analysis; furthermore following radiochemical separation the isotopes of Ra-226, U-234 and U-238 have been measured by alpha spectroscopy (see MacKenzie et al., 1983 for experimental details and data); and also the total organic and nitrogen contents have been measured on a Perkin-Elmer 240 elemental analyser.

In Figure 7 are depicted the down-core bulk dry weight concentration profiles for elements Ce, Cs, Br and I. Broadly these patterns do not accord with our expectations from the above discussion; the halogens appear to have suffered virtually no post depositional transport whereas Ce and Cs reveal no clear gradients. A major difficulty in interpreting the bulk distributions for Ce and Cs lies in not being able to distinguish a migration signal as a result of fluid processes from the background "noise" present in the mineralogy whether it be detrital or authigenic in origin.

Ideally, if the Cs deposited within the marine sediments had been labelled isotopically its subsequent diffusion with sorption path would have been made easily determinable. However, there is one way of trying to monitor this process and that is to measure the porewater abundance in a freshly collected core. This is being carried out at the moment with special regard to iodine.

The completed activity profile for Ra-226 is illustrated in Figure 8 where there is a clear display of enhanced activities close to the junctions of the marine band. Figure 8 compares the radium profile with data accumulated for ^{238}U and $^{234}U/^{238}U$ activity ratio. Although ^{238}U and ^{226}Ra are not in secular equilibrium their depth relationships are broadly similar which would support the idea that disequilibrium was established before deposition. The enrichments in U and Ra measured within the marine sediments would appear to have a common origin possibly associated with scavenging of the elements by organic particulates or clays from sea water under relatively anoxic conditions. This is consistent with the known geochemistry of Ra (Koczy, 1958; Conlan et al., 1969; Moore, 1969; Edmond, 1970; Kaufman et al., 1973; Broecker et al., 1977). Analysis of the organic content of LLRD1 would support this hypothesis. Catastrophic events at the beginning and end of the marine transition probably caused the mortality of substantial numbers of planktonic organisms leading to the deposition of large quantities of organic matter plus any materials scavenged by these organics.

The $^{234}U/^{238}U$ ratios exhibit values in excess of the secular equilibrium value of 1.0 and seem to approach a value of 1.15 in the marine sediment horizon. A ratio of 1.15 is fairly typical of seawater and surficial marine sediments (Burton, 1975). The fact that the ratios are generally in excess of 1.0 implies that the U containing minerals are relatively new, either forming in the catchment area and being washed into Loch Lomond, or, forming authigenically within the loch itself.

Figure 9 illustrates the depth variations in the abundances of total organic carbon and nitrogen. A comparison with Figures 7 and 8 reveals distinct correlations between the enhanced organic component of the core residing within the marine deposits and the distributions of I, Ra and U lending credence to the idea that biogenic particulates were responsible for concentrating these elements. However, the processes underlying these positive correlations remain unclear; associated siliceous rather than carbonaceous organisms could have been responsible for the transfer of Ra from ocean to sea bed sediments (Ku et al., 1970; Edmond, 1970); soluble organic uranyl (U VI) complexes could have been fixed by sorption onto clay minerals of detrital or authigenic origin; and the mechanistic detail for iodine is still open to debate, the formation of N-iodoamide compounds being favoured by Harvey (1980) while Wong (1980) stresses the potential of hypoiodite to react with organics to immobilise the element.

CONCLUSIONS

The laboratory experiments involved the sorption/desorption of radionuclides in solution contact with subsamples of core LLRD1 and revealed that the sorption processes were commonly irreversible controlled by mineralogy and chemical reaction. Modelling from this basis is difficult.

Evidence for post depositional migration of elements out from the marine deposits has not been found (with the possible exception of U-234) which accords with the general findings of Mackereth (1966) when he examined lake sediment cores from the Lake District of Northern England. The identification of diffusion processes is more likely to be made by determining the porewater elemental concentration profiles.

More detailed study of the inter-relationships of I, Ra, U and organics is required in order to elucidate the mechanisms of their enhanced concentration and subsequent apparent retardation within the marine sediments.

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Table 1. Sorption/desorption data onto Loch Lomond sediments.

a) Nuclide (input conc. g/ml)	Expt*	Eh (mV)	pH (sorp)	pH (desorp)	K_{sorp}+ (ml/g)	K_{desorp}+ (ml/g)
^{131}I	1	568	6	6	4.1	18
(1.8×10^{-7})	2	461	6	6	0.9	3.8
	3	610	4	4.5	3.3	7.1
	4	607	4	4.5	2.1	5.1
^{139}Ce	1	513	6	6	830	1850
(1.8×10^{-7})	2	424	6	6	1100	2700
	3	608	4	4.5	9.1	18
	4	607	4	4.5	8.5	19
^{60}Co	1	545	6	6	330	720
(9.5×10^{-8})	2	426	6	6	390	1000
	3	607	4	4.5	6.6	7.3
	4	606	4	4.5	6.5	7.2
^{95m}Tc	1	579	6	6	<1	<1
(2.2×10^{-13})	2	495	6	6	<1	<1
	3	582	4	4.5	2.8	5.0
	4	578	4	4.5	3.0	5.2
^{235}Np	1	737	4.5	4.5	3.0	5.2
(4.8×10^{-13})	2	764	4.5	4.5	<1	<2
	3	670	3	4	3.6	7.0
	4	665	3	4	3.5	6.1

b) Isotherms

Fit of data to equation $C_R = \alpha\, C_W^{\beta}$

r = correlation coefficient for linear least squares fit on log/log transformed data.

In all cases, expt 1, 2 pH sorp = 6, pH desorp = 6
expt 3, 4 pH sorp = 4, pH desorp = 4.5

Nuclide (input range g/ml)	Expt*	Eh (mV)	Sorp α	Sorp β	Sorp r	Desorp α	Desorp β	Desorp r
^{137}Cs	1	516	3.1	0.7	0.996	1.7	0.7	0.996
(2×10^{-8} - 9×10^{-4})	2	452	2.9	0.7	0.994	3.2	0.7	0.993
	3	602	0.7	0.7	0.998	0.4	0.6	0.996
	4	599	1	0.7	0.998	0.3	0.6	0.995
^{85}Sr	1	520	6.2	0.8	0.99	6.2	0.8	0.99
(2×10^{-8} - 8×10^{-4})	2	421	2.5	0.7	0.98	5.9	0.8	0.99
	3	609	1000	1.3	0.89	670	1.3	0.98
	4	606	2300	1.5	0.92	-	-	-

*Expt 1 = LLL/air 3 = LLM/air
2 = LLL/N_2 4 = LLM/N_2

+ mean value; variation between duplicates generally ~10%.

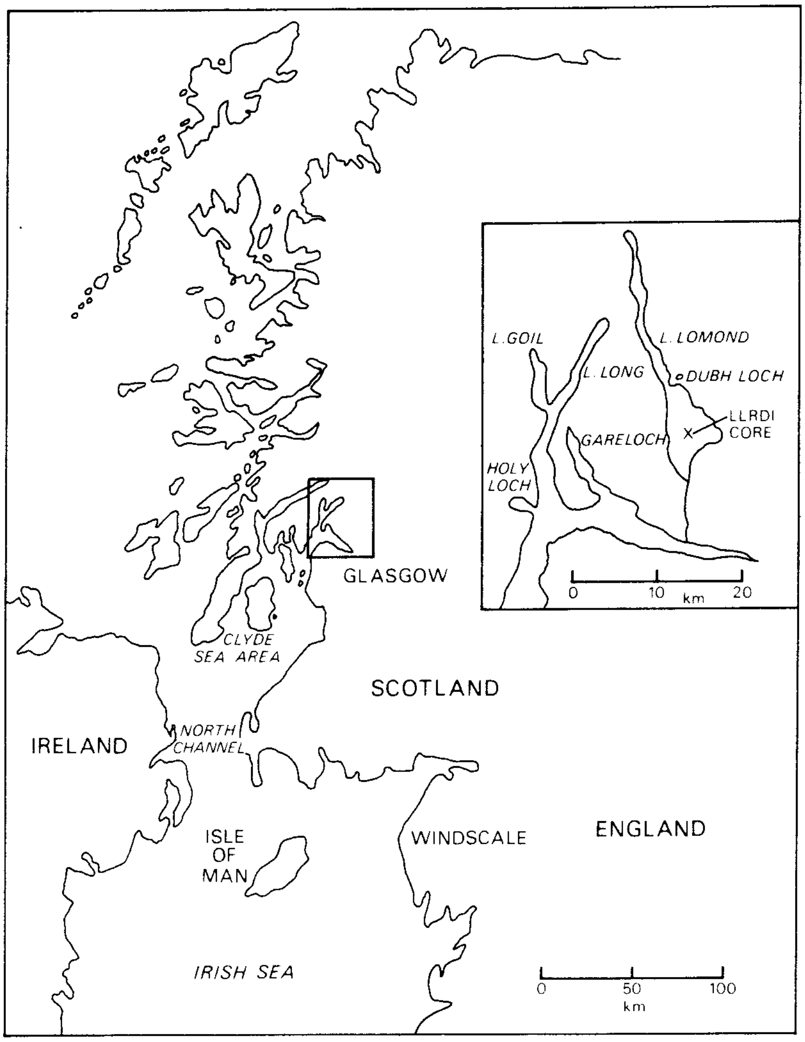


Figure 1. Location map for Loch Lomond, Scotland showing where core LLRD1 was recovered.

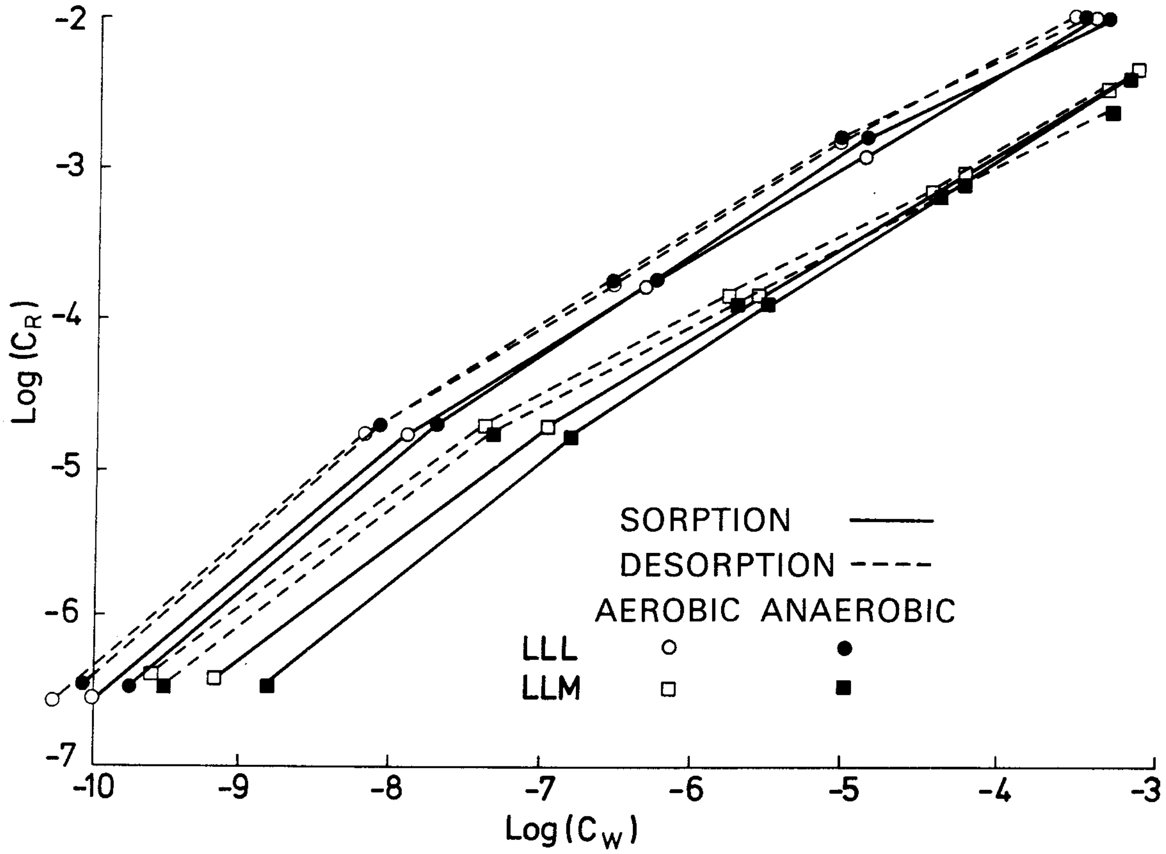


Figure 2. Sorption and desorption isotherms for Cs on sediments from core LLRD1; LLM refers to a sample of the marine layer, LLL to the overlying freshwater material.

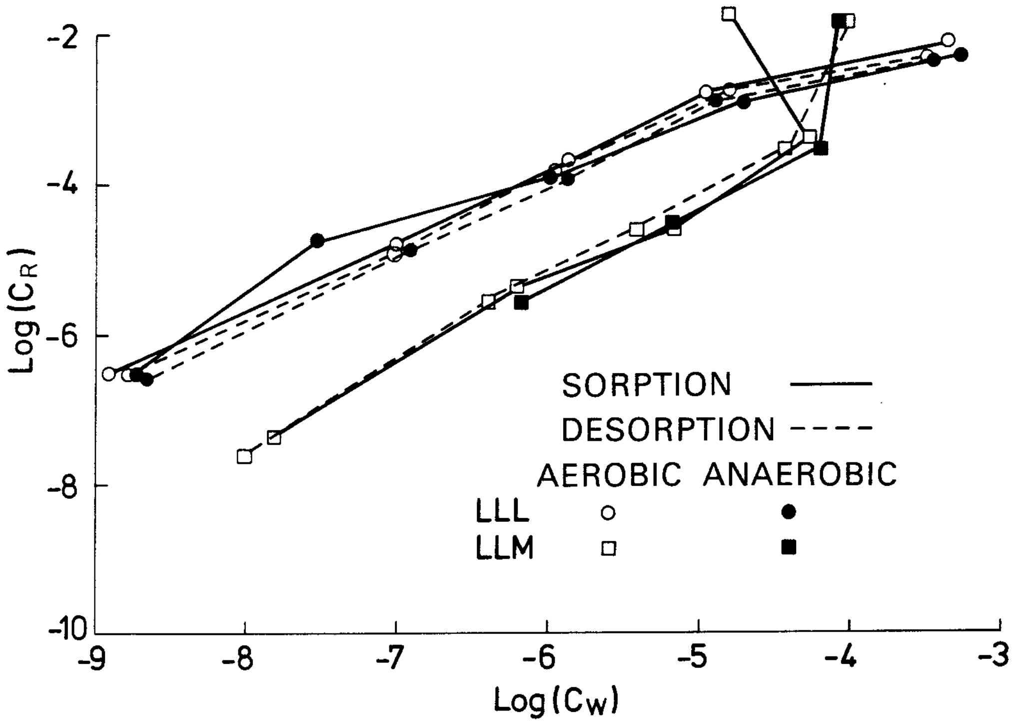


Figure 3. Sorption and desorption isotherms for Sr on sediments from core LLRD1; LLM refers to a sample of the marine layer, LLL to the overlying freshwater material.

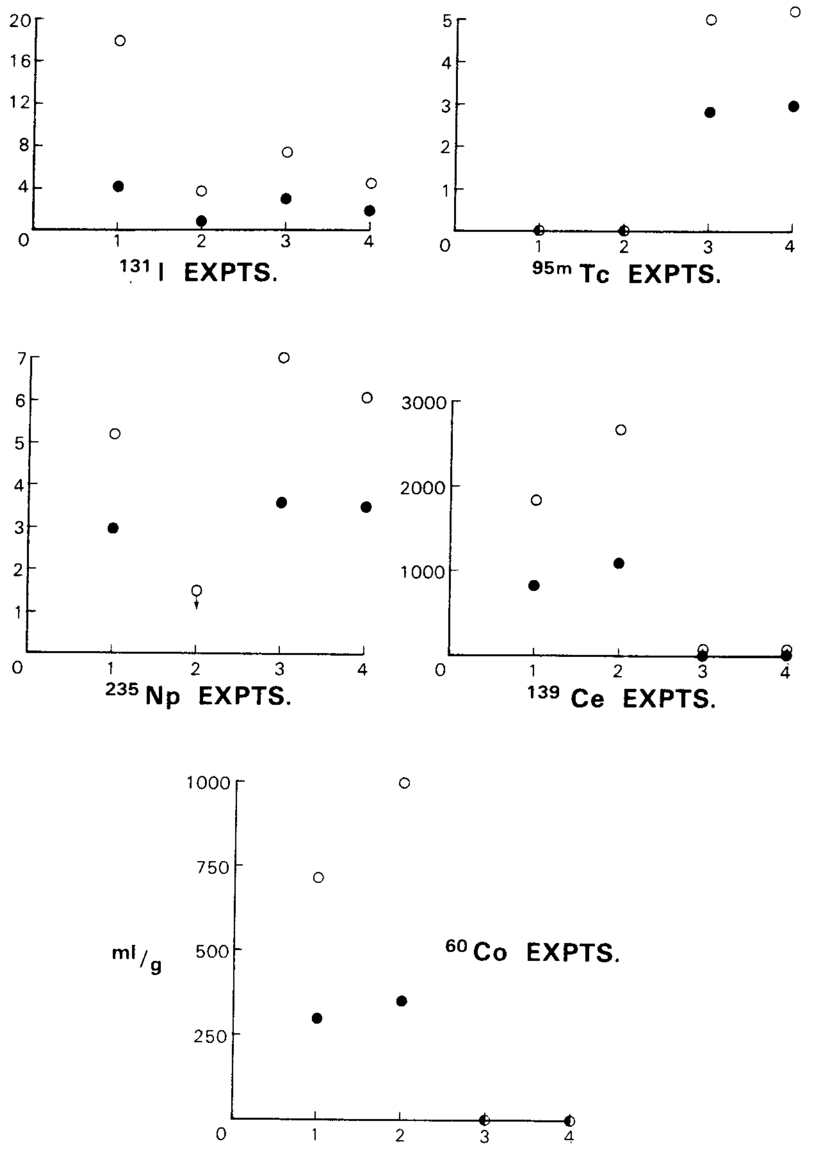


Figure 4. A display of the different sorption and desorption characteristics of five radionuclides on sediments from core LLRD1. See Table 1 footnote for the description of the 4 types of experiment. The K_{sorp} and K_{desorp} values (ml/g) are shown as filled and open circles respectively.

	ELEMENT	I	Ce	Cs	Sr	Co	Tc	Np
MARINE SEDIMENTS	REVERSIBLE SORPTION			■	■	■		
	IRREVERSIBLE	■	■				■	■
FRESHWATER SEDIMENTS	REVERSIBLE			■	■		○	
	IRREVERSIBLE						○	■
	INCREASED	■	■			■	○	

Figure 5. The sorption behaviour of radionuclides on sediments from core LLRD1. Open circles indicate no measurable uptake. The main trend is towards irreversible sorption.

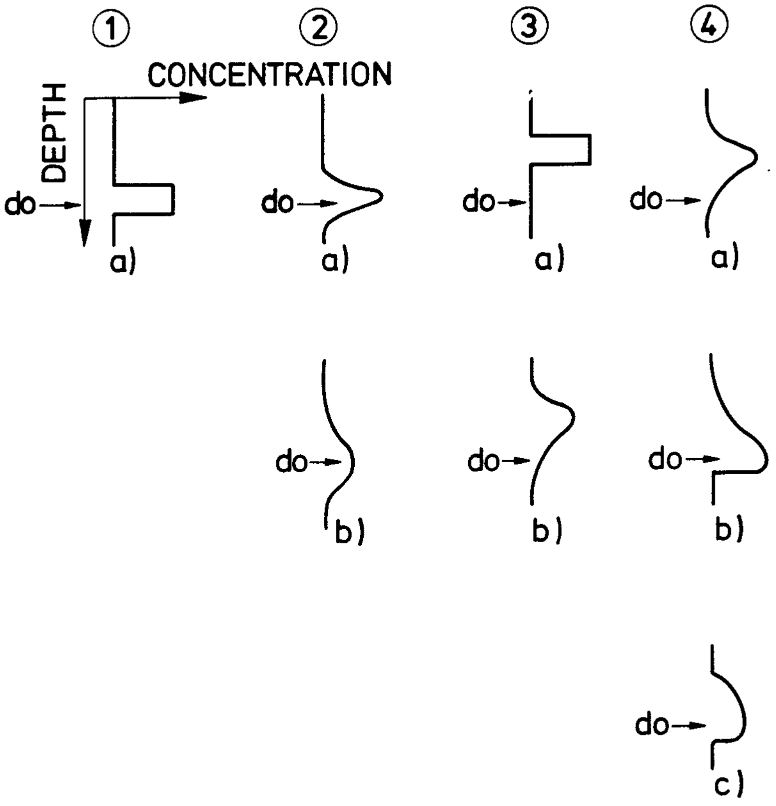


Figure 6. A number of hypothetical concentration with depth profiles as a result of a chemical discontinuity at depth do. See text for explanations.

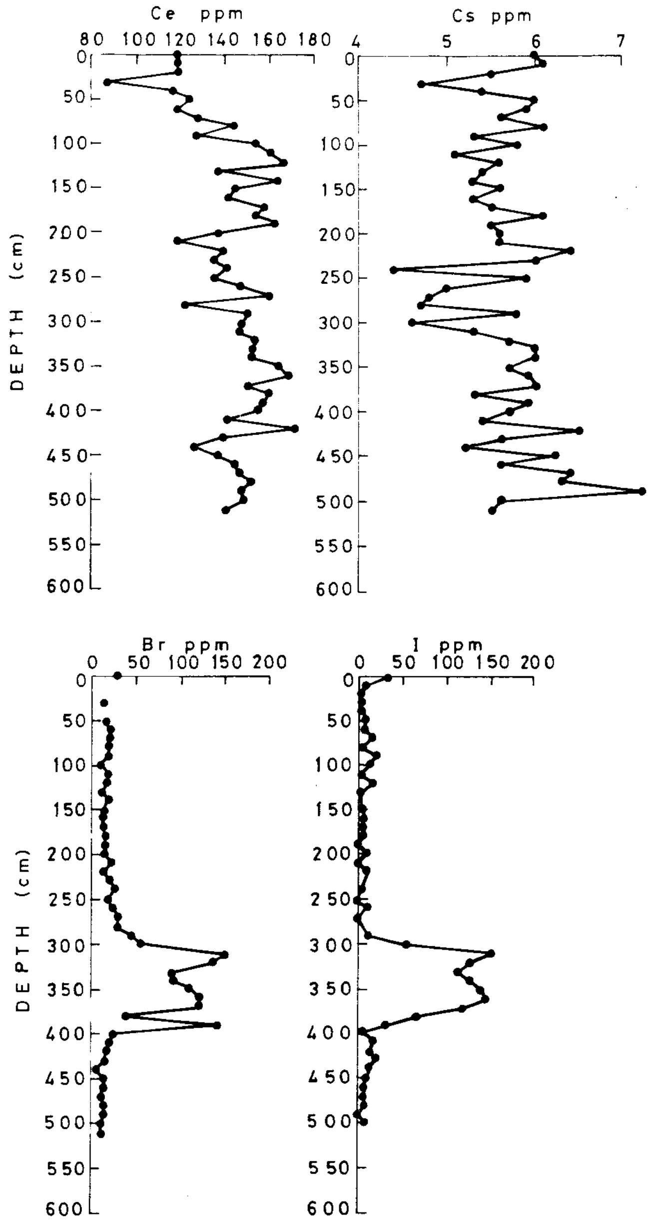
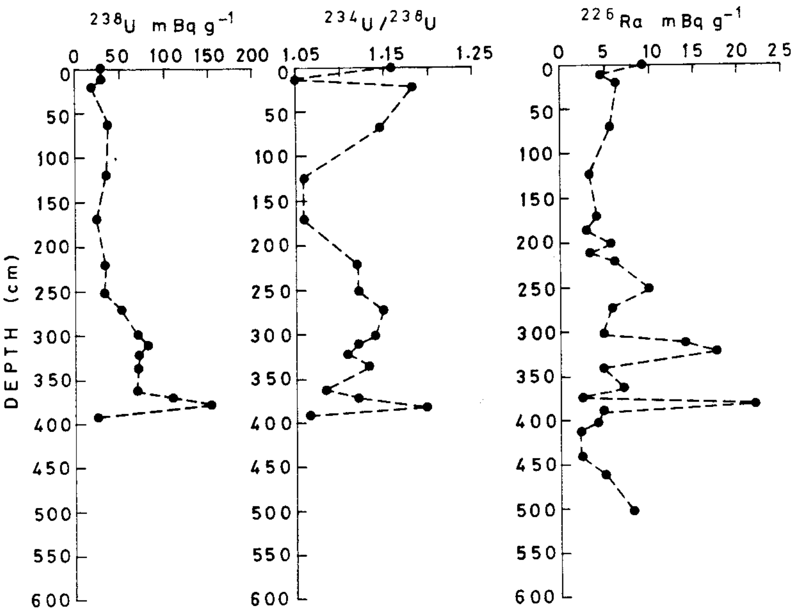


Figure 7. Depth concentration profiles measured on bulk dried samples of core LLRD1 for the elements Ce, Cs, Br and I. Note the distinctive enhancements of Br and I in the marine material between 300-400 cm depth.



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PROFILES FOR LLRD 1

Figure 8. The peak activity of U-238 corresponds to 12 ppm U. The activity peak for Ra-226 corresponds to 6.1 x 10^{-13} g/g and would have been 1.16 x 10^{-11} g/g 6900 years ago, assuming a closed system since then.

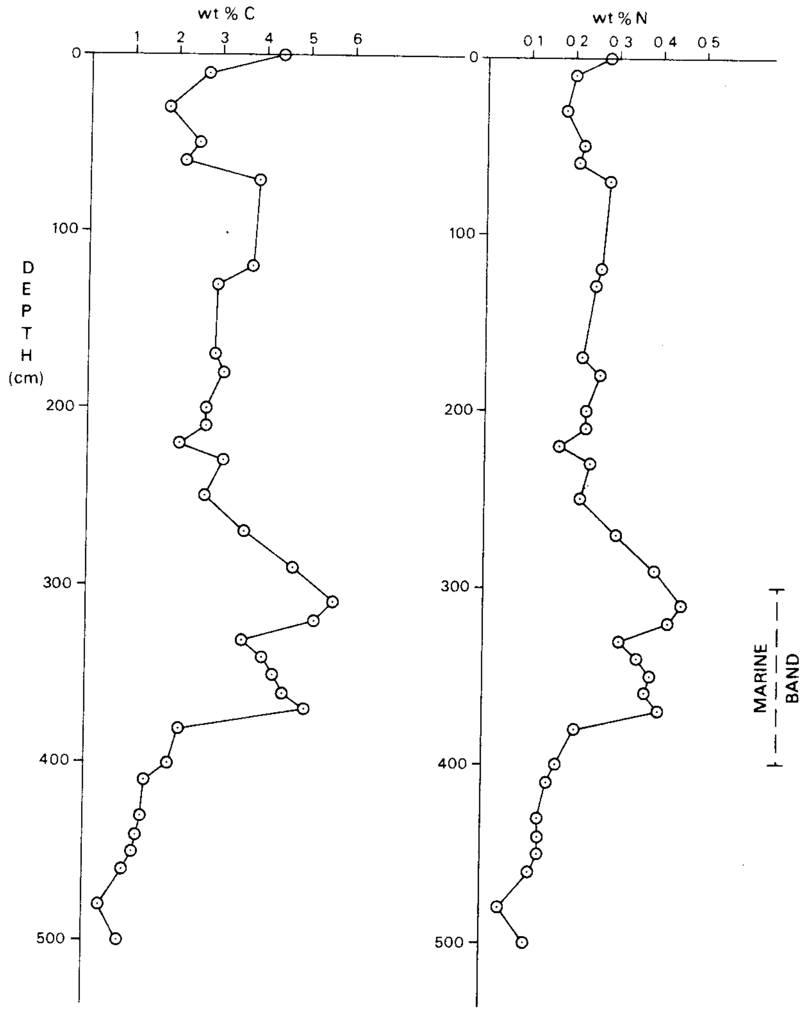

Figure 9. Total organic carbon and nitrogen contents within core LLRD1. Note the enrichments within the marine band.

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